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ANALYTICAL-GEOMETRICAL METHOD FOR ASSESSING THE OREBODY GEOLOGICAL COMPLEXITY

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ABSTRACT
The method proposed for assessing the geological profile complexity and the orientation of changeability can be used for determining the geometry of the development and extraction workings, for devising a methodology for standardising ore loss and contamination, for building up a quality control system, etc.

The orebodies which are being mined by the mining companies are pulsating systems. The natural factors and the raw materials market situation determine the pulsation of the geological (industrial) reserves of the company (Topalov S. et. al. 2000). The quantitative evaluation of the natural conditions and, in particular, the company and market reserves, is probabilistic. Despite the strictness of the design and engineering solutions on working the orebody, their implementation depends on a certain probability. It is close to 1 for well-explored orebodies with simple chemical, mineralogical, structural, etc. composition and close to 0 for geologically complex and insufficiently explored orebodies.

The degree of exploration of the orebody and its geological complexity are closely interrelated for well-known reasons. The exploration methodology depends on the geological complexity. Unfortunately, no quantitative standard has been elaborated so far for regulating the geological complexity of the Bulgarian ore deposits. Such a standard would solve the problems related to: the ratio between drilling and mining exploration works; the geometry and density of the exploration grid; the methods and techniques of sampling; the obtaining of single solutions by applying the three-index classification of reserves and resources adopted in this country.

The methodological approach to assessing the geological complexity would significantly facilitate: the standardization, planning and control of losses and contamination in mineral extraction, subsoil protection, etc.

The difficulty in assessing quantitatively the geological complexity of the orebody (or its sections) arises out of the hypothetical character of the output geological data. The methods of interpolation and extrapolation, limited by the location of the sampling points (selected statistical sample) are essential for the geological solutions.

The complexity of the orebody, depending on the stages and tasks of the geological exploration and mining cycle, is proposed to be subdivided into geological and mining-geological (Попов В.Н. и др. 1996). The assessment is designed to be made by using an *integral index* which should involve: geological factors by degree of their changeability which assess the deposit quantitatively and have an influence on the accuracy of evaluation of the predicted mineral resources, on the rational extraction of valuable minerals from the Earth’s crust and on the technical and economic indices for the activity of the mining company. We suggest that the mining-geological complexity model be grapho-analytical and be expressed by the topofunction of the type $V = f(x,y,z)$.

According to (Попов В.Н. и др. 1996), the assessment of the mining-geological complexity should be carried out by an index which has to meet the following requirements:

- zero dimension - the different geological indices are expressed by dimensionless variables without losing the physical sense thus enabling us to compare the orebody areas;
- spatial relationship - reflecting the character of change when solving particular engineering problems;
- taking into account the discrete and continuous character of the geological indices;
- possibility for formalisation of the qualitative and descriptive factors;
- versatility, flexibility and reliability of the constructed volumetric model capable of being used in the planning and management of mining operations.

The requirements to the index mentioned above can be implemented by a method based on the mining-geometrical relationships (Христов Ив. 1974). In its analytical part the method is based on the theory of random functions - the normalised correlation function:

$$\rho_x(\tau) = \sigma_1^2 e^{\alpha_i(\tau)} + \sigma_2^2 e^{\alpha_j(\tau)} . \cos \beta_j(\tau)$$

where:

σ_1^2 and σ_2^2 are variances of the random and regular (periodic) components in the distribution of the geological index;

$\alpha_{i,\,j}$ - an index of the degree of reduction of the correlation between the spatial indices;

ß - angular velocity of the periodic (regular) component of the changeability in the geological index.

Fig. 1 shows the graphs of the normalised, reduced to a variance=1, auto-correlation function of the change in the copper content along a given direction in the orebody which is being extracted by open-pit mining methods. 1 designates the graph plotted on the basis of data from detailed exploration drill-holes and 2 designates data from the exploitation exploration. The figure shows clearly that along with the random component whose variance for graph 1 equals σ_1^2, with a standard deviation σ_1 = 0.87 (basic component), there is also a regular component with a variance of σ_2^2 and a standard deviation σ_2 = 0,38, with a period T_1 equal to four times the sampling grid size.

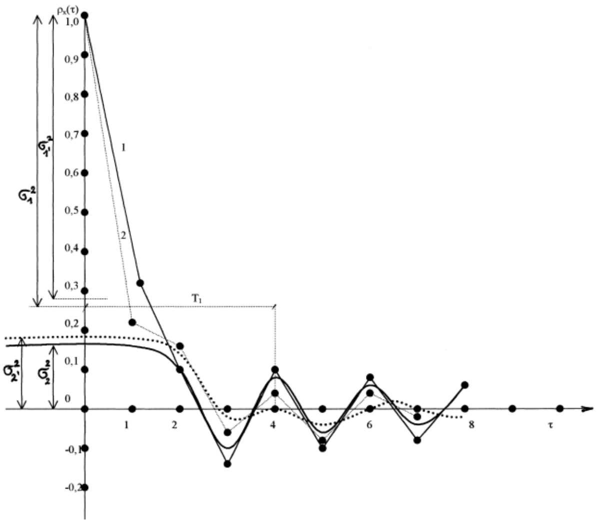

Figure 1

The graphical part of the proposed model is expressed both by what has already been shown in its analytical part and by the following sequence of graphic constructions:

- for each level the centre of gravity is defined hypothetically on the basis of a geological profile;
- straight lines are drawn through the centre of gravity whose orientation is defined by the value of a true bearing;
- the sampling points are defined for each straight line in order to study the geological index determining the orebody complexity and the values of s_1 and σ_2^2 are also defined;
- the values of σ_1 and σ_2 are plotted on separate radial diagrams whose origins coincide with the values of X and Y of the gravity centre of the mine level;
- the final points are connected with a closed polygon line which defines the dimensionless area of the random (regular) component in the changeability of the index; the orientation of the two types of changeability in the coordinate system of the mining operations;
- the circumference P in the figure is defined (the length of the closed polygon line) whose length is used as a decisive factor in assessing the complexity of the geological index.

Fig. 2 shows radial diagrams for the random component of the copper content for levels 1090, 1075, 1060 and 1045 (according to data from the detailed exploration at the Elatsite Mine), which are constructed on the basis of the character of the auto-correlation function (the values of the radius of auto-correlation) for the eight defined directions. The graphical basis for assessing the regular component is a derivative of the one shown in Fig. 2.

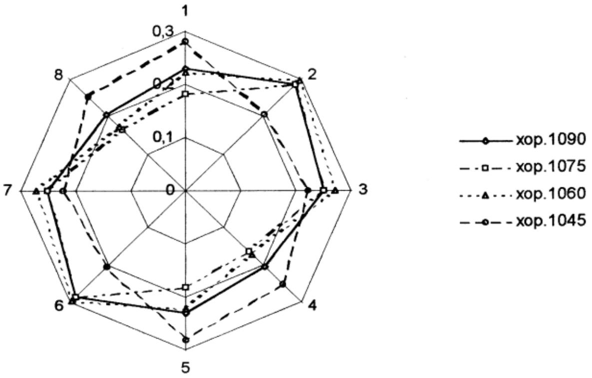

Figure 2

The results were obtained by using some standard application software packages (e.g. "*Statgraph - Plus*"), applications of Microsoft Office (Excel), application of a series of logical operations, etc.

From the analysis of the applied graphic models of the random component for the levels under study, viz. 1090, 1075, 1060 and 1045, with regard to copper content, it is possible to draw the following important conclusions:

1. In terms of non-homogeneity (based on data from detailed exploration) - level 1090 can be said be the most complex one, levels 1060 and 1045 can be said to be of similar complexity and level 1075 can be considered the least complex one with respect to the distribution of copper content.
2. With increasing the bulk of information (sampling data from the exploitation exploration) on the copper content, the random component for each level decreases as follows:

    on level 1090 by 61,5 %;
    on level 1075 by 62,0 %;
    on level 1060 by 63,5 % and
    on level 1045 by 55,9 %.

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CREATING AN ALGORITHM AND TECHNICAL SOLVING TO CHOOSE OPTIMAL METHOD OF OPENING FOR UNDERGROUND MINE

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ABSTRACT
One of the main stages in underground mining of deposit is their opening. The opening of mine field is described with specific features, which continuously maintains the actuality of their investigation. According to developed algorithm an object function is created and a method, for investigating the extreme value, is chosen. A suitable mathematical model is created for economic evaluation of the method of opening which is based on generating a great number of variants and multicriteria approach. The following results are achieved by means of formulating the problem for choosing the optimal method of opening: an object function for underground transport; hoisting transport; surface transport to the consumer. The problem is solved in 3 Dimension (3D).

Key words: algorithm, bed, ore, vein, minerals, mine field.

INTRODUCTION

The design and practical implementation of mine fields opening is carried out under conditions of least reliability of information about the environment. Often this information is based on data gathered while developing analogous deposits or data gathered during the process of driving prospecting workings.

The term of exploitation of the basic development workings corresponds to the period of development of the mine field and every mistake or inaccuracy made when deciding on the deposition of openings has got serious economic consequences. Their gravity may turn out to be crucial and a premature close down of the mine company be reached at a later time.

PROBLEM FORMULATION FORMING OBJECT FUNCTIONS TO SOLVE THE PROBLEM

Solving the problem of choosing a location for the opening was posed as early as the times of the first attempts to introduce strict calculation methods when deciding on the elements of the underground mining technology. For the first time the problem was treated scientifically in the works of the Russian scientists B.I. Bokiy and L.D. Shevyakov. From a modern perspective, the formulation and the solution of the problem are considered by all means three-dimensionally. In addition to the choice of a location for the main haulage gateway, another particularly important problem is the way the deposit is uncovered. In this way a general problem consisting of two mutually connected conditions is formed, the solution to which should be regarded as an example of the use of a comprehensive approach in the present day computer technology used in mining.

When determining the opening’s location in the case of bedded deposits, the problem has got fairly representative solutions. They are universal, i.e. they can be used irrespective of the degree of dip and number of beds representing the deposit. Construction expenses for the openings and transport expenses along them are used as criteria published by (Vellev M. 1986). The object function is of the form:

$$w = f(x,y,z)\ , \qquad (1)$$

where x,y,z are the running coordinates of a reference coordinate system possessing pre-arranged rules for its orientation. The problem’s solution is made easier if the actual earth surface is approximated with the plane:

$$z = ax + by + c\ z, \qquad (2)$$

where a, b, c are number coefficients. Then the object function w depends solely on the coordinates x and y. From the system of irrational equations:

$$\frac{\partial w}{\partial x} = 0; \qquad (3) \qquad \frac{\partial w}{\partial y} = 0, \qquad (4)$$

by means of successive approximations are determined the coordinates of the optimum location of the basic development working published by (Vellev M. 1986).

When developing ore deposits the problem is further complicated by at least three additional, but at the same time essential factors:

- Very often ore veins have got uneven distribution of useful components, they are represented by separate ore poles, which further on for convenience will be called ***geological blocks***;
- The separate geological blocks in the ore veins have got clearly identifiable inclination, which in depth has considerable influence on the dimensions and boundaries of the mine field, i. e. inclination influences the topology of the network of extraction workings for the opening and preparation of the levels;
- The thickness of ore veins (geological blocks) is uneven, which means that the amount of loads corresponding to the reserves in the separate blocks on the separate levels will be different.

To these characteristic features we should add the features of the surface terrain and the distance to the consumer. In this way premises are created for the development of a general algorithm for the choice of a technical solution for the opening of the mine field, based on the three-dimensional formulation of the problem. A reference coordinate system is introduced, oriented in such a way that the whole mine field is situated in the positive octant. The (y) axis coincides with the ore vein's strike line, while the (x) axis is oriented crosswise to the strike line, i.e. along the way of dipping.

The object function (w) is composed to measure transport work along the level haulage gateways and crosscuts, respectively w_g and w_{cr}, lifting work along the vertical shaft – w_l and surface transport work to the consumer w_c.

The authors' main claim is that geological blocks situated on the separate levels can be described very precisely in space using their indices and coordinates. In this case it is necessary to identify the centres of gravity of the geological blocks on the separate levels by means of the distance R to the origin of coordinates for the reference coordinate system, the transfer stations P on the levels and crosscuts, the amount of loads Q from each stope block within the boundaries of the level, the intersection point F, determining the intersection point of the vertical shaft with the earth surface, the location of the consumer K. The problem is considered taking for granted that the consumer's location has been determined in advance, i.e. its coordinates are known $K(x_k,y_k,z_k)$. The problem thus formulated necessitates the introduction of triple indexation - i, j, k where:

i = 1..n – the index showing the sequential number of the geological blocks (poles), located on the level, and situated along the ore veins' strike line;

j =1..m – the index showing the location of the following vein, determined crosswise to the strike line;

k =1..t – the index showing the level's sequential number within the mine field.

In this case, when the stope block's geometry is predetermined (length L_{bl} and height $H_{bl} = H_l$, where H_l is the level's height) it is possible to calculate the amount of reserves, respectively amount of loads Q[ijk], to be transported to the surface and then to the consumer.
Clearly

$$\sum_{i=1}^{n}\sum_{j=1}^{m}\sum_{k=1}^{t} Q[ijk] = \frac{z_{bal}(1-a_e)}{1-b}, t \qquad (5)$$

where: z_{bal} – is the balance reserve in the mine field; a_e – exploitation losses; b – ore dilution. In this case z_{bal}, a_e, b are constants, i.e. the influence of the mining technology is not taken into account.

When the geological blocks' coordinates on the separate levels are known it is possible to calculate the geometrical dimensions, the amount, the productivity and the location on the separate levels by means of three angles (fig.1):

- The angle of dip α of the vein or the geological block in the plane 0xz, α varying on the interval $0 \le \alpha \le 180°$;
- Angle of inclination φ of the geological block on the separate levels in the plane 0yz, φ varying on the interval $0 \le \varphi \le 180°$;
- The angle of azimuth β of the geological block on the separate levels in the plane 0xy, β varying on the interval $0 \le \beta \le 360°$.

The calculation of parameters such as geometrical dimensions, amount, productivity, takes place once the angles α, β, φ have been determined by means of the geological blocks' coordinates on the separate levels (fig.1):

Projected length (S) of the [ijk]-th geological block on the separate levels as the remainder of the maximum and minimum (y) coordinates:

$$S[ijk] = y^{max}[ijk] - y^{min}[ijk], m \qquad (6)$$

Actual length (S_r) of the [ijk]-th geological block on the separate levels as the remainder of the maximum and minimum (y) coordinates:

$$S_r[ijk] = (y^{max}[ijk] - y^{min}[ijk]) / \cos(\beta[ijk]) = S[ijk] / \cos(\beta[ijk]), m \qquad (7)$$

* *actual thickness* (m_r) of the [ijk]-th geological block on the separate levels as the remainder of the maximum and minimum (x_r) coordinates:

$$m_r[ijk] = x_r^{max}[ijk] - x_r^{min}[ijk], m \qquad (8)$$

* *projected thickness* (m) of the [ijk]-th geological block on the separate levels as the remainder of the maximum and minimum (x) coordinates:

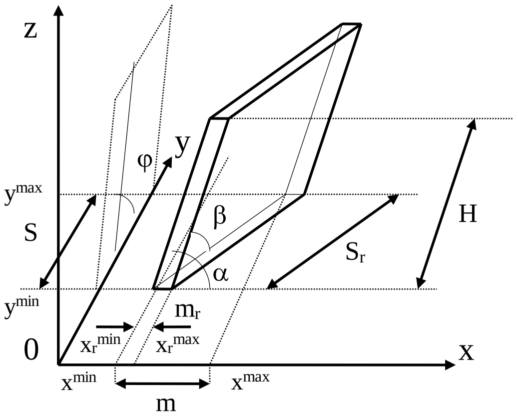


Figure1. Geological block on a separate level in (3D) space

* *actual thickness* (m_r) of the [ijk]-th geological block on the separate levels as the remainder of the maximum and minimum (x_r) coordinates:

$$m_r[ijk] = x_r^{max}[ijk] - x_r^{min}[ijk],\ m \tag{8}$$

* *projected thickness* (m) of the [ijk]-th geological block on the separate levels as the remainder of the maximum and minimum (x) coordinates:

$$m[ijk] = x^{max}[ijk] - x^{min}[ijk] = S[ijk].\cos(90 - \beta[ijk]) = \\ = S[ijk].\sin(\beta[ijk]),\ m \tag{9}$$

* *the distance from the origin of coordinates to the centre of gravity* of the projected [ijk]-th geological block on the respective level along the (y) axis:

$$R[ijk] = (y^{max}[ijk] + y^{min}[ijk]) / 2,\ m \tag{10}$$

* *the distance from the origin of coordinates to the centre of gravity* of the projected [ijk]-th geological block on the respective level along the (x) axis:

$$R_x[ijk] = (x^{max}[ijk] + x^{min}[ijk]) / 2,\ m \tag{11}$$

* *productivity* per square metre (1m^2) of the geological blocks on the separate levels:

$$p[ijk] = m_r[ijk].\gamma,\ t/m^2 \tag{12}$$

where γ - is the density of the deposit, t/m^3.

In the case of inhomogeneous deposits $\gamma[ijk]$ is used to determine the productivity of each geological block on the separate levels.

- *Quantity of reserves* in each [ijk]–th geological block on the separate levels:

$$Q_r[ijk] = S_r[ijk].H[ijk].p[ijk] = S_r[ijk].H[ijk].m_r[ijk].\gamma,\ t \tag{13}$$

where H[ijk] – the inclined height of each of the [ijk]-th geological blocks on the separate levels. That height is constant, when α stays constant. It is determined by the location of horizontal workings.

* *The projected quantity* along the (y) axis is:

$$Q[ijk] = Q_r[ijk].\cos(\beta[ijk]),\ t \tag{14}$$

* *The projected quantity* along the (x) axis is:

$$Q_x[ijk] = Q_r[ijk].\cos(90 - \beta[ijk]) = \\ = Q_r[ijk].\sin(\beta[ijk]),\ t\,. \tag{15}$$

The optimum work of *underground transport* along horizontal workings solely (drifts, crosscuts) without vertical transport is represented by an object function. The object function is divided into five global intervals along the respective axis of study, one of the global intervals being subdivided. If y is taken as a running coordinate on the interval [0, R_y] depending on the intervals studied for the function we get:

interval $0 \le y \le y^{min}[1jk]$ (formula 16):

* interval $y^{min}[1jk] < y < y^{max}[1jk]$ (formula17)

$$w_1(y) = \sum_{j=1}^{m}\sum_{k=1}^{t}\sum_{i=1}^{n}\{Q[ijk].(R[ijk] - y)\},\ t.m \tag{16}$$

$$w_2(y) = 0.5\sum_{j=1}^{m}\sum_{k=1}^{t}\{\{(y - y^{min}[1jk])^2 + (S[1jk] - y)^2\}.H[1jk].p[1jk]\} + \sum_{j=1}^{m}\sum_{k=1}^{t}\sum_{i=2}^{n}\{Q[ijk].(R[ijk] - y)\},\ t.m \tag{17}$$

- interval $y^{max}[1jk] \le y \le y^{min}[njk]$ (formulas18 and 19):

On this interval, divided into two subintervals, it is necessary to introduce the following additional conditions:

i = 1...n; r = 2...(n-1); 1 < r < n; When i = r,

where r shows the location of the fixed element i as an ore body or a geological block on a separate level. The running coordinate y (or x) either intersects or does not intersect the projection of the i^{-th} element. This element is called - r :

- irst subinterval $y^{max}[ijk] \le y \le y^{min}[i+1jk]$ from the global interval $y^{max}[1jk] \le y \le y^{min}[njk]$, where y does not intersect the projection of the i$^{-тия}$ element (formula 18):
- second subinterval $y^{min}[ijk] < y < y^{max}[ijk]$ from the global interval $y^{max}[1jk] \le y \le y^{min}[njk]$, where y intersects the projection of the i^{-th} element (formula 19):

* interval $y^{min}[njk] < y < y^{max}[njk]$ (formula 20):

* interval $y^{max}[njk] \leq y \leq R_y$ (formula 21);

$$w_{31}(y) = \sum_{j=1}^{m}\sum_{k=1}^{t}\sum_{i=1}^{r-1}\{Q[ijk].(y - R[ijk])\} + \sum_{j=1}^{m}\sum_{k=1}^{t}\sum_{i=r}^{n}\{Q[ijk].(R[ijk] - y)\}, t.m \tag{18}$$

$$w_{32}(y) = \sum_{j=1}^{m}\sum_{k=1}^{t}\sum_{i=1}^{r-1}\{Q[ijk].(y - (R[ijk])\} + 0.5\sum_{j=1}^{m}\sum_{k=1}^{t}\{\{(y - y^{min}[rjk])^2 + (S[rjk] - y)^2\}.H[rjk].p[rjk]\} + \\ + \sum_{j=1}^{m}\sum_{k=1}^{t}\sum_{i=r+1}^{n}\{Q[ijk].(R[ijk] - y)\}, t.m \tag{19}$$

$$w_4(y) = \sum_{j=1}^{m}\sum_{k=1}^{t}\sum_{i=1}^{n-1}\{Q[ijk].(y - (R[ijk])\} + 0.5\sum_{j=1}^{m}\sum_{k=1}^{t}\{\{(y - y^{min}[njk])^2 + (S[njk] - y)^2\}.H[njk].p[njk]\}, t.m \tag{20}$$

$$w_5(y) = \sum_{j=1}^{m}\sum_{k=1}^{t}\sum_{i=1}^{n}\{Q[ijk].(y - R[ijk])\}, t.m \tag{21}$$

$$w(y) = w_1(y) + w_2(y) + w_{31}(y) + w_{32}(y) + w_4(y) + w_5(y), t.m . \tag{22}$$

The optimum work of underground transport has got the same form if the other x axis is taken as a running coordinate on the interval 0 to R_{xx} in order to study the function. This may be obtained under the following conditions: $Q[ijk] = Q_x[ijk]$, $R[ijk] = R_x[ijk]$, $S[1jk] = m[1jk]$, $S[njk] = m[njk]$ and $R_y = R_{xx}$.

In the isolated case of parallel running veins which do not exhibit considerable variability along the strike line, the optimum work of transport along the horizontal workings – drifts and crosscuts, taking into account vertical transport along the z axis and transport to the consumer could be represented by the object function:

$$w(x, y, z) = 0.5\sum_{j=1}^{m}\sum_{k=1}^{t}\{\{(y - y^{min}[ijk])^2 + (S[ijk] - y)^2\}.H[ijk].p[ijk]\} + \sum_{j=1}^{m}\sum_{k=1}^{t}\sum_{i=1}^{n-1}\{Q[ijk].|(y - R[ijk])|\} + \\ + \sum_{j=1}^{m}\sum_{k=1}^{t}\sum_{i=1}^{n}\{Q[ijk].|\{x - (R_x[ijk] \pm \Delta x)\}|\} + \sum_{j=1}^{m}\sum_{k=1}^{t}\sum_{i=1}^{n}\{Q[ijk].(t.H - k.H + H)\} + \sum_{j=1}^{m}\sum_{k=1}^{t}\sum_{i=1}^{n}\{Q[ijk].H_p\} + \\ + \sum_{j=1}^{m}\sum_{k=1}^{t}\sum_{i=1}^{n}\{Q[ijk].\Delta z\} + \sum_{j=1}^{m}\sum_{k=1}^{t}\sum_{i=1}^{n}\{Q[ijk].\sqrt{(x - x_k)^2 + (y - y_k)^2 + (z - z_k)^2}\}, t.m \tag{23}$$

where Δx is the correction of coordinates along the x axis, due to the non-coincidence between the coordinates of the centre of gravity of each [ijk]-th body and the crosscut transfer station;

H – constant vertical height of the level;

H_p– height, measured from the highest point of the closest to the surface level to the lowest elevation of the surface (the terrain);

Δz – vertical height, measured from the lowest elevation of the surface to the highest elevation of the surface (topography relief);

x_k, y_k, z_k – consumer's fixed coordinates on the surface;

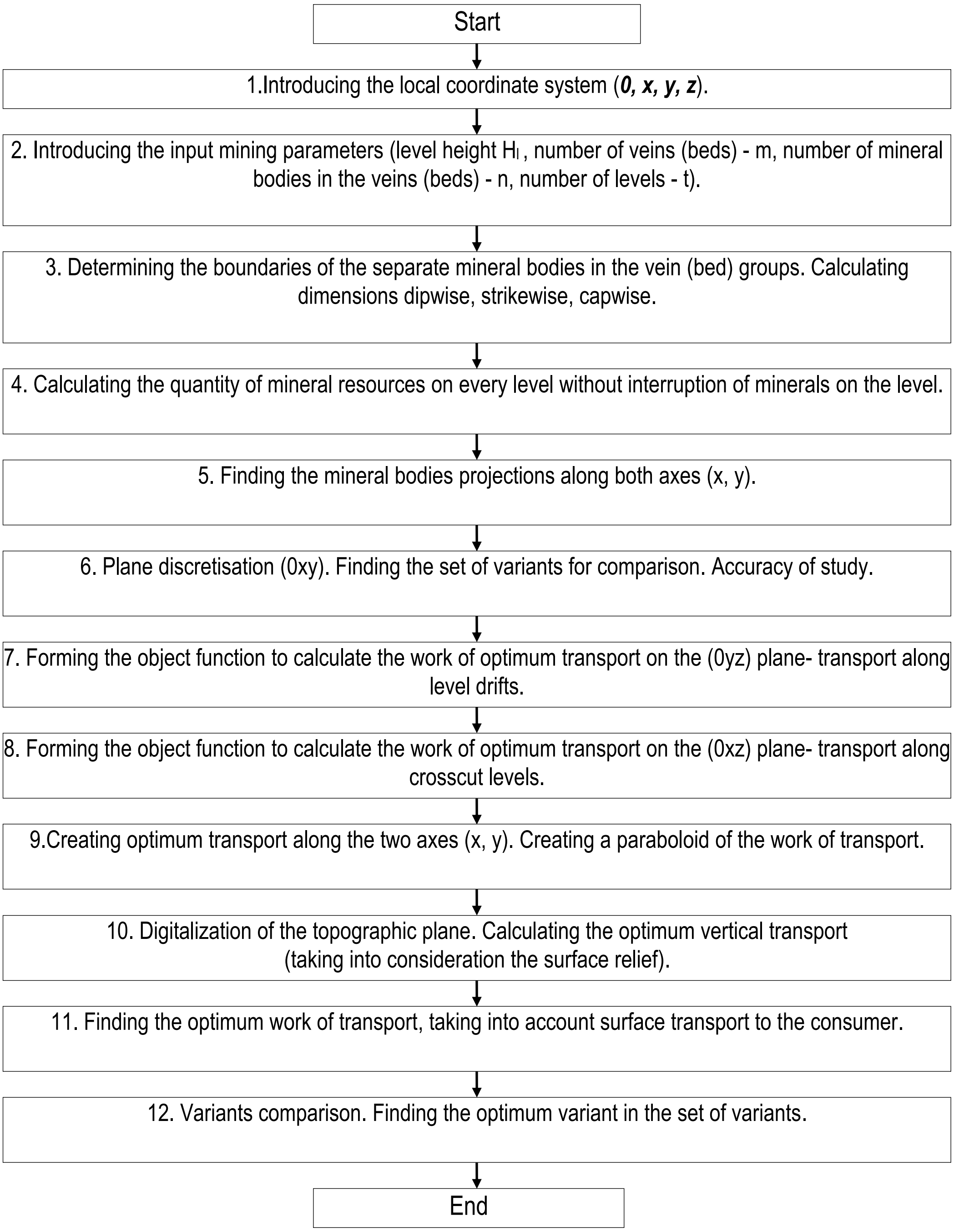
x, y, z – running coordinates.

GENERALIZED ALGORITHM FOR LOCATING INTO SPACE THE OPEN HOLE OF A BASIC DEVELOPMENT WORKING. ALGORITHM FOR THE 3D PROBLEM

The whole procedure for choosing a deposition for a vertical mine shaft and determining the optimum opening plan is in itself the algorithm, represented by means of a flow chart in fig.2. The main elements of the algorithm have been developed. The algorithm is an open structure allowing the unhindered addition of new elements pertaining to its improvement when additional limiting conditions are introduced.

CONCLUSION

The elaborated algorithm and the results obtained while solving the problem of choosing an optimum location for the deposition of a basic development working show that the object function has got a clearly identifiable minimum which facilitates its formalization. At the same time the functions describing the work of transport are in themselves curved surfaces, and this fact necessitates looking for an optimum solution in three-dimensional space.



Start

1.Introducing the local coordinate system (***0, x, y, z***).

2. Introducing the input mining parameters (level height H_l, number of veins (beds) - m, number of mineral bodies in the veins (beds) - n, number of levels - t).

3. Determining the boundaries of the separate mineral bodies in the vein (bed) groups. Calculating dimensions dipwise, strikewise, capwise.

4. Calculating the quantity of mineral resources on every level without interruption of minerals on the level.

5. Finding the mineral bodies projections along both axes (x, y).

6. Plane discretisation (0xy). Finding the set of variants for comparison. Accuracy of study.

7. Forming the object function to calculate the work of optimum transport on the (0yz) plane- transport along level drifts.

8. Forming the object function to calculate the work of optimum transport on the (0xz) plane- transport along crosscut levels.

9.Creating optimum transport along the two axes (x, y). Creating a paraboloid of the work of transport.

10. Digitalization of the topographic plane. Calculating the optimum vertical transport (taking into consideration the surface relief).

11. Finding the optimum work of transport, taking into account surface transport to the consumer.

12. Variants comparison. Finding the optimum variant in the set of variants.

End

Figure 2

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INFLUENCE OF ENGINEERING GEOLOGICAL FACTORS ON THE CHOICE OF WAY OF AN UNDERGROUND WORKING

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ABSTRACT
Article defines the term “competent rock mass”. Taking the definition as a cryterium, a classification for the contour stability of an underground opening is proposed. Engineering- geological aspects, influencing rock mass competency are discussed.
On the base of analysis of rock mass competency, general principals of tunnel rout choice, support systems and tunnelling technologies are proposed.

To drive an underground working is a challenge to nature. It leads to instantaneously stress release of contour of the opening and change of natural field of stresses in the rock mass. Under certain geological conditions, this could cause serious problems in driving and maintaining the underground workings, such as:

- rock bursts;
- rock falls or cavings;
- floor heaving or rock squeezing;
- water inflow: dripping, inrush, impoundment;
- inrush of quicksand.

All this leads to higher costs of construction and maintenance, accidents and manlife losses even to impossibility to use the working.

Forecasting and avoiding or minimizing the influence of the above mentioned adverse events could be reached only as a result of careful engineering- geological investigations and correct estimation the obtained information about the way underground working is to follow.

The underground construction terminology includes the term “competent rock mass”, not giving definition about it. We suggest for competent rock mass to understand such one, which assures stable condition of the opening without any support during all the time of it existence. In other words an opening is stable if there are not any fragments to split and fall from the contour of the working and convergencies can not be observed without any instrumentation.

Rock masses poses different competency and it is result from the geologic and technical conditions. On this basis the authors propose to classify them into four classes:

- ***competent*** - as they were defined above. If they are mine workings, no need of support. If they are tunnels because of the higher safety standards and longer service period, support is shotcrete or even cast in situ concrete;
- ***of middle competency*** - the contour of the opening is stable for a period from a week up to several months. After that period from the back and the walls small or not so small rock pieces split and fall and small rock cavings are possible. The radial convergencies of the contour are from 0 to 2 cm The more often used supports are shotcrete, combination of rock bolts and shotcrete or cast in situ concrete with some higher load bearing capacity than in previous class;
- ***of low competency*** - rock mass assures stability of the contour from a day to a week. In such rock mass, if permanent support is built in above- mentioned period, temporary support is not necessary. The convergencies of the contour could reach for the boundary period values of 10 cm. In this conditions supports must poses high bearing capacity, or to be yielding ones (with predetermined yield);
- ***incompetent*** - rock masses, in which the contour is stable from 0 to 24 hours. In them radial convergencies of upheaving or rock squeezing reach tens of centimeters or even could lead to total closure the opening. In the same class are the high water bearing rock masses, in which water or quicksand inrush is possible. Driving mine workings in such conditions is possible by using temporary or fore supports or by using not conventional technologies (earth pressure balance machines, rock freesing or grouting e.t.c.). Supports must be with maximal bearing capacity (and yielding ones in development mine workings), in water bearing rocks- impermeable.

Rock mass competency is influenced by many factors: genesis, mineral staff, rock properties, folding, faulting and fissuration, water logging, natural field of stresses, tectonic disturbances and many other factors.

Analysis of above mentioned factors permits, by rational choice the way working must follow, to avoid or minimize their unfavorable influence on rock mass.

One of the most important factors concerning rock mass competency is the origin of rocks. The best conditions for tunneling propose igneous rocks. Intrusive ones poses high strength, and negligible porosity. They are resistant against weathering, particularly if they content abundant quantity of quartz. Some lower competency poses extrusive rocks. Their porosity is bigger, strength lower and permeability higher.

Sedimentary rocks, in accordance with their mineral staff, cementing material and degree of lithification are taking place in all four classes of competency. Monomineral rock masses of limestone, plasterstone and rock salt assures enough competency to a definite depth. For clastic rocks, the most important thing, influencing rock mass stability is the binding matter. If binding material is silica, rock mass could be as competent as igneous one. In lowering order could be mentioned carbonate and hematite cement. The worst competency could be waited from clay binding, especially in the cases, when rock contains abundance of water or quicksand.

For clayey rock masses very important factor is the degree of lithification. The higher degree of lithification, the higher density, the better binds between particles, the more competent rock mass.

Igneous and sedimentary rocks could be altered by metamorphism or metasomatism. In general if an igneous rock passes trough metamorphism, the competency of the rock mass gets lower because of anisotropism, lamination, changes of mineral staff. A typical example is alteration of granite into gneiss.

Just the opposite, if a sedimentary rock passes metamorpism, as a result of recrystallization processes, rock mass upgrades its properties. Good examples are marbles, clay schists, and calcareous shales.

More of metasomatic changes lead to deterioration of rock mass stability. Argillization, pyritization, chloritization, propilitization are processes which alter low resistant to hydrothermal impact rocks into clayey minerals.

Dolomitization of carbonate rocks leads to higher rock porosity, and if later they are put under weathering, in certain geological conditions- to disintegration to sand.

Quartzitization of sedimentary rocks is allays a reason for better competency of the rock mass.

Fissuration and jointing strongly deteriorate rock mass stability. Reasons for rock fissuration and jointing are too much: rock origin, tectonics, weathering, conditions of lava cooling, metamorphism, metasomatism, tunneling technology. The exiting jointing planes lead to increasing filtration properties, make rotation and tangential convergences of rock blocks much easier.

The influence of fissuration and jointing on rock mass competency is in functional relations with natural field of stresses and roughness of jointing planes. This influence is minimal if there are high compressive stresses perpendicular to jointing planes and the surface of above- mentioned planes are rough. In this sense, unfavorable are geologic conditions, where above- discussed stresses are tension ones or negligibly small compressive.

In a jointed rock mass, competency is a function of the angle between the direction of tunnel axis and direction of jointing planes. The most favorable is the case, when the angle between them is about 90°. Less favorable are the cases in which tunnel axis and jointing planes are parallel. The worst situation is when tunnel axis crosses jointing planes at 60°- 80°.

When a rock mass consists of strong, brittle rocks at depth over 800- 1000 m, its natural jointing assures energy dissipation as a result of rotation and displacements of rock blocks, forming the contour of the opening. By this way danger of rock bursts and rock spitting is lower.

But it is well- known fact, that going to depth intensity of fissuration becomes smaller and smaller, and width of fissures negligible narrow (in other words possibilities for rotation an displacements of rock blocks are very small) and the danger of rock bursts increase, especially in the area with compressive stresses concentration. In smaller depth rock bursts are connected to older rock formations and areas with stress concentration as a result young folding or residual stresses from older tectonic processes.

The practice showed, that not allays enough attention is paid to this question. Later it becomes a cause for larger tunneling time, higher cost and useless risks. A bad example of such an error is Western tube of. **V**itinya tunnel. Improper placement of tunnel way caused many rock falls, additional expenses and risks for supporting occurred cavings, longer period for tunnel construction, higher cost of maintenance. Nowadays the water, infiltrating trough concrete lining will destroy it in very short time.

Another reason for bad rock mass competency is weathering. Weathered rocks become much more fractured, water impermeable and less stable. Buried weathered rocks could be found in bigger depth in earth crust. Tunneling and later maintenance in such conditions are more expensive.

What are leading requirements for the choice of the way tunnel is going to follow?

Everything must start with a profound engineering- geological prospecting of the region. It must find all factors, influencing rock mass competency, such as: geological formations, postgenetic geodynamic processes and changes, caused into rocks: folding, faulting, weathering, underground water, jointing e. t. c.

Discovered tectonic forms must be discussed in aspect natural stress field. If safety standards for the future working are too high, quantitative results of earth crust stresses must be obtained.

It is advisable to be avoided all zones, where the rock mass is incompetent or of low competency. Usualy, this zones are in connection with dynamically fed water bearing strata or quicksand, rocks undergone metasomatic changes, clastic rocks on low degree of lithification with clay binding between particles.

The way, tunnel is going to follow must avoid areas with highly developed fissuration systems. If this is not possible, the best decision is tunnel to intersect jointing planes at right angle. Going back to Vitinya tunnel example, we can say that the length of the working was quite enough faulted zone to be avoided or crossed at right angle.

When working is at shallow depth and must cross jointed rock, the rout it must follow should be laid in areas, where horizontal compressive stresses are maximal and their direction is perpendicular to the jointing planes. But if there is a danger of rock bursts, just the opposite- the way, tunnel should follow must be led in distressed areas, proposing possibilities for potential deformation energy dissipation.

It is not advisable to drive a working trough buried weathered rocks. Possibilities should be searched to go round them.

In coal mines at great depth in hard, strong host rock good results are obtained when future tunnel way is previously undermined and after dome of equilibrium formation, underground working is placed into the distressed zone, near the top of natural arch.

Choice of the tunnel rout must be made on the basis of minimum two well analyzed in engineering- geological aspect variants, brought roughly to full cost, including the risk estimation (as in financial, so in safety aspects). For an example, in ore mines, exploiting vein deposits, always must be compared variants: in vein working, or stone drift.

Good results offers the system “engineering”, which unites designing and driving the working. It permits if unfavorable geologic circumstances occur during tunneling, rational correction to tunnel road to be introduced.

Never should be forgotten the fact, that correct choice of the way tunnel must follow is possible, if specialists, engaged with designing and driving it poses certain level of qualification. This may be impose the need for some changes into educational programs of mine specialists and engineering- geologists too, where more profound study of hard rock to be included.

CONCLUSION

The analysis of engineering- geological factors, influencing radically rock mass stability permits the specialists to create rational choice of the rout an underground working must follow. This will assure minimal risks, costs and good standards of safety during tunneling and exploitation period of the working.

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NEW EFFECTIVE AND ECOLLOGICALLY FRINEDLY TECHNOLOGY FOR DEMOLITION OF BLAST DEMOLITION OF EXCISE DIMENSION ROCKY PIECES WITH CUMULATIVE ACTION CHARGES

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SUMMARY

As a result of the work performed under a US AID—Ecolinks sponsored project, developed was a new technical process for Blast demolition of excise dimension rocky pieces with cumulative action blast charges for the condition Skakavitsa Rock Quarry, State Bulgarian Railroad Company. At the previously used technology the fragmentation of the excise dimension rocky pieces was achieved through utilization of open charges with various weight placed above the rocks. The simultaneous detonation of several rocky pieces was accomplished through Detonation cords, which led to large expense of explosives, large quantity of flying rocks and substantive air blast. The developed new technology included:

1. Introduction of the newly developed charge construction for demolition of excise dimension rock pieces
2. Classification of the oversize rock in four types by the location of the primary flat surface for the purpose of achieving a more effective placement of the charge.
3. Development of a new scheme of charge initiation, according to rock’s size and location;
4. Proposing a change in the blasting agent and its packaging.

The following targeted objectives were reached through the implementation of the new technology for secondary blasting operations:

- Reducing the quantity and cost of explosives for demolition of a 1m^3 rock piece by over 50% ;
- Decreasing, by over 50%, the toxic gas emissions resulting from demolition of oversize rock;
- Eliminating flying rock and largely minimizing the air blast in the blasting field;
- Over 25% reduction in the costs of the secondary blasting operations

All this measures contribute to more ecologically friendly and effective demolition of excise dimension rocks.

The new technology was developed under contract with Ecolinks, initiative of the US Agency for International Development, conducting assistance for quarry Skakavitsa, the Bulgarian State Railroad Company. This technology could be successfully used for varied conditions in extraction of inert materials.

The goals and main objectives of the developed technology were:
1. Reduction the relative cost of explosives for demolition of 1m excise dimension rocky piece with over 50 % -- from 2-3 кg/m^3 to 1-1,3 кg/m^3;
2. Decrease of over 50 % the toxic gas emissions resulting form demolition of excise dimension rocky pieces;
3. Elimination of flyrocks and substantial reduction of the shock wave at demolition of excise rocky pieces in the blasting field;
4. Over 25 % reduction in the cost of secondary blasting operations.

These main objectives are achieved through the implementation of the following technological solutions, part of the new technology:
1. Classification of the resultant excise dimension rocks and their organization in four major groups, based on rock’s volume. The excise dimension rocky pieces are compactly built up of sand, small to medium grains, and on rare occasions coarse. Their weight is between 2,2 and 2,5t/m^{3m} and have Protodiakonov coefficient for firmness of 6 to 8.

The characterizing proportions of the excise dimensions rocky pieces are given in Table 1.

Table 1 The characterizing proportions of the excise dimensions rocky pieces

№	Length,m	Width,m	Height,m	Volume,m^3
1	1.5	1.2	1	1.5-1.8
2	1.5	1.2	1.2	1.9-2.2
3	1.5	1.5	1.2	2.2-2.7
4	2	1.5	1.2	3-3.6
5	2	1.5	1.5	3.8-4.5
6	2	2	1.5	5-6
7	2.5	2	2	8.8-10
8	3	2	2	10.5-12

2. Classification of the excise dimension rocky pieces by the location of the primary flat surface for the purpose of achieving more effective placement of the charge.
3. Introducing new charge construction for demolition of excise dimension rocky pieces. The charges are prepared with cumulative gaps at Skakavitsa quarry.

4. Achieving blasting of a group of excise dimension rocks based on their size and location through the use of a new process of charge initiation with a millisecond delay.
5. Deployment of more suitable from ecological and effective standpoint cartridged emulsion-type explosive with brand name Lazarit, chosen after extensive testing and examination at the Minenergo Ltd. testing center. Determined was that this explosive emits fewer toxic gases in the environment, fragments the excise dimension rock pieces more efficiently, and has a relatively low market price compared to other available explosives.
6. Use of stemming over blast charges aiming at reduction of toxic emissions and attaining of better rock fragmentation.

The charges are prepared at the field from the cartridged emulsion type explosive Lazarit and explosive type Amonit 6, as in the contact area between the charge and the rocky piece is formed cumulative gap through placing a V-shaped thin laminated iron sheet with size of 0,35 to 0,5mm.

Figure 1 below shows a prepared charge for Secondary Blasting operations.

Table 2 gives the charge parameters according to the size and location of the excise dimensions rocky pieces.

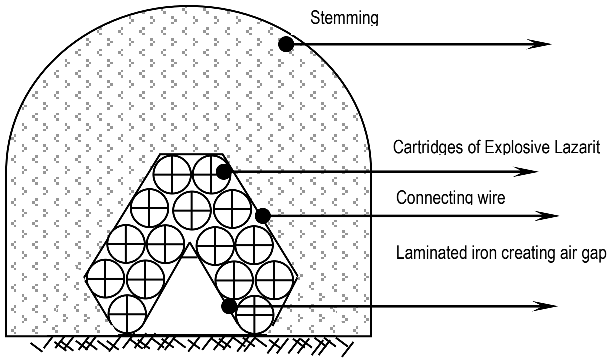

Figure 1. New charge construction for secondary blasting

Table 2 Blasting Parameters,types and modifications of the CHARGES WITH CUMULATIVE ACTION

Charge №	Modification	Charge mass, kg	Charge length, mm	No of explosive, cartridges	No of cartridge lines	No of blasting caps ЕДМР-25	Volume of oversize rock, m^3	Size of stemming, dm^3
1	I	2	240	5	1	1	до1	15
2	I	2,2	240	11	2	2	1,5-2,2	30
	II	4,4	460	22	2	2	2,5-4,5	60
3	I	3	240	15	2	2	2-3	40
	II	6	480	30	2	2	4-6	80
	III	9	480	45	2+1	2	6-9	150
4	I	4,8	240	24	3	2	3,6-4,8	70
	II	9,6	480	48	3	2-4	7,5-9,5	120
	III	10	480	50	3+1	2-4	8,5-10	150

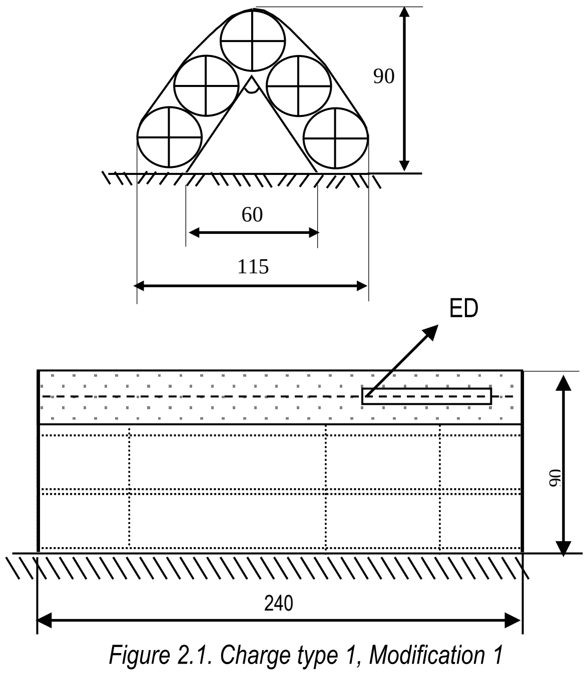

Figure 2.1. Charge type 1, Modification 1

The principal charge construction corresponding to the four groups of excise dimension rocky pieces are presented in the documentation of the developed and approved technological process.

For fragmentation of the excise dimension rocky pieces at quarry Skakavitsa are applied four types charges prepared according to the size of the V-shaped profile, the number of the cartridges and the number of the lines of the explosive cartridges placed on the profile. The four types charge constructions corresponding to the four groups of rocky pieces described in Table 2 are shown in Figure 2.

Charge №1 is prepared of five 200 g- cartridged explosive evenly placed on the V-shaped laminated iron sheet, representing an equilateral triangle with length of the side 60 mm. This charge construction is designed for small rocky pieces (up to 1 m^3) and demolition of peaks. The length of the charge is 240mm.

Charge № 2 is constructed of 2 lines 200g cartridged explosive placed evenly on the V-shaped profile as in charge № 1. This charge is designed for rocky pieces with volume 2-4 m^3. There are two modifications based on the length of the charge -- 240 and 480 mm applied for 2,4 и 4,4 kg sized rocks respectively.

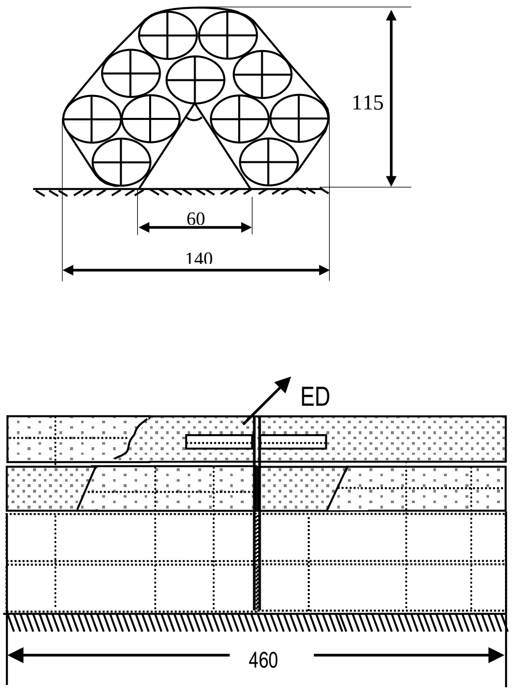

Figure 2.2.. Charge type 2, Modification II

Charge № 3 is composed of two lines explosives with the charge of the cartridge 200g placed on the sides of the triangle of the V-shaped laminated iron with length of the sides 90 mm. This charge type is used with excise dimension rocky pieces with volume from 2 to 9 m^3. Developed are three modification of this charge type for lengths of 240,480 and 480 and respective mass of 3 to 9 kg.

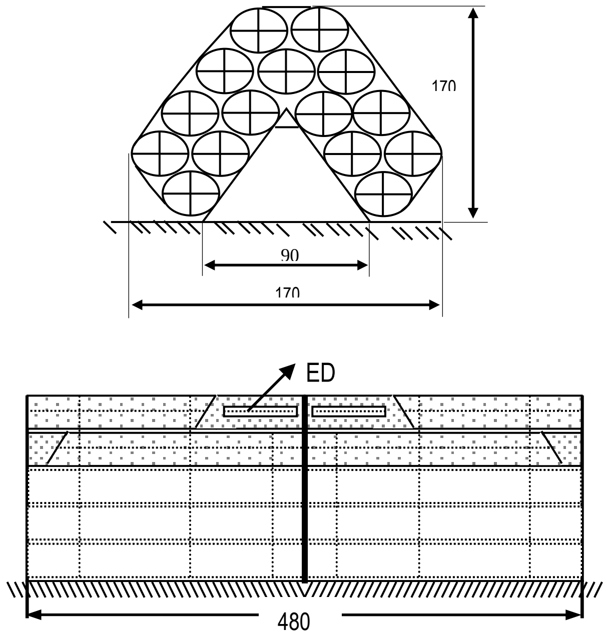

Figure 2.3. Charge type 3, Modification II

Charge № 4 represents three lines of cartridged explosive arraigned on the V-shaped laminated iron profile. Developed are three modifications with the length of the charge as follows: 240 mm - 4,8 kg; 480 mm - 9,6 kg; 480 mm - 10kg. The charge is used for the fragmentation and partial demolition of relatively large sized rocky pieces in the range of 4 - 10m^3.

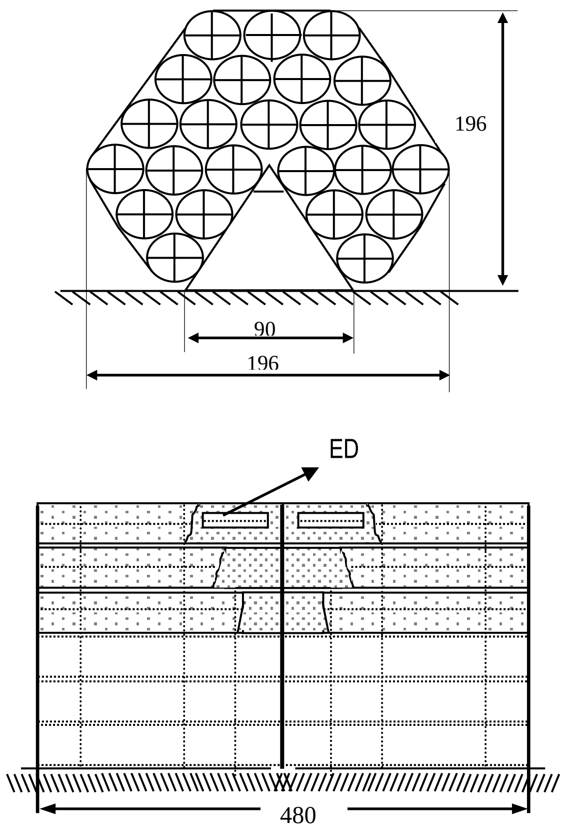

Figure 2.4. Charge type 4, Modification II

The preparation of the charges is conducted on the blasting field by two technologies:

- Technology 1. The charge is assembled from wrapped cartridges of explosive – five or seven, depending on the type of the charge to be used. The cartridges are strapped up with recycled wires of electric detonators. The advantages of this technology include: ensuring absolute compactness of the charge, rapid assembly of the charge at place of application, and its suitability for steep, vertical terrains. Disadvantage of the technology is the relatively large extensive preliminary preparation.
- Technology 2. The charge is constructed above the excise rocky piece as the stemming is applied simultaneously. Advantages of this technology are the firm securing of the charge to the object to be detonated and the fewer preliminary preparations. The technology, however, requires extra attention and skill for the preparation of the charge. Another disadvantage is that this technology is not applicable at steep and vertical terrains.

Figure 3 presents scheme for situating of the prepared cumulative charge on rocky piece with applied stemming.

The implementation of the newly developed technology for Blast demolition of excise dimension rocky pieces with cumulative action blast charges achieved the main objectives of more effective and ecologically friendly secondary blasting operation at quarry Skakavitsa.

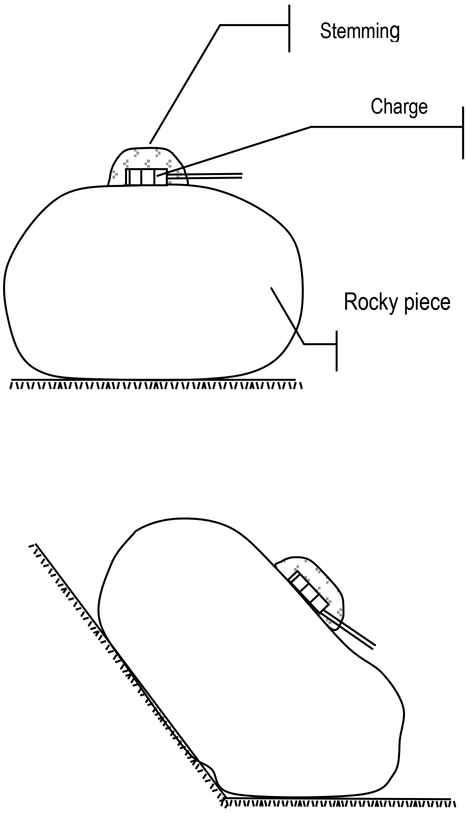

Figure 3. Placement of charges over rocky pieces

The developed and implemented at quarry Skakavitsa new technology for demolition of excise dimension rocky pieces, utilizing charges with cumulative action lead to the following conclusions:

1. The developed technology is practical, feasible and allows the preparation of the cumulative charges at the location of their usage.
2. The new technology achieves:

- Reducing the quantity and cost of explosives for demolition of a 1m^3 rock piece by over 50% ;
- Decreasing, by over 50%, the toxic gas emissions resulting from demolition of oversize rock;
- Substantially reducing the flyrock in the blasting field ;
- Significantly minimizing the air blast and sound at secondary blasting operations;
- Simultaneous demolition of many rocky pieces with the application of the electrical scheme of millisecond delay.

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STANDART REQUIREMENTS AND CONDITIONS OF RAILWAY TRACK INSIDE LINES IN MP DEBELT

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SUMMERY

It presents research of railway track regarding with publishing a “Complex technology for work at industrial area in MP Burgas”, 1990. The problems of inside railway lines are actual now with regarding recommendation of railways and bad condition of railway track. A summery of problems leads to conclusions in the following directions:

- Proposals for modifying of standards and conditions.
- Proposals for decisions regarding with track maintenance and organisation of capital repairs.

Kay words: designing, railway and track maintenance.

INTRODUCTION

Inside railway lines possess a number of special features in comparison with normal-gauge railway:

- They are constructed and operated for needs of some industrial company, accordingly with her technology of work.
- They have a temporary character and are subordinated of standards and conditions, different from these in use in railway administration.
- They are maintenance by special group in the plant, but special companies do capital repairs.
- Loads and pollution are differing from operating conditions in railway net.

At the base of comparison with existing railway net, structure and special features of the railway line, connecting MP Debelt (Promet) with st. Dolno Ezerovo, is checked. Conclusions and deductions have a more general application about inside lines in Maritza – Iztok, Kremikovtzi and so on.

GENERAL CHARACTERISTIC AND FEACHERS OF THE RAILWAY TRACK

Inside railway lines are basic kind of inside industrial transport. The first railway tracks origin for the needs of industry. Industrial lines are divided into outsides and insides.

Outsides railway lines

They connect the main railways with the plant. In accordance with speed they are classified. The highest in three different categories is I-st (speed from 40 to 65 km/h). Outside railway lines in MP Debelt beginning from st. Dolno Ezerovo to st. Metal (Table 1 and 2).

Table 1. General length – outside lines

Railway section	D. Ezerovo – Vaia	Vaia - Ravnetz	Ravnetz - Debelt	Debelt - Metal	General length, m
Length, km	1,600	8,700	9,840	3,410	23,650
Reduced length	1,678	9,080	10,211	4,540	25,509

Table 2. Railway lines – station tracks

Station	Vaia	Ravnetz	Debelt	Metal-outsides	Metal-insides	General
Km	0^{+000}	11^{+235}	22^{+000}			
Station tracks	4,460	1,000	6,270	2,200	2,200	6,438
Reduced length	9,000	1,000	13,175	4,395	4,395	13,620
R. switch	20	2	47	13	13	45

Ground bed and geometry of the railroad are designed for 130 km/h. Only the variants, connecting with st. Dolno Ezerovo are designed for speed of 40 km/h. Curves with radius 350 m and 265 m are permitted.

Inside railway lines

They service production of plant (Table 2, Metal - inside). The technological processes in plants, especially in metallurgical ones influence the construction of the track and features of their exploitation. The minimal radius of curves might reach up to 60-100m. Even in low speed, the loading up of outside rails from centrifugal forces in large. In MP Debelt, minimal radius of the horizontal curves is 190m. It corresponds railway switches to the used 49-1:9-190m. The crossings with roads in one level, inside the plant are 8 and the outside of plant – 9, but in the area of inside railway lines in st. Metal.

CONSTRUCTIVE CONDITIONS AND GEOMETRY OF RAILWAYS TRACK

Outside railway lines are designed for maximal speed of 130 km/h. In accordance with prognosis loads, the railway must be to the I-st category of main railway (Table 3).

Table 3. Superstructure

Element	Description
Rails	type S49, 25m, standard-gauge road
R. Clips	РАК 68И (type “K”)
Sleepers	ST4, 1480 sl./км (in straight) 1600 sl./км (in curve)
Ballast prism	40 cm, type IV by TU
R. switch	type 49-1:9-190; 49-1:7-190; 49-1:9-300

In practice, from the beginning of plant, there are no loads close to prognoses. In the section, only goods trains with considerable smaller speeds, move. Therefore, the railroad is builder with very high requirements and his construction doesn’t answer to real the conditions.

The longitudinal section of railway could be seen on fig.1 and fig.2. The elevation course is accepted at 0,72m under railhead level. Elevations are from Baltic benchmark. The maximum longitudinal slope is 15‰, according to the standards of designing of railway lines of I-st category.

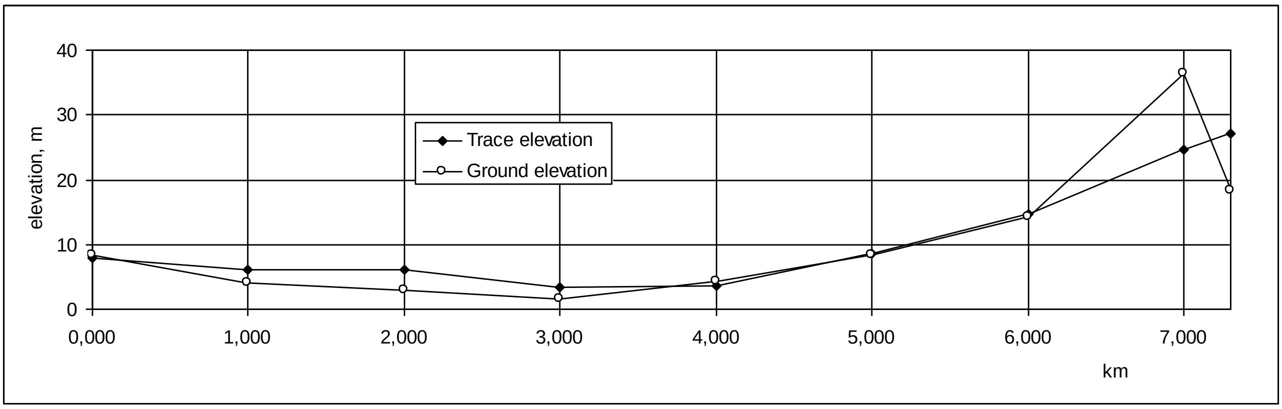

Figure 1. Dolno Ezerovo – Debelt - Plant km 0^{+000} – 7^{+300}.

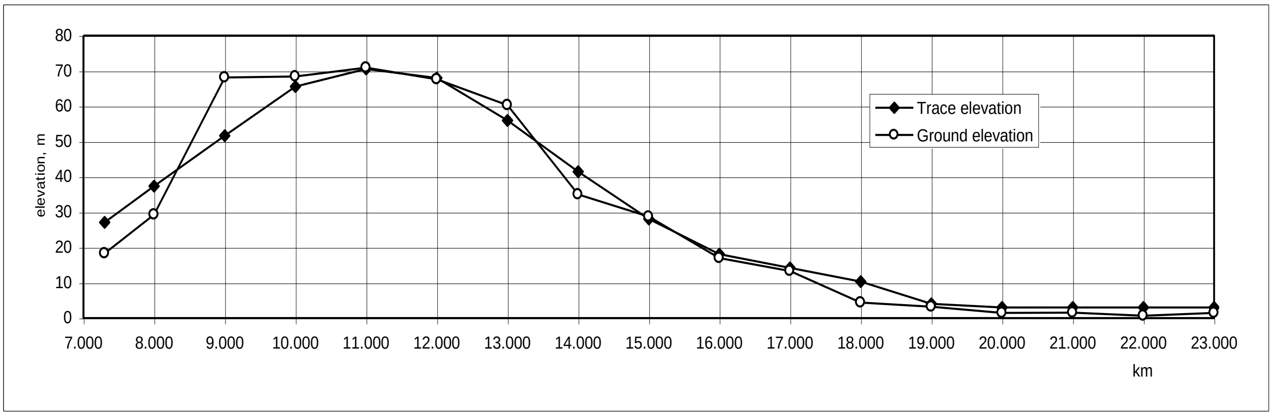

Figure 2. Dolno Ezerovo – Debelt – Plant km 7^{+300} – 23^{+000}.

Ground elevation is very low. At km 2+000 it reach’s 1,51m altitude. After that, it reach’s 70,91m at km 11+000 and near st. Debelt, ground level vary from 0,64 to 1,50m. (km 21+000 to km 23+000) at course elevation at 3,00m. These low elevations (close to see level) usually are accompanied with loose soil.

Soil subsidence is appeared to all length of line particular in embankments. Bridge-abutment bankseat in km17+937 is subsidence.

Loose grounds and higher ground water demand to build a lot of water – intake structures (Table 4 and 5).

Table 4. Water-intake structures

Type of culvert	number	General length, m
Assembled culvert L=1,00m	15	15
Assembled culvert L=1,50m	13	19,5
Assembled culvert L=2,00m	10	20
Platy culvert L=1,00m	3	3
Drain culvert Φ=1,00m	1	0,8
General	42	58,30

Railway area is crossed with a lot of roads. There are forests:

- 5 crossing in two levels.
- 2 temporary watched crossing.
- 5 automatic crossing (refused).

Railways crossing in inside lines are 16: 8 in industrial area and 8 near to the plant.

Table 5. Bridges

Type of equipment	km	length, m	General length, m
Reinforced concrete bridge	2^{+272}	3x13,50	40,50
Railway overhead crossing	2^{+318}	8,00	8,00
Railway overpass	2^{+440}	120	120,00
Reinforced concrete bridge	5^{+675}	8,00	8,00
Road underground crossing	6^{+735}	8,00	8,00
Reinforced concrete bridge	7^{+360}	3x12	36,00
Road overhead crossing	7^{+975}	6,00	6,00
Road overhead crossing	9^{+895}	6,00	6,00
Reinforced concrete bridge	11^{+471}	6,00	6,00
Road overhead crossing	14^{+200}	6,00	6,00
Reinforced concrete bridge	17^{+937}	3x13,50	40,50
General			285,00

TRACK MAINTENANCE AND REPAIRS

Track maintenance of line is serviced of personal, working for a plant accordingly publication of Todorov and Nikolov, 2000. Therefore requirement for maintenance for I-st category railway, and a lot of equipment's was rotten reduced length of railway (Table 1 and 2).

Accordingly her and accepted standard is determined necessary number of workers with correspondent qualification. In practice appointment workers and specialists is been 4 to 5 much under necessary. That leads to development of heavy permanent deformation in railway track and shorts inter repair periods.

Capital repairs are made from inside for the plant specialisation repair company.

CONCLUSION

Presented analysis for state of railway track of inside industrial lines in MP Debelt lead to some conclusions:

- Railway line is designed for speed 130 km/h, but goods trains are moved with the maximal speed 60-70 km/h. Only passenger trains must be moved project speed, but they are very little for a industrial railway line. Goods wagons are designed for the maximal constructional speed 70-80 km/h.
- Requirements for track maintenance of railway for 130 km/h are in contradiction with requirements for speed in ratio of size of rise-to-distance ratio and length of transition curve. The contradiction are leaded to no assumed loading, which in combine with loose soil is one of reason for bad state of railroad.

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A PROBABILITY APPROACH TO ANALYSING AND ASSESSING SOME NATURAL AND TECHNOGENIC FACTORS AND THEIR INFLUENCE ON THE RISK LEVEL IN SELECTING AN OPTIMAL MINING TECHNOLOGY SOLUTION

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ABSTRACT

The stability number N′, calculated on the basis of the Stability Graph Method developed in 1981, has been widely used in selecting the mining technology. The indices determining the stability number N′ have a random character so that its calculation is suggested to be performed by applying simulation based on the Monte-Carlo method. The hydraulic radius S is considered as a random variable along with N′. The procedure demands the introduction of limiting conditions resulting from the structure of the mining method and extraction technology. This approach requires analysis and assessment of alternative solutions, each characterised by a certain risk level. Criteria for the final selection of optimal technology are the technical and economic indices and, in particular, production costs, damage caused by losses and ore contamination, safety costs, accident prevention costs. The procedure thus presented allows to select a strategy based on a reasonable risk in taking the final solution.

In working steeply inclined ore deposits, the orebody thickness and physico-mechanical properties of the ore and wallrock are some of the strictest limiting conditions for determining the mining method to be applied in the stope. The most favourable conditions for mining and the highest technical and economic indices, respectively, can be achieved for stable ores and wall rocks and orebody thickness of over 5 m. Preconditions are created for high intensity of mining operations with low ore contamination, which is typical of sublevel blasting stoping with caving mining methods. With decreasing the degree of stability of the wallrock, the application of open stoping methods becomes impossible. Then the proportion of sublevel caving methods rises significantly. By degree of mining intensity these methods are not less effective than the open stoping methods but their major drawback is ore contamination since most of the ore is drawn while in contact with caved rock.

Transition zones exist where it is difficult to determine with certainty the expediency of applying one of the two mining methods mentioned above. The degree of stability of the wallrock can be evaluated by different criteria and approaches but the stability number N’ is a sufficiently representative index judging by its wide application in practice. The stability number N’ allows to assess the varying geometry of the stope and, mostly, its length L_s and width B_s. Then, besides the economic indices of prime cost, damage caused by losses and ore contamination, we can use the stope dimensions and especially those structural components related to the use of highly productive mechanisation for drilling holes, their charging, loading and ore delivery. From this point of view, the tendency to increase the height of the sublevel is obvious. A volume extracted at one time is directly proportional to the sublevel height. That means higher mining intensity and rate of development of mining operations.

The categorization of the ore and wallrock into medium-stable to unstable leads to considerable changes in the tendency mentioned above. When working medium-thick (2-5 m) orebodies, splitting (mining in splits) is applied, the split height depending on the mining and rock pressure control methods. Practice has shown that in working thick ore deposits (5-15 m), top slicing, mostly horizontal slicing is used. In those two cases, viz. splitting or cut-and-fill, either ascending or descending order of mining is used. The choice of ascending or descending order of mining has a decisive role on the nature of mining technology. The separate variants differ with respect to both mining intensity and ore quality, particularly concerning losses and contamination. As a natural property, the stability of ore and wallrock has the greatest effect on the mining method. The ascending order of mining requires a preliminary assessment of the stope back stability of the exploitation split, i.e. it (the stability) is a limiting condition for using ascending order of mining. If this condition is not satisfied, then the extraction should be carried out by dividing the orebody into slices with the necessary use of hardening fill. The other alternative, i.e. descending order of mining, is more versatile. It allows to cut both splits and slices using hydraulic and hardening fill. An essential drawback of that method is the lower mining intensity due to the large volume of support operations. In this case, the choice of ascending order as a more productive technology should be related to the stability number N' which appears to be the most appropriate parameter for stability assessment of the extraction workings.

Following the results from previous studies, it was found that the relationship N' = f(S) exists where S is the hydraulic radius of the open stope mined. On the other hand, $S = \frac{a.b}{2.(a+b)}$, where *a* and *b* are two mutually perpendicular dimensions of the open stope. Then, if the dimension corresponding to the stope length is L, and *b* is the dimension corresponding to the horizontal thickness of the orebody is M (M = B_s), we can determine the degree of stability of the stope back in relation to the selected stope length L_s and orebody thickness (the slice width, respectively) B_s. In other words, L_s = *a* ; B_s = M = *b*. The orebody thickness should be taken as a random variable. Therefore, the hydraulic radius S will also be a random variable. The approach to presenting the stability number N' as a random variable was discussed in Mihaylov, G., Trapov, G. (2001). Nevertheless, the choice of an engineering solution there is based on the fixed value of variable S. The identification of S as a random variable provides for a more detailed analysis of possible solutions. This is of particular significance for transition zones where the task of selecting a mining technology in relation to the stable state has no single answer. The procedure proposed evaluates both the random character of the natural factors and the risk level in the final selection of the mining technology for the particular natural and mining conditions.

In choosing an optimal engineering solution, the assessment criterion should take into account the income (I), expenditures (E) and risk level (R). These three parameters can be expressed as values thus making it possible to determine the anticipated average (average statistical) “profit” Q as a difference between the anticipated average income and expenditures:

$$Q=(1-R).I-R.E=I-R(I+E). \qquad (1)$$

The anticipated income (I) is usually higher when operating under higher risk conditions. For example, income as a result of operating larger stopes, decreasing investments for protection measures, etc.

The expenditures (E) are financial means to redeem losses, eliminate consequences of inflicted damage and safety costs (investments in protection measures, training of personnel for adequate response to an undesired event, etc.).

The risk level (R) is the probability for an undesired event to happen. Here the following sequence for its determination is adopted. Two variables are considered - N' (stability number) and S (hydraulic radius).

Factors (RQD, J_n, J_r, J_a, A, B, C) on which N' depends, have a probability character with certain probability laws of distribution.

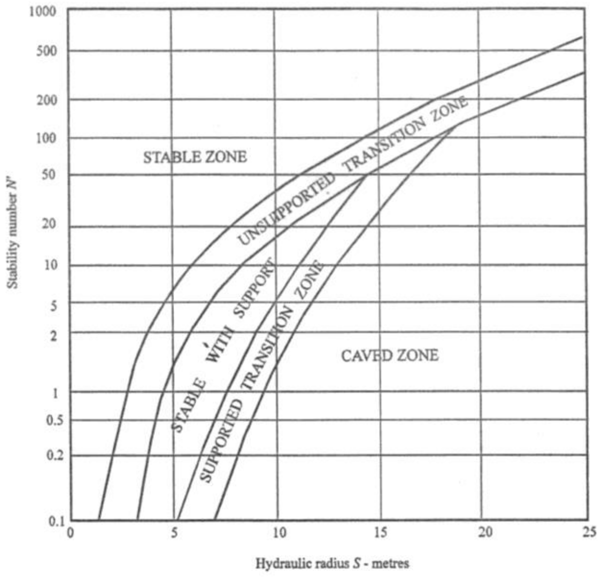

Figure 1

As was already mentioned, the hydraulic radius is obtained by the formula $S = \frac{a.b}{2.(a+b)}$, where *a и b* are the two mutually perpendicular dimensions of the open stope. The value of variable *a* is usually assumed to be within [40*m*; 100*m*]. For the particular simulation of the model we assumed *a*=60*m*. The values of variable *b* depend largely on the natural factor, i.e. the thickness of the ore vein being mined. Its consideration as a random variable taking values in the interval [2; 5] or [5; 15] is of particular interest. Then the hydraulic radius is also a random variable taking values in the intervals [0.97; 2.31] or [2.31; 6.00] and obeying certain probability laws.

The two random variables N’ and S, considered jointly, present a two-dimensional random variable X=(N’; S). The Monte-Carlo method has been applied in this paper and as a result, after taking into account the laws of distribution of N’ and S, we have obtained a set of values for X. This is the empirical law of distribution of that random variable. Now it becomes easy to find the risk level in adopting a strategy for operation corresponding to each zone in Fig. 1 (zone no.1 – STABLE ZONE; no.2 – UNSUPPORTED TRANSITION ZONE; no.3 – STABLE WITH SUPPORT; no. 4 – SUPPORTED TRANSITION ZONE; no. 5 – CAVED ZONE).

The values assumed for variables I and E as well as the values obtained for R and Q for a case corresponding to operation under competent rock conditions, are presented in Tables 1 and 2. They comply with the two probability laws (in the two intervals) of change in the hydraulic radius. The boundary risk values are given in the fourth row of the tables which are calculated by (1) of the condition Q=I-R(I+E)=0, i.e. $R_l = \frac{D}{D+E}$. These numbers allow to assess the maximum risk for which the anticipated average “profit” will be positive applying the respective strategy.

Table 1

Zone	1	2	3	4	5
I	60	65	70	62	55
E	40	48	50	40	35
R_l	0,6	0,58	0,58	0,61	0,61
R	0,05	0,95	1,00	1,00	1,00
Q	55	-42,4	-50	-40	-35

Table 2

Zone	1	2	3	4	5
I	65	65	70	60	55
E	40	50	55	40	38
R_l	0,62	0,57	0,56	0,60	0,59
R	0,08	0,94	0,98	1,00	1,00
Q	55,8	-43,1	-52,5	-40	-38

The analysis of the results obtained on the average “profit” shows definitely that the only winning strategy is no. 1. With all others the anticipated average profit will have a negative sign, i.e. when adopting any of those strategies, the anticipated average “profit” will actually be a loss in the average statistical sense. This is due primarily to the high risk level in adopting strategies corresponding to zones 2 - 5 for the two ranges of change in the hydraulic radius.

The values of variables I and E as well as the values obtained for R and Q for a case corresponding to operation under conditions of weak rock are presented in Tables 3 and 4. They correspond to the two probability laws (in the two intervals) of change in the hydraulic radius.

Table 3

Zone	1	2	3	4	5
I	60	65	70	62	55
E	40	48	50	40	35
R	0,54	0,53	0,94	1,00	1,00
Q	6,00	5,11	-42,8	-40	-35

Table 4

Zone	1	2	3	4	5
I	65	65	70	60	55
E	40	50	55	40	38
R	0,919	0,553	0,548	0,980	1,0
Q	-31,50	1,405	1,5	-38	-38

The analysis of the results obtained on the anticipated average “profit” for a change in the hydraulic radius by the first probability law (Table 3) does not show definitely which strategy, i.e. no. 1 or no. 2, should be preferred. If the aim is to operate at a lower risk level, strategy 2 should be chosen. The risk level will be 0.53, i.e. it will have a minimum value. Provided a strategy is chosen that will lead to a maximum anticipated average profit, then strategy 1 should be chosen since in that case the anticipated average profit will have the highest value, i.e. will be equal to 6.00 units.

When changing the hydraulic radius by the second probability law (Table 4), the anticipated average profit will be positive only with strategies 2 and 3. The best choice in this case should be the third strategy where the risk level is considerably lower (0.548) and the anticipated average profit (1.5 units) is a little higher.

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EXPERT SYSTEM FOR ASSESSMENT OF RISK FROM SPONTANEOUS COMBUSTION

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INTRODUCTION

Estimation of spontaneous combustion risk in mining of mineral resources, liable to self-heat, should start in the pilot stage of design and carry on during the whole lifecycle of a mine. Even after mine closure the self-heating risk remains an issue of environmental expertise.

Experience in many countries as well as experience in Bulgarian coal mining proved that underestimation or absolute lack of prediction for risk of self-heating in the stage of design had developed the application of exceptionally effective technological and other special preventive methods for self-heating risk mitigation either technologically impossible or economically unadvisable.

Number of technological parameters of methods for development and mining, laid down in the pilot stage of design, together with mine life-assuring systems specify the preliminary basis of the investment project. Right in the pilot stage, not only a prediction of risks but also a preliminary risk analysis of spontaneous combustion in the future mine is needed according to modern concepts for safety. This procedure is compulsory as it specifies requirements toward construction and detailed technological design of mine systems in the next stage.

In next conceptual stages of design, an optimization of different systems is required by comparing the $\frac{benefit}{risks}$ ratio for each option and selecting the system of maximum ratio. Each of the risks should be brought to an acceptable level in advance. However, materialization of spontaneous combustion risk involves hazard of not only economic but also severe human losses, and it may not be neglected in optimizing and decision making.

Real consequences of each spontaneous combustion depend on efficiency of methods applied to control its development. That is why assessing future consequences at the pilot stage of design seems unrealistic. The only reasonable approach at this stage is focussing the efforts on minimization of risk, i.e. reducing the probability or frequency of spontaneous combustion at the mine. Acting safety guides regulate a general principle for downward mining of coal seams liable to self-heat. Developing a specific instruction for prophylactics and extinguishing of spontaneous combustion in the mines is an obligation for each coal basin.

After a comprehensive analysis of the systems operating in other countries, the present article suggests a new system **SES** (SPONCOM EXPERT SYSTEM) for assessment of spontaneous combustion risk.

RECENTLY EXISTING EXPERT SYSTEMS

Severe consequences of underground mine combustions directed efforts of researchers toward investigating the reasons for high combustion risk in coal mines. As a matter of tradition, each country started its investigation by categorizing coal seams according to their natural predisposition to oxidation under low temperatures by analyzing coal ability to self-heat.

Later investigations were directed to influence of other natural factors on spontaneous combustion risk. Variety of methods of mining and technological parameters, which effected combustion risk, involved a search of approaches for categorising the mining technologies and ventilation schemes, according to combustion risk. Attempts for statistical differentiation of these factors into different groups of combustion risk did not provide a sufficiently reliable reason for applying this approach for categorization even in countries of extremely powerful mining industry. Modeling the effect of those factors on intensity of self-heating and a comparative expert estimation of combustion risk related to mining systems, ventilation schemes, abandoned coal losses, air leakage though fractures and porous media were the categories for grouping of mining and technological factors, at a particular grade level, in modern systems for spontaneous combustion risk analysis.

The system of the National Coal Board (NCB) (*Gill et al., 1971*) for estimation of self-heating risk included 6 natural characteristics F_i of the coal seam. The estimation itself of spontaneous combustion risk F_E was calculated by the dependency:

$$F_E = \left(\sum_{i=1}^{4} F_i \right) . F_5 . F_6 \qquad (1)$$

where: F1 – rate of coal metamorphism [grade];
F2 – pyrite mineralization of coal [grade];
F3 – hardness of coal [grade];
F4 – humidity of coal [grade];
F5 – natural temperature of coal [grade];
F6 – thickness of coal seam [grade];

There were 3 categories for risk of coal self-heating ability – low, medium and high risk. The system of former NCB, in spite of claiming to allow an estimation of spontaneous combustion risk in mines did not take into consideration the natural liability of coal seams to self-heat. Evidently, the authors definitively connect the natural liability of coal to oxidation under low temperature to the first four $\left(F_1 ... F_4\right)$ characteristics. However, mining practice did not confirm an analogy like that one. An example would be the comparison of spontaneous combustion risk of lignites at the West Maritsa basin to combustion risk of brown coal at the Bobov dol basin. This conceptual omission, in the NCB system, of the only characteristic that might be directly determined made impartial analogies to already developed coalfields impossible. The absence of coal seam ability to self-heat made the system rather approximate and even an analogous verification of expert results was not possible.

Relation between characteristic of natural ability of coal to self-heat and mining and technological factors, effecting on spontaneous combustion risk might be found out in the Polish system for estimation *(Karpov et al., 1981*). In the estimation (*PS*) the grade values S_i of the following factors were summed up:

S1 - Method of Mining [°C/min];
S2 - rate of coal recovery [°C/min];
S3 - Direction of mining the coal seam [°C/min];
S4 - Approach for isolating the goaf area [°C/min];
S5 - humidity of coal [°C/min];
S6 - Rock stress and fractures in the coal seams [°C/min];
S7 - intensity of ventilation of mine workings in the coal seams [°C/min],

With the characteristic of ability to self-heat, as follows:

$$PS = S_z^b + \sum_{i=1}^{7} S_i \text{ , [°C/min]} \qquad (.2)$$

Coal fields were subdivided into non-combustion risky, semi- and combustion-risky according to propensity for spontaneous combustion **PS**. The criterion of Olpinski (S_z^b) was accepted as a characteristic of coal ability to self-heat. It was determined by speed of temperature rise of heated coal for 1 min under laboratory conditions (*Maciejasz Z., 1972*). There were four categories for self-heating ability – lower, intermediate, upper intermediate and higher according to the value of S_z^b .

The described system made an attempt for binding natural liability of coal seams to self-heat to the technological factors for combustion risk estimation. Even more, the expert system reflected also factors, which reduced spontaneous combustion risk. A more common application of the system was restricted due to the following difficulties:

- Results of the method of Olpinski were not reliable for ability to self-heat of brown and lignite coals;
- The enormous weight appropriated to the factor S_z^b of ability to self-heat of coal in the overall estimation (2) of combustion risk was unrealistically high. Furthermore, all the methods for determining coal ability to sel-heat gave results, which varied within a wide range along the coal seam. The method of Olpinski was not an exception.

Not avoiding above remarks about significance of S_z^b it was worth emphasizing that factors S_i of that system provided an estimation of spontaneous combustion risk more complete than any other one.

The German system for estimation of spontaneous combustion risk (*Sudilovskii et al., 1988*) appropriated higher weight to the ventilation scheme and ten geological and technological factors B_i. Estimation was calculated for each ventilation scheme by the dependence:

$$D_e = \sum_{i=1}^{10} \left(B_i \bullet W_i \right) \qquad (3)$$

The expert appropriated to each factor B_i a weight W_i within the range from 1 to 10 and selected estimation B_i within discretely defined boundaries of the system. The expert gave his estimation for the following ten $(i = 1...10)$ factors B_i:

B1 - grade of metamorphism of coal [grade];
B2 - angle of coal seam dip [grade];
B3 – thickness of coal seam [grade];
B4 - pyrite content [grade];
B5 - tectonic faults [grade];
B6 - presence of admixtures in the roof [grade];
B7 - pillars [grade];
B8 - filling up of the goaf [grade];
B9 - filling up of caved out area in the shafts [grade];
B10 – air leakage [grade];

That system was more realistic in the aspect of technical factors. Weight, appropriated by the expert to each factor made incomparable the estimations of different experts. In this sense, the insufficiency of information for formalizing the estimation was substituted by the expert estimation, which was heavier than unbiased grades of factors in it. The system took indirectly into account the type and concentration of losses of coal along the caved out area, where most of spontaneous combustion originated, but that consideration was not relevant to modern mining technologies.

In 1995 the Pittsburgh Research Centre (PRC) of the former US Bureau of Mines put into practical use a computer program for estimation of spontaneous combustion risk, called **SPONCOM** (Spontaneous Combustion). Risk within that program was assessed according to grade effect of the following factors:

⇨ ***Characteristics of coal***, which effected on the rate of heat generation – reactivity, moisture content, pyrite and other inclusions. Three categories for ability to self-heat of coals were introduced: higher, medium and low. Coal critical self-heated temperature (SHT) was used for categorizing the relative reactivity of coal for spontaneous combustion. Black coal of different coal basins and seams revealed significant correlation between content of oxygen and spontaneously heated temperature SHT, and therefore the critical temperature was (*Guide on occupational …, 1992*). Humidity of coal was also considered an important factor for development of self-heating.

⇨ ***Geological factors*****,** considered as decisive for the system are: depth and angles of dip of the coal seam, thickness of coal seam, geothermal gradient, number and frequency of coal seams in the coal formation (seam density), availability of geothermal sources and old combustion sources, availability of geological faults, availability of an over-layer and pyrite formations immediately close to the mined out seam.

⇨ ***Mining conditions****:* method of mining; functions of pillars (supporting or isolating); rate of fitting of ventilation flow to the caved out area and refreshing of the ventilation scheme; slope of bottom of mined out area; sizes of panel and longwall, quantity of air for ventilating the longwall and leakage in the caved area; sources of spontaneous combustion in mined out areas or working zones, incoming or outgoing openings in mines, in pillars, hoppers or other mines exploiting the same seam; air temperature and humidity.

An undoubted advantage of the SPONCOM program was the attempt for specifying in details the mining and technical factors and involving of data about factual combustion risk of coal seams. The unrealistically high weight of self-heating ability, which had been defined in the Polish system, was overcome in the SPONCOM program. Disadvantages of the system for estimation, employed as a SPONCOM basis, were the high precision of formalisation of some of the factors without allowing their natural variation and the genetic impossibility for determining spontaneous combustion risk of mines, operated by different mining technologies. As all other systems of that kind it suggested an expert opportunity for determining self-heating risk as a probability. In spite of the evident advance it did not allow an estimation of sel-heating risk, because it did not present an approach for predicting the consequences of spontaneous combustion. Referring to brown and lignite coals that will be of increasingly higher interest in the future, obtaining of stable and formalized average estimations of SHT will be a serious difficulty.

FACTORS IN THE SES SYSTEM FOR ASSESSMENT OF RISK FROM SPONTANEOUS COMBUSTION

The **SES** system is especially useful for development of new deposits, sectors and coalfields in the case of insufficient statistical data for assessment of self-heating ability risk under similar conditions. It might be successfully applied into the search of technological changes, schemes for uncovering and mining in the aspect of prediction.

The following important natural and technogenic factors for estimation of spontaneous combustion risk were selected and incorporated in the suggested system.

1. Self-heating ability of coal seams

Self-heating ability of coals S^1	Factor *S* depending on coal metamorphism, determined by temperature interval				Grade estimation S^1
	Anthracites (150 – 200)°C	Black (150 – 200)°C	Brown (125 – 175)°C	Lignites (100 – 150)°C	
Lower ability	**< 8**	**< 9**	**< 10**	**< 4**	**1 - 2**
Intermediate ability	**8 - 12**	**9 - 15**	**10 - 16**	**4 - 8**	**2 - 6**
Higher ability	**> 12**	**> 15**	**> 16**	**> 8**	**6 -10**

2. Thickness of coal seam

m	< 1.20	1.20 - 2.40	2.40 - 3.20	> 3.20
S^2	**1**	**2 - 3**	**3 - 5**	**6 - 10**

3. Slope of coal seam

deg	0 - 15	15 - 30	30 - 45	45 - 90
S^3	**1**	**2**	**3**	**4 - 5**

4. Release of methane

$q,\ m^3 / Mg$	0	less than 5	5 - 10	10 - 15	> 15
S^4	**0**	**1**	**2 - 3**	**3 - 5**	**6 - 8**

5. Tectonic faults

faults	Not available	Low frequency	High frequency
Frequency along the strike	0	Less than 2/500m	More than 2/500m
S^5	**0**	**1 - 3**	**4 - 6**

6. Fitting of ventilation flow to the caved area

Rate of fitting	Ventilation schemes	S^6 for speed of air, *m/s*		
		≤ 0.5	$> 0.5 \leq 1$	> 1
Single fitting	UR, WR	**1**	**1.5**	**2**
Double fitting	YR, ZR, ZA	**3**	**3.5**	**4**
Triple fitting	HA, HR,YA, UA	**6**	**6.5**	**8**
Four-time fitting	WA	**8.5**	**9**	**10**

7. There are pillars, unmined coal seam, co-seams that belong to the zone of caving in the caved out area

Loss of coal	No	Limited	High
S^7	0	1 - 4	5 - 10

8. Natural temperature of coal in the massif

t^n_{coal}	15-20	20-25	25-30	30-35	> 35
S^8	**1**	**2 – 3**	**3 - 5**	**5 - 8**	**8 - 10**

9. Temperature and humidity of ventilation flow in risky zones for self- heating ability

t_{air}	S^9 for relative humidity of air, %		
deg C	< 65	65 - 80	> 80
15 - 19	**-3**	**-2**	**-1**
20 - 25	**0**	**1**	**2**
26 - 30	**2-3**	**3-4**	**3-5**
> 30	**5-6**	**6-7**	**6-10**

10. Prophylactic work for the caved area - S^{10}

Hydraulic filling	**- 10**
Inertizing of media	**- 8**
Pneumatic filling	**- 7**
Injection of frothed structures	**- 7**
Blocking with slurry	**- 5**
Powdering, blowing and injection of antipirogens	**- 3**
Necessary but not applied	**0**

11. Prophylactic work for pillars and ventilated contour of the caved area - S^{11}

Construction of artificial pillars for the shafts	**-10**
Filling of caves behind the support with hydraulic binding materials	**-8**
Filling of caves behind support with frothed materials	**-7**
Construction of artificial isolating pillar in the entry	**-6**
Injection of antipirogens in the shafts	**-4**
Necessary but not applied	**0**

The following conditions should be considered in the estimation of significant factors. Self-heating ability S^1 was estimated by the apparatus of Maevskaya (*Maevskaya et al., 1972*). Some unpublished data are presented below from investigations on gaseous characteristic of coal seams from the West Maritsa basin and the Dobroudja basin, which were used for determining the S^1.

In the type of schemes for ventilation, coded in the characteristic S^6, where indexes of schemes have the following two meanings:

- ∗ Inverse order of excavation -“R”;
- ∗ Direct order of excavation - “A”.

The characteristic S^2 showed the average thickness of coal seam within the boundary or coal field. High variations in the thickness of coal seam were shown by the characteristic S^5.

Last two characteristics have a negative grade value, corresponding to rate of reduction of spontaneous combustion risk in the sites of the most frequent self-heating. Those sites form a significant portion of the risk from spontaneous combustion, which is assessed in the aspect of prediction.

Categories, introduced by each of those 11 factors may be supplemented under observation of relative grade distance of the new category from the known and fixed ones.

FORMALIZING THE ESTIMATION AND CATEGORIZATION OF COMBUSTION RISK IN SES

These characteristics are used for calculating the spontaneous combustion risk according to the dependence :

$$D_S = \sum_{i=1}^{11} S^i \qquad (4)$$

Depending on the value of D_E fields and sites are categorized as:

$$\left.\begin{array}{ll} \textit{lower risky} & D_S < 22 \\ \textit{threathened} & 23 < D_S < 39 \\ \textit{risky} & 40 < D_S < 60 \\ \textit{higher risky} & D_S > 60 \end{array}\right\} \qquad (5)$$

When a spontaneous combustion is registered in the same seam in the vicinity of planned for mining field, the planned field appropriates a category of spontaneous combustion risk one unit higher than the category, determined by (5).

An example of the application of the system is shown in table 1. The threatened seam should be referred to the category “Risky” if an spontaneous combustion is registered in the same seam close to the projected field. The threatened seam from table 1 with a value $D_S = 24$ may be re-categorized in the aspect of prediction, as low risky if some antipirogens or blocking with slurry is applied - see tables of values for S^{10}.

Similarly to each other expert system, the SES also involves specifying the reliability of estimation of different experts. Critical is the case, when different experts put the projected site into different categories by their estimation (5). In those, and only those cases, experts are allowed to give different value Đå of analyzed factors, as this is shown in table 2. During the re-estimation experts re-order factors, according to their view about importance of factors and give them a consecutive number, from one to the number of factors in the table – for the example in the table – from 1 to 9.

Table 1

F A C T O R	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**Estimation of system** S^i
1. Self-heating ability of coal seam						**5**						**5**
2. Thickness of coal seam				**3**								**3**
3. Slope of coal seam			**2**									**2**
4. Release of methane			**2**									**2**
5. Tectonic faults		**1**										**1**
6. Fitting of ventilation flow to the caved area		**1.5**										**1.5**
7. There are pillars, unmined coal seam, co-seams that belong to the zone of caving in the caved out area				**3**								**3**
8. Natural temperature of coal in the massif			**2**									**2**
9. Temperature and humidity of ventilation flow in risky zones for spontaneous combustion					**4**							**4**
TOTAL		**2.5**	**6**	**6**	**4**	**5**	**0**	**0**	**0**	**0**	**0**	**23.5**
ESTIMATION OF SPONTANEOUS COMBUSTION RISK	**THREATENED**											**24**

Table 2

F A C T O R	Expert opinion Pe	Pe x S^i	0	1	2	3	4	5	6	7	8	9	10	Estimation of system S^i
1. Self-heating ability of coal seam	**7**	*49*								**7**				**7**
2. Thickness of coal seam	**6**	*30*						**5**						**5**
3. Slope of coal seam	**2**	*2*		**1**										**1**
4. Release of methane	**8**	*32*					**4**							**4**
5. Tectonic faults	**3**	*9*				**3**								**3**
6. Fitting of ventilation flow to caved area	**1**	*2*			**2**									**2**
7. There are pillars, unmined coal seam, co-seams in the caved out area	**9**	*54*							**6**					**6**
8. Natural temperaure of coalin the massif	**5**	*25*						**5**						**5**
9. Temperaure and humidity of ventilation flow in riskous areas	**4**	*16*					**4**							**4**
TOTAL	**45**	**21**	**0**	**1**	**2**	**3**	**8**	**1**	**6**	**7**	**0**	**0**	**0**	**37**
ESTIMATION OF SPONTANEOUS COMBUSTION RISK	**43.8**		**R I S K Y**											**37**

In those cases calculation of re-estimation is carried out according to the dependence:

$$DE = i \times \frac{\sum_i \left(S^i \times \left| P_i^E \right| \right)}{\sum_i P_i^E} \qquad (6)$$

For the example in table 2, two experts refer the analyzed seam to two different categories – threatened and risky. In the last column of the table, the estimation of the expert referring to a lower category is shown as an estimation of system.

After re-ordering of factors in column two according to their significance, and dividing the total $\sum_i \left(S^i \times \left| P_i^E \right| \right)$ in column 3 to the total $\sum_i P_i^E$ of column two and multiplying to the number of factors, used in the estimation $i = 9$ the re-estimation adopts the value DE = 43.5 and the threatened seam transfers into the category of risky ones.

The described procedure was performed by at least two experts as follows. First of all, each of the two experts completes his estimation S^i in the last column of table 1. If the total estimation D_s calculated by (4) refers the seam to one and the same category (5) the final estimation is adopted within boundaries of variation of individual estimations of the experts.

However, engineering prophylactic decisions – groups S^{10} and S^{11} have to be transferred to a lower risk category from a higher one.

When the total estimation D_s of two experts, calculated according to (4) refers the seam into different categories (5) the data, the have completed into sample-table 1 are re-copied in the last column of the sample of table 2. Each expert is given a table, which contains the estimation of the other expert and he has to re-order the factors in the second column, according to his own opinion. This crossing of estimations usually brings the re-estimation closer to only one category (5). If there is no bringing closer, the re-estimation is repeated and each expert works with his own initial estimation.

SELF-HEATING ABILITY OF COAL SEAMS

In the period 1979-1986, according to requirements of (*Guide on occupational …, 1992*) the employed coal seams in Bulgaria were categorized according to Self-heating ability (*Markov et al., 1989; Hristov et al., 1982, 1984; Michaylov et al.., 1984, 1980; Nanovska et al., 1985*), by the method of gaseous characteristic. Later, in 1993 the same method was applied for analyzing also samples from the deposit near the town of Bitolia in the Republic of Macedonia. The method of investigation (*Markov et al., 1989*) and data about self-heating ability of coal seams from the Bobov dol basin, which showed the highest value of the gaseous characteristic S, were published in (*Markov et al., 1989*).

A generalization of results and conclusions from investigations (*Markov et al., 1989; Hristov et al., 1982, 1984; Michaylov et al.., 1984, 1980; Nanovska et al., 1985*) is done in the table of the first factor S^1 of the SES system. The effective use of SES requires publishing of available data for the factor of gaseous characteristic S from investigations on coal basins in Bulgaria. Nevertheless of conservation taking place nor closure of some mines and sectors, reserves that may not be extracted in an economically acceptable way now, are supposed to be utilized in the future by either traditional or innovative methods. Due to restrictions of this edition only bench marking data for self-heating ability of coal from the West-Maritsa basin and Dobroudja coalfield will be presented.

Lignite coals, mined at the West-Maritsa basin, according to results in (*Michaylov et al., 1980*), are characterized with significantly lower propensity for oxidation. The gaseous characteristic S is calculated in the temperature interval 100 – 150 °C. This temperature interval is confirmed by the analysis of self-heating ability of coal from the East-Maritsa basin and the Sofia basin. The highest is self-heating ability of the "roof" seam, followed by "extra" seam and "bottom" seam. The lowest self-heating ability of coal, according to average data, in the West-Maritsa basin has the "Shompol".

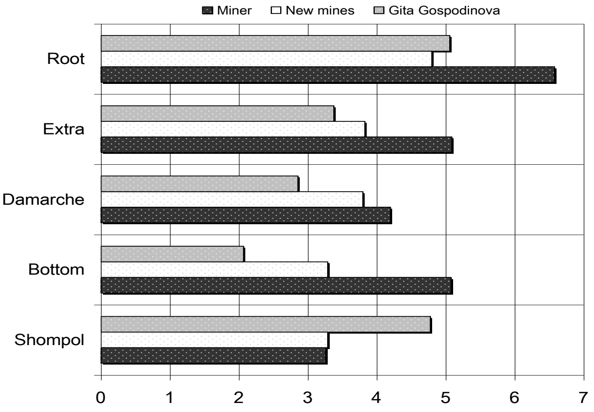


*Figure 1. Minimum values of **S** (on the x-axis) in the mines of the West-Maritsa basin*

A comparison of minimum and maximum values of self-heating ability is shown in figures 1 and 2. In the scale of generalization it may be considered that there is a tendency of reduction of self-heating risk along the thickness. Minimum values of spontaneous combustion risk vary within the boundaries from 2.1 to 6.5. The lowest spontaneous combustion propensity (absolute minimum observed) has the "bottom" seam at the "Gita Gospodinova" mine (fig. 1).

Maximum values of self-heating ability is shown by the coal seam in the field of "Miner" mine, as a whole and especially the first two sub-seams (fig. 2). Similar, but a little lower are the values, established in control analyses at the "Zfravets" mine.

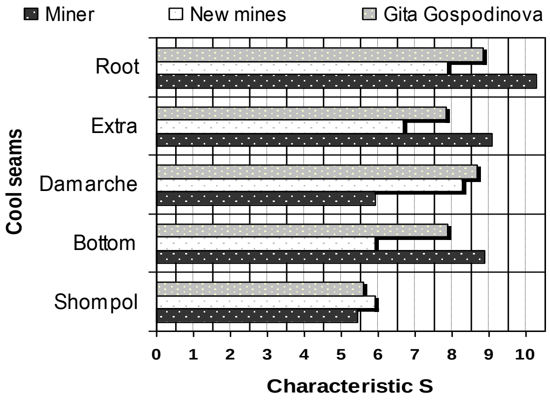


*Figure 2. Maximum values of **S** (on the x-axis) in the mines of the West-Maritsa basin*

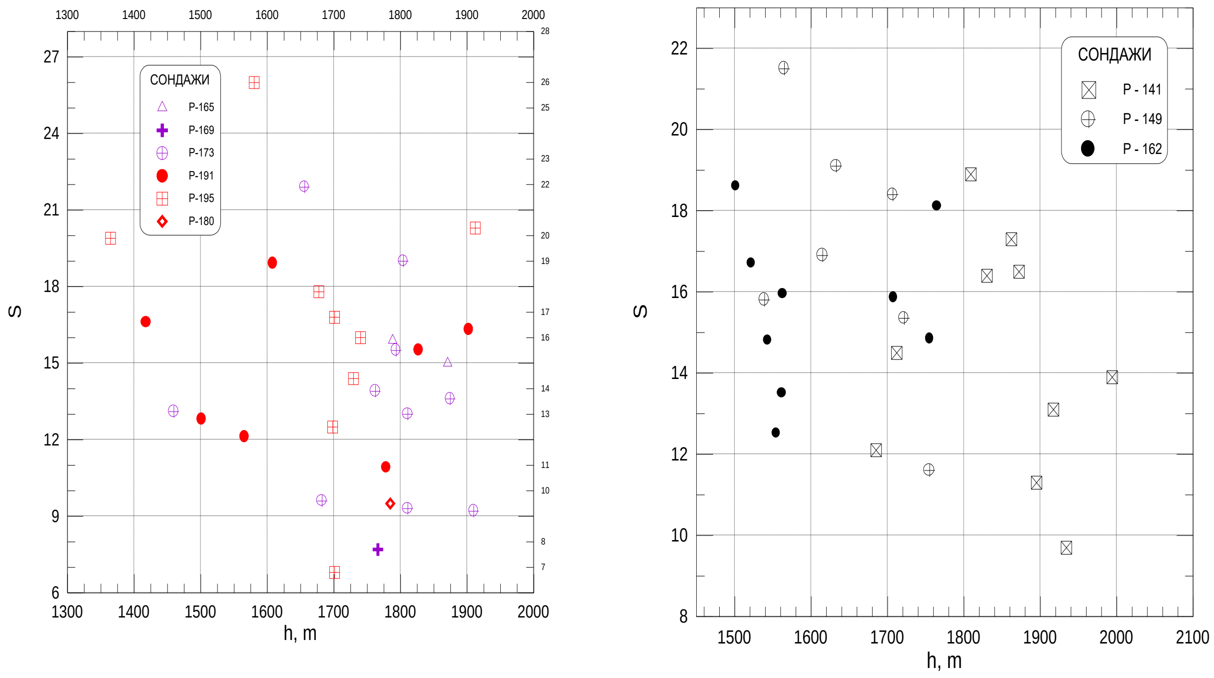
Even generally lower than ability of Bobov dol brown coal, self-heating ability of lignites from the West-Maritsa basin are variable enough for their categorization. The value of the characteristic S of that propensity varies for the sub-seams of coal layer from 2.07 to 10.28, i.e. 5 times. This is a rather wide range for their categorization.

The highest variation is shown by the "bottom" sub-seam. The highest variation of self-heating ability of coal seams is shown in the field of "Gita Gospodinova" mine, followed by the "Miner"mine.

The characteristic of self-heating ability S of coal samples (*Michaylov et al., 1980*) from the Dobroudja coal deposit varies as it is shown in fig. 3 – fig. 5. Denotations in fig. 3 and fig. 4 show the numbers of relevant wells.

With the increase of depth from the surface self-heating ability (fig. 3) decreases. This tendency is important and favorable but it should not be forget that S^1 is only one of the factors, determining the estimation of combustion risk.

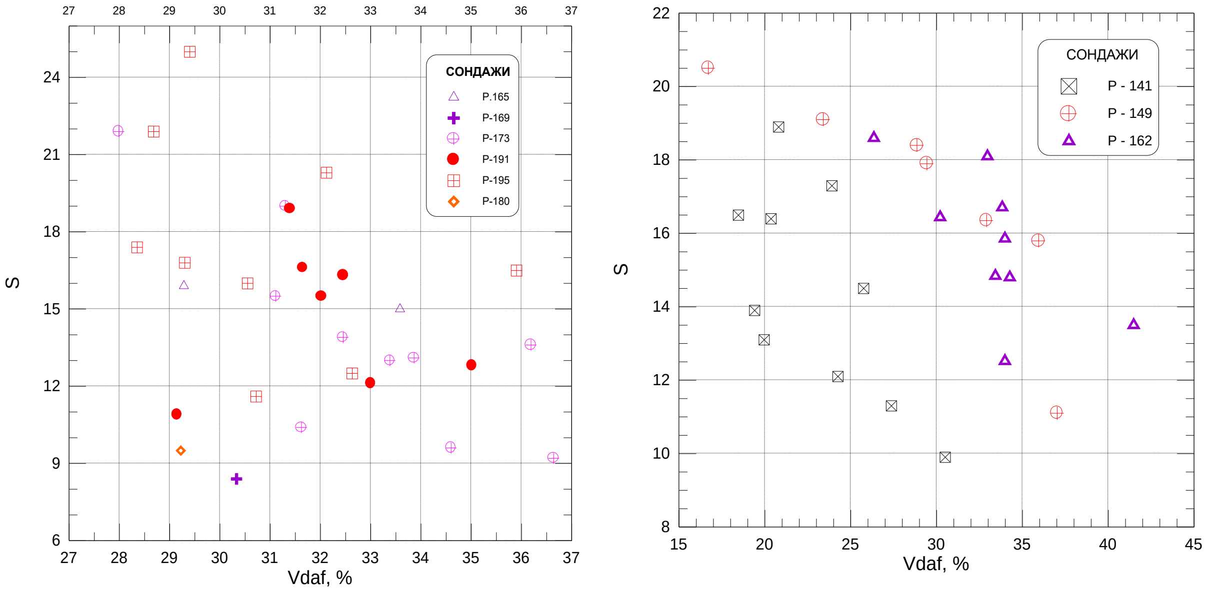
The tendency, even a fuzzy one, for reducing the factor S was observed and it increases with the increase of volatile content (Fig. 3).



a

b

Figure 3. Effect of the depth of occurrence h on the characteristic S for wells of ID numbers, shown in the denotations



a

b

Figure 4. Effect of volatile content V_{daf} on values of S for wells of ID numbers, shown in the denotations

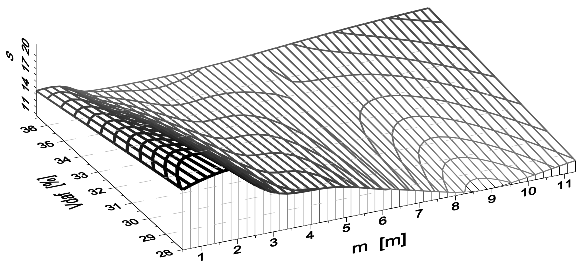


Figure 5. Effect of volatile content and seam thickness on self-heating ability

This tendency is more typical than unexpected. Its fuzz, according to data from analysis (Nanovska et al., 1985) may be explained by the differences of endogenous fracturing of coal and less with the character of pyrite mineralization.

Deviation from that tendency is observed for coal seams and sub-seams of thickness lower than 2.5 m (fig. 5) for which the natural propensity for oxidation under normal temperatures remains higher and reduces very little with the increase of content of volatiles.

CONCLUSION

A System for estimation of spontaneous combustion was developed in the aspect of prediction. The system overcame some disadvantages of well known similar methods for estimation by a selection of factors and definition of their importance, reasoned by experience of coal mining in Bulgaria. Two of the factors considered also the mitigation of combustion risk due to engineering prophylactic decisions. Two categorizations were suggested: categorizing of coal according to liability to self-heat depending on class of metamorphism and exploitation sites – according to spontaneous combustion risk. A procedure for approximating the estimations of two groups of experts was developed in the case of significant differences in the categorization of sites according to spontaneous combustion risk.

Data from studies on gaseous characteristic S of coal from the West-Maritsa basin and borehole samples from the Dobroudja coal basin were revealed. Data illustrated typical tendencies in the differentiation, variation and influence of different factors on coal ability to self-heat.

The SES system allowed an estimation of spontaneous combustion risk for mining of new coal deposits, fields and sectors. In recently acting mines it may be applied to estimating the efficiency of changes in technology and application of new methods for prophylactics of spontaneous combustion in the aspect of prediction. The system is universal enough and the only requirement to be adapted for application into other countries is the way of calculation of S^1 according to the method for investigating the self-heating ability of coal.
No matter if potentially prospective deposits and abandoned reserves in Bulgaria will be developed by traditional mining technologies or non-traditional methods, without coal excavation, will be applied the spontaneous combustion risk will significantly effect the selection of future method of exploitation and its parameters.

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CHANGE OF PARAMETERS OF ROCK DEFORMATION IN GIPSUM MINE "KOSHAVA" DEPENDING ON THEIR STRAINED STATE

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ABSTRACT

The results of experimental laboratory researches for definition of some parameters of deformation (modulus of elasticity and Poisson's Ratio) of gypsum raw materials from "Koshava" deposit are adduced. Parameters have been measured when appearing different values of stress in trial samples put on monoaxial impact. The same results have been received about changes of these parameters depending on values of stress when using static and dynamic methods. These dependences can be used for efficient definition of rock massif strained state around mine workings and pillars with help of seismic and acoustic methods.

Improvement of system for exploitation and technology of underground mining is connected with prognostication of rock massif state when changing of some parameters of applying systems or their perfected variants.

Except this for guaranteeing of safety during working it is necessary to receive information about strained and deformated state of rock massif around mine workings.

For receiving fast and constant information about state of rock massif large volumes different physical method are used. Especially successful is application of acoustic methods. They are based on the fact that parameters of elastic wave spreading in rock medium change when changing medium strained state. Important characteristics defining passing waves trough given rock are the velocities of their spreading. They depend to great degree on parameters of medium deformation. Thus, in order to judge about strained state of massif it is necessary to determine changes of these rock parameters depending of stress. For the purpose experimental laboratorial researches has been made. The main results of researches are adduced in this work.

Subject of researches is gypsum raw material from "Koshava" mine. The necessity of solving a number geomechanical tasks have appeared when working this mine.

It is exploited by the chamber and pillar system. The most using are band pillars, which length is 100 m, width is 17.5 m, height is 15 m and square pillars with section 20 x 20 m. Removed spaces are filled up by sand. This raise the coast price of raw material. Physical and mechanical properties of gypsum are studied by a number of authors but in spite of practical needs purposeful researches for determination of strained state influence upon the mechanical parameters using physical methods haven't been made.

In laboratorial conditions modulus of elasticity and Poisson's ratio have been determined. For this purpose cylindrical samples have been loaded with impact force P. Four indicators of clock type for measuring of longitudinal deformation and also four of such indicators for measuring transversal deformation have been fastening with the help of special device. Samples have been loaded by stepped way. Load has been increased until utter destruction of samples. Indicator readings have been averaged and relative longitudinal deformation $\varepsilon^{\uparrow} = \Delta l_{av} / l$ has been calculated by average Δl_{av} of base of measurement change. By average Δd_{av} of diameter d change relative transversal deformation $\varepsilon^{\rightarrow} = \Delta d_{av}/d$ has been calculated. After calculation of impact strain a static modulus of elasticity has been calculated as $\sigma/\varepsilon^{\uparrow}$ and μ ratio as $\varepsilon^{\rightarrow}/\varepsilon^{\uparrow}$. The strength of monoaxial impact *Rc* (σ_H) has been determined by value of destroying force P. Parameters of deformation are determined by ratio: strain/strength of monoaxial impact. Generalized diagram expressing typical dependence between this ratio and deformation (longitudinal and transversal) in the widest spread variety fine-crystalline gypsum with mediofoliated texture is shown on figure 1.

Independently of the fact that studied samples have been taken from different drills and are different to a certain extent in their structure, a number of common appropriateness's can be determined. Curvilinear part is observed at the beginning of diagram (picture 1). Further function becomes practically linear up to value of strain that is 80%-90% of strain impact. Experimental ratio strain / transversal deformation also has linear part but it is shorter. When value of strain reaches 60%-80% of destroying strain, the sharp growth of this deformation is observed – function becomes curvilinear. Ratio of transversal deformation $\mu = \varepsilon^{\rightarrow}/\varepsilon^{\uparrow}$ in linear parts of both dependences is constant, which corresponds to Poisson's ratio. Sharp growth of $\varepsilon^{\rightarrow}$ when strain is (0,6-0,8)Rc causes quick growth of transversal deformation ratio and it reaches values greater than 0,5. This is confirms by other investigators e.g. (Baklashov, I. V., 1988).

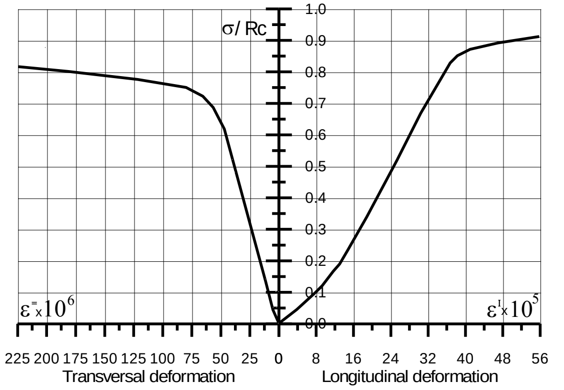
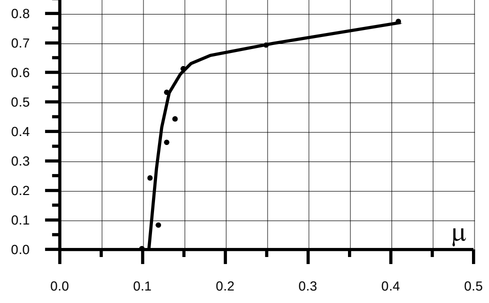


Figure 1. Dependence between ratio strain σ to strength monoaxial impact Rc – longitudinal $\varepsilon^{\uparrow} = \Delta l/l$ and transversal $\varepsilon^{\rightarrow} = \Delta d/d$ deformation

The character of received dependences strain/deformation gives possibility to judge about processes proceeding in samples. Primary curvilinear part of diagram of $\sigma(\varepsilon^{\uparrow})$ is conditioned by consolidation of sample as the result of micro fractures and pores closing. Linear parts of both diagrams characterize elastic pressing of mineral skeleton of rock medium. It is interesting to mention that almost right lines in dependences $\sigma(\varepsilon^{\uparrow})$ are approximately parallel, when loading and unloading accomplishes by stepped way. This mean that modulus of elasticity, which depends on quantity of reversible deformations, is close to modulus of deformation which depends on total deformation, and this correlation keeps up to great values of strain. Fast growth of transversal deformation when strain is 60% - 80% of destroying one can be explained by formation and solution of vertical microfractures which are parallel to acting load, since the dependence $\sigma(\varepsilon^{\uparrow})$ remains linear. Process of microfractural formation up to certain strain values to some extent is reversible, that is fractures close after external force stops acting. This is determined after unloading of sample. Presence of considerable remanent deformation is evidence of the fact that closing is not complete. Further growth of strain up to values that are 80% - 90% of strength when dependence $\sigma(\varepsilon^{\uparrow})$ also deviate from linear, loads to process of swift formation of fractures. These values of strain can be taken for long-term strength of strain. If value of strain is bigger than this, then destruction begins. Quickness of destruction is proportional to increase of the strain.

Changes of Poisson's ratio and modulus of elasticity depending on increase of strain (which is to destroying strain) is shown on the figure 2.



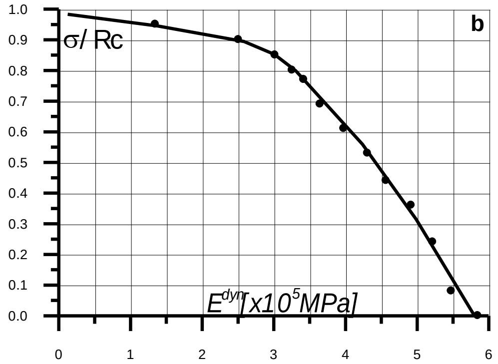


Figure 2. Dependence between a) Poisson's ratio and ratio strain/strength of monoaxial impact; b) static modulus of elasticity and ratio – strain/ strength of monoaxial impact.

Experimental determination of parameter of deformation of gypsum samples has been made with the help of dynamic method. For this purpose the velocity of elastic waves spreading has been measured when loading samples. Generalized results receivied during ultra-sonic research of samples are shown on figure 3.

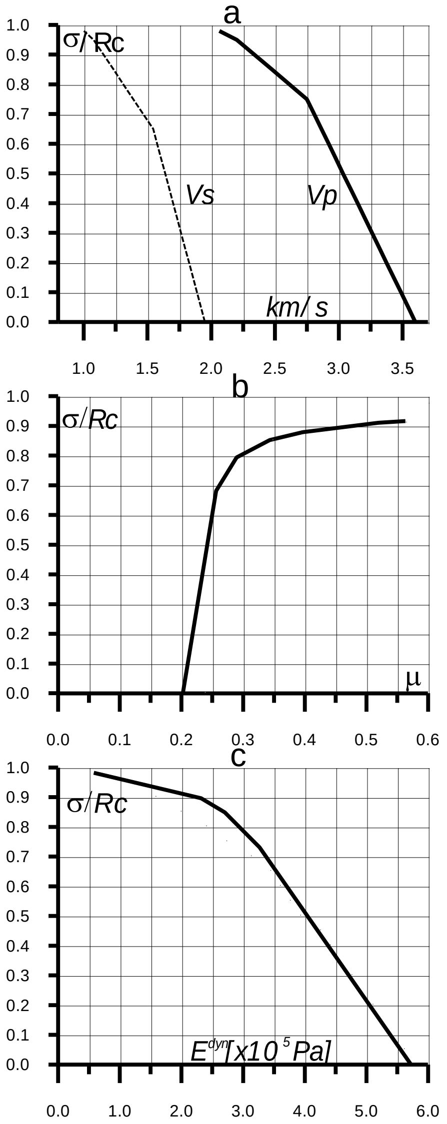


Figure 3. Dependences between ratio strain/strength of monoaxial impact and a) velocity of longitudinal (V_P) and transversal (V_S) waves; b- Poisson's ratio (μ); c- dynamic modulus of elasticity (E^{dyn}).

On adduced diagrams it could be seen that character of change of dynamic elastic characteristics that are determined by measuring of velocities of elastic waves is the same as that for static elastic modules and ratios that are determined by mechanical test of samples, to wit: there are considerable increasing of Poisson's ratio when strain is (0,6-0,8)Rc and decreasing of dynamic modulus of elasticity E^{dyn} when strain is (0.8-0.9)Rc.

The conclusion can be made that you can judge about change of strain state of rock massif (e. g. in pillar) by change of velocities of elastic waves and also by change of modulus of elasticity and Poisson's ratio, which have been measured using these velocities.

These open wide possibilities for constant periodic control of strain state of massif by seismic and acoustic methods.
It is very favorably in this case that accumulated potential power in the loading volume is released gradually. That is why it is possible to measure deformations when strain in rock massif approximate to destroying strain.

The undesirable processes in rock massif (formation of fractures, first stage of destruction) can be established when strain in rock massif is considerably less than destroying strain. This gives possibility to take measures for safe working in mine. When destroying samples frequent of waves is changed. These changes are the same that where described by R. Goodman, 1080.

Researches that have been carried out in laboratorial conditions give possibility to make conclusions that seismic and acoustic methods can be used successfully for division of pillars in two classes by degree of loading accordingly smaller and larger that conventional level 0.7Rc. Using measuring values of Poisson's ratio directly in massif can make this division.

For caring out researches of pillar's state mine "Koshava" is provided with specialized three- canal seismic station, set of geophones for registration of longitudinal and transversal waves and also with method of measuring. It is necessary to work out technological software, which gives possibility to receive space distribution of strain in massif automatically, and which doesn't demand special knowledge and skills from operator.

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A METHOD FOR SELECTIVE TECHNOLOGICAL FLOWSHEETS SYNTHESIS

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ABSTRACT
In process of the mineral treating it is obtain several products with very low grade for concentrate, but very grade for tailing. That middling products have to be input in some places of the flowsheet. The choice of the place is very imported for all technological results. That is the main decision in process of flowsheets construction.

INTRODUCTION

The most commonly used method for development of selective technological flowsheets for ore processing is based principally upon the chemical composition of the products, while the objective is to achieve maximum recovery of the target components at a higher possible grade for the concentrates obtained. Based upon the flotation kinetics of the principal component, either the time needed for its rougher flotation in the case of direct selective flowsheets or the time needed for collective flotation in the case of collective selective flowsheets is estimated. Further on step by step, the number and the flowsheet type for the cleaning and scavenger operations are tested. This procedure is a rather lengthy one. Its principal drawback and a source of mistakes lies in the fact that the place for middling return, in case of locked tests, is determined on the basis of the concentration of the principal component only.

Based upon technological studies performed over several years in six Bulgarian processing mills treating copper sulphide ores, it was established, that the decisive factor concerning the point of middlings return is the granulometric and mineralogical composition, rather than the concentration of the principal component. Both mining itself as well as overgrinding occurring during ore grinding and middlings and concentrates regrinding cycles could be a potential sources of slimes generation. Usually for regrinding operations the products are classified in advance, the slime classes being directed towards cleaning operations. Thus the fine ore and gangue particles which have different susceptibility to flotation report together with the normal sized particles into rougher, scavenger and cleaner flotation circuits. This contributes to overall recovery decline both for the fine and for the normal sized particles.

PRINCIPAL EXPERIMENTAL SET-UP AND COMMENTS

In the suggested method for selective flowsheets design, a principal emphasis is placed on minerals recovery from the middlings. This characteristic is linked to mineral composition, degree of mineral liberation, granulometric characteristics and the content of the different mineral types. A technological flowsheet is designed in the following sequence:

1. The objective of the selection is figured out precisely. This is accomplished via punctual economic analysis: owing to the content of various components in the ore; the existing and the anticipated prices of mineral concentrates with different metal and impurities content; the market niche of the products locally and abroad; last but not least - the technological possibilities for realisation of the various options.
2. The parallel flotation kinetics for the whole range of components met in the ore is estimated.
3. The mineralogical characteristic of the different fractions of concentrates and the reasons for tailing losses is determined using up-to-date instrumentation.
4. Based upon the findings from p. 1-3 above, a flotation flowsheet is synthesised and is further validated on lab scale via closed cycle tests.
5. Based upon the results from the locked cycle tests, flowsheet alterations are envisaged if needed.

The above described procedure tested for the copper ore treated in Elatzite processing plant has suggested that for this ore the optimal flowsheet is the one illustrated at Figure 1. It has been designed taking into account the following peculiarities of the ore and requirements:

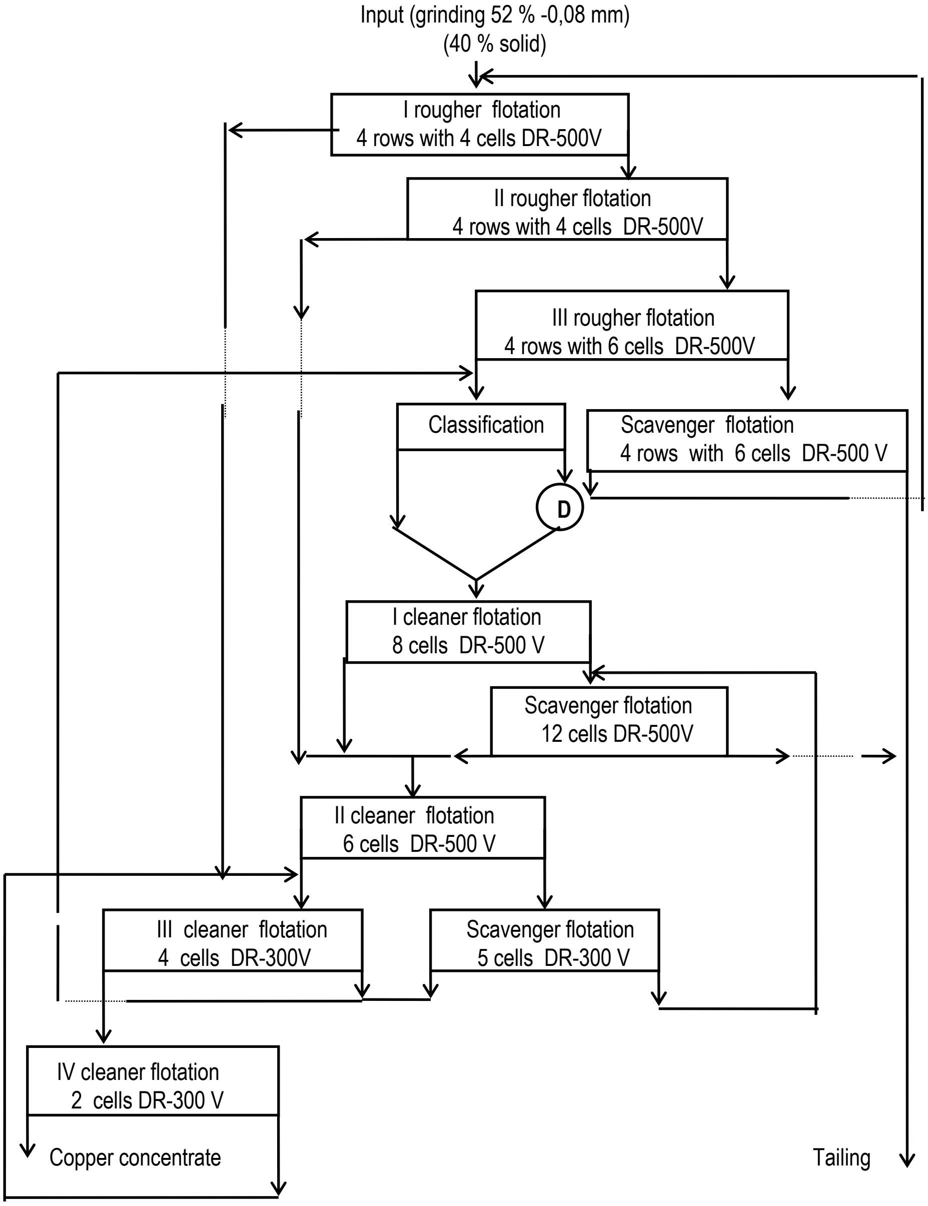

Fig. 1. Suggested technological flowsheet for Elatzy copper ores selection

1. Collective copper concentrate with Cu grade 22-24 % has to be produced, at a maximum recovery of copper minerals and gold.
2. Major ore components are copper, gold and molybdenum. Flotation kinetics curves obtained under lab scale are presented at Figure 2.
3. The mineralogical characteristic of the separate concentrates (obtained at pH 9 – $Ca(OH)_2$ maintained) taken as fractions at the end of minute two, four, six, eight and fourteen (see Fig.3) is the following:

- During the first two minutes free chalcopyrite grains predominately report in the concentrate. No intergrowths are met, both between chalcopyrite-gangue and chalcopyrite-pyrite. Free molybdenum grains are met.
- From minute three to four, about 30 % of the grains recovered in the concentrate are present by free chalcopyrite, chalcozine and bornite particles. The rest particles are intergrowths of copper minerals with pyrite and gangue minerals.

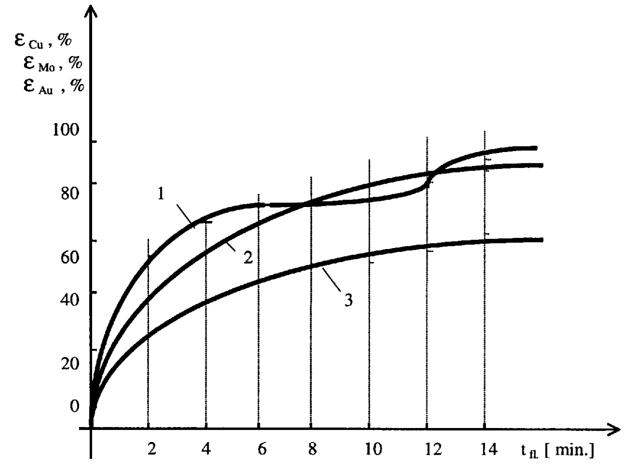

Fig.2. Kinetic of the copper (1), gold (2) and molybdenum (3), recovery for Elatzy ores

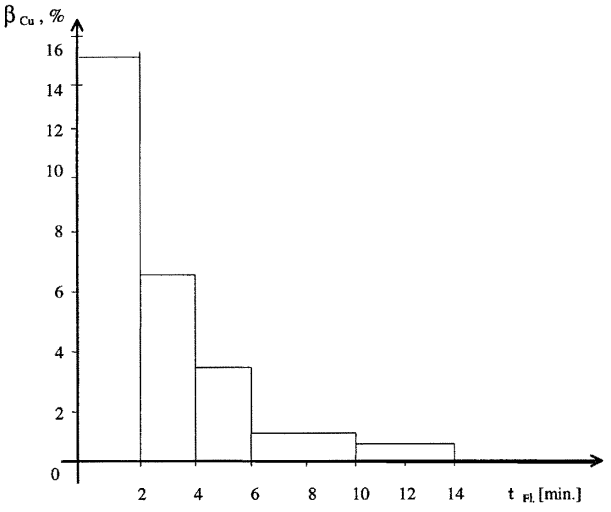

Fig.3. Copper containce in concentrates like function of the time

- From minute four to six the grains recovered are rich in copper bearing intergrowths. Only free pyrite grains are met as free particles.
- From minute six to ten, lean intergrowths of copper minerals and pyrite are recovered. Free molybdenum grains are met as well.
- From minute ten to fourteen, lean intergrowths are predominantly recovered.
- About 30 % of copper in intergrowths and 50 % in classes below 0.02 mm is lost with final tailings. The majority of gold is met as dispersed phase in quartz grains.

By the help of the flowsheet presented at Figure 1, a possibility is offered for the middlings to report in a particular flowsheet points, which are in line with their floatability. Table 1 presents comparative data from lab tests: following the flowsheet existing under which the mill operates and the alternative flowsheet designed according to the presented method. In order to secure the required flotation time of 14 minutes for the existing flotation line in the mill, pulp density needs to be increased from 32 % to 38-40 %.

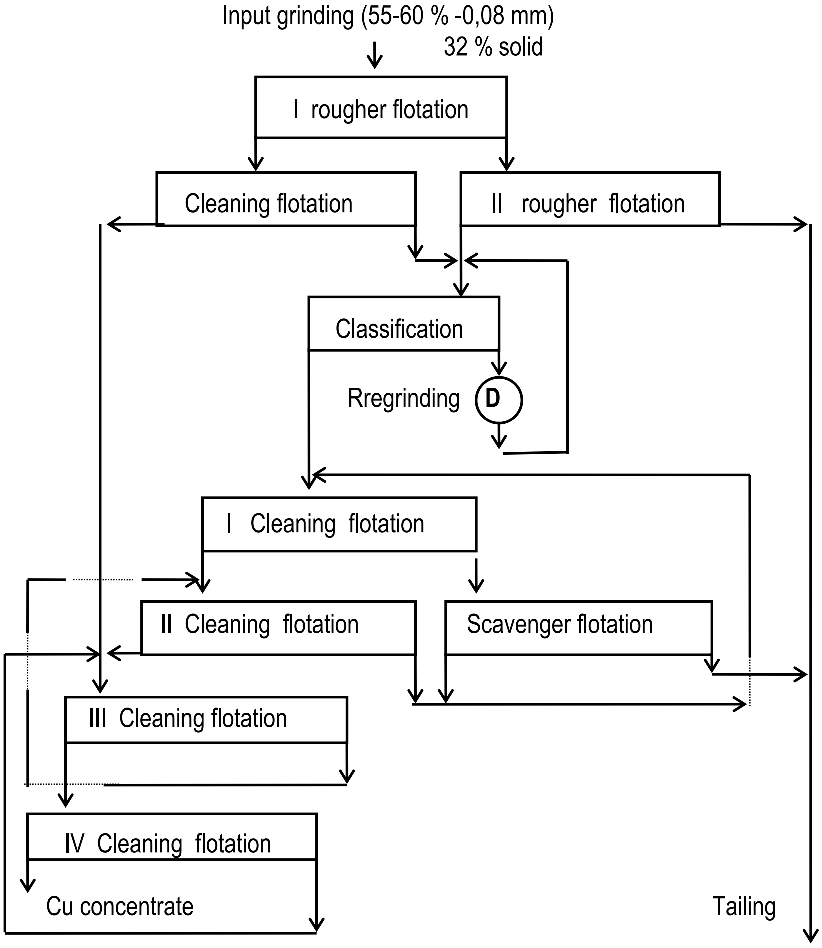

Fig. 4. Technological flowsheet in Elatzy plant

Table 1. Technological results by laboratory tastes

Technological flowsheet	Products	Yield, %	Contains Cu, %	Contains Au, g/t	Recovery Cu, %	Recovery Au, %
Flowsheet now	Cu c-te	1,50	28,80	7,4	86,92	89,38
	Tailing	98,50	0,066	0,0192	13,08	14,62
	Ore	100,00	0,497	0,13	100,00	100,00
Suggested flowsheet	Cu c-te	1,46	26,69	8,2	89,37	92,92
	Tailing	98,54	0,047	0,0093	10,63	7,08
	Ore	100,00	0,436	0,13	100,00	100,00

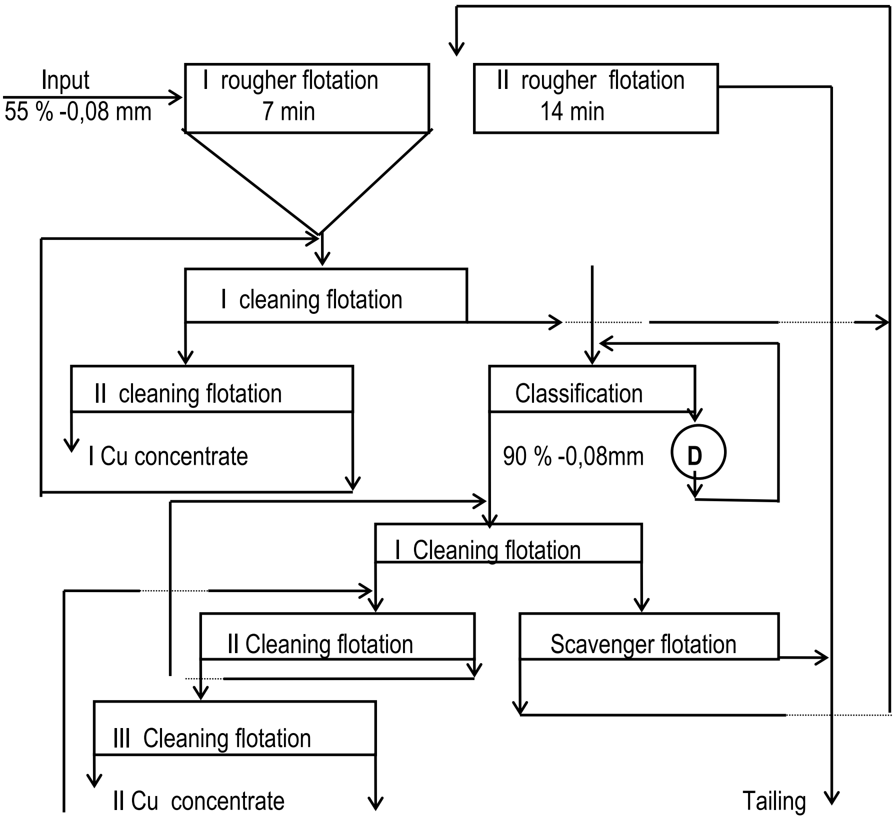

Fig. 5. The suggested technological flowsheet for Chelopech ore treatment

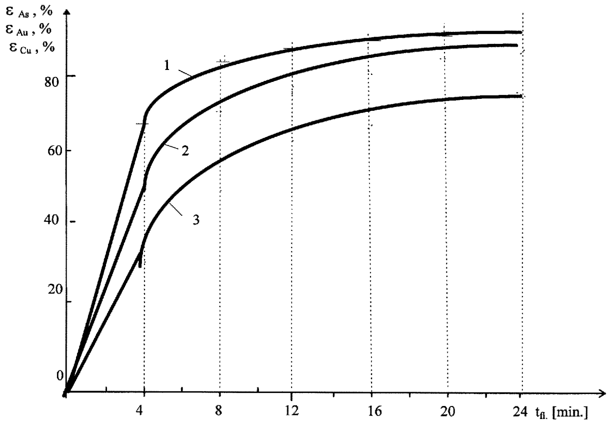

Fig.6. Kinetics flotation of the minerals Cu, As and Au containing in Chelopech ore

1 – recovery As, 2 – recovery Cu, 3 – recovery Au.

Following the above described sequence, a flotation flowsheet aimed for processing of the ore treated in Chelopech mill is designed as well. A characteristic feature of that ore is the relatively high content of arsenic and gold. Copper minerals are presented by sulphosalts and chalcopyrite. Significant amount of pyrite is also met in the ore. Gold is evenly distributed between copper minerals and pyrite. The principal objective in this case is isolating arsenic in a product with a minimal yield and minimal gold recovery in it. The majority of arsenic associates with the sulphosalts like tetrahedrite and enargite. The sulphosalts are slightly prone to slime generation. The majority of the sulphosalts mineral grains are liberated when grinding is maintained 55 % , 0.08 mm undersize. The amount of sulphosalts intergrowths with pyrite and gangue minerals is relatively small. Sulphosalts intergrowths with chalcopyrite are absent.

Chalcopyrite grains are often covered with fine particles arising from sulphosalts overgrinding. The flowsheet shown at Figure 5 is designed on the basis of kinetics (Figure 4) and product characteristics. The advantages of this flowsheet have been confirmed on the basis of comparative tests on the background of the results obtained from the existing flowsheet.

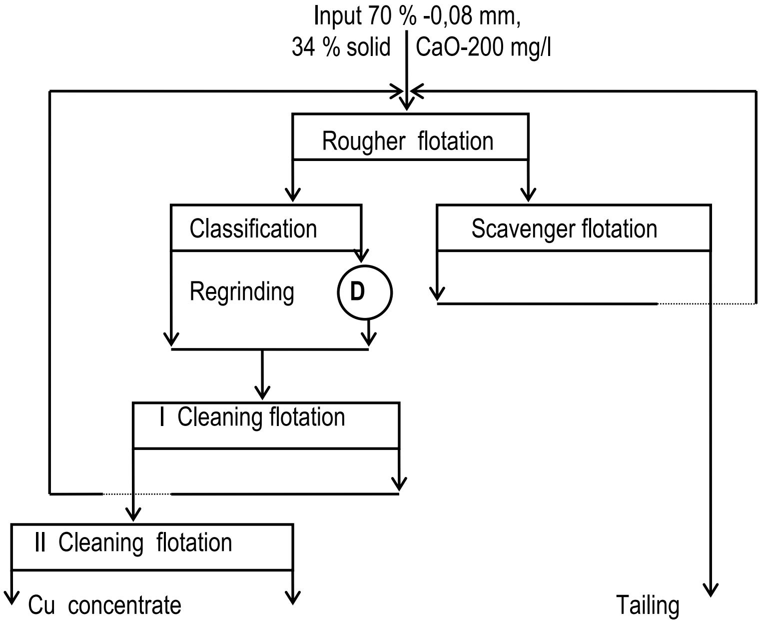

Fig. 7. Technological flowsheet in Chelopech plant now

Table 2. Technological results by laboratory taste

Technological flowsheet	Products	Yield, %	Contains			Recovery, %		
			Cu,%	As, %	Au, g/t	Cu	As	Au
Flowsheet now	Cu c-te	8,32	18,12	2,41	28,3	90,24	67,47	77,71
	Tailing	91,68	0,178	0,11	0,77	9,76	32,13	23,29
	Ore	100,00	0,31	3,03	100,00	100,00	100,00	100,00
Suggested flowsheet	I Cu c-te	4,49	18,01	5,90	26,17	44,68	80,29	42,27
	II Cu c-te	5,02	19,16	0,207	22,83	53,14	3,16	41,22
	Tailing	90,49	0,043	0,06	0,507	2,18	16,55	16,51
	Ore	100,00	1,81	0,33	2,78	100,00	100,00	100,00

CONCLUSION

The described investigations performed at Elatzite and Chelopech flotation mills, give us the possibility the drawn up the following conclusions:

1. The research method suggested for development of selective flotation flowsheets offers the possibility to reduce the amount of laboratory work needed, while placing an accent on the use of up-to-date instrumentation for quantitative mineralogical studies. The introduction of the middlings at the most optimal point inside the flowsheet guarantees reaching satisfactory technological results and leads to energy savings and more flexible unit arrangements.
2. The suggested method is an universal one. It could be used for various mineral processing technological flowsheets design, encompassing gravity, magnetic, electrostatic, hydrothermal, flotation and combined methods.

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MAGNETIC SEPARATION OF CHROMIUM-CONTAINING LATERITES

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ABSTRACT

Investigations on the separation of ore, utilizing the difference in magnetic properties of the minerals were performed. The influence of the magnetic induction and the cross slope of Franz-isodynamic separator were studied in a laboratory scale. Experiments with ore ground for different durations were made. Experiments with semi-industrial separators – flat Jones separator and cross band separator were performed with the estimated optimal particle sizes. The optimal conditions for mineral processing of chromite material were found.

INTRODUCTION

The exploitation of less-important and poor deposits attracts growing attention along the recent development of mineral processing technologies. For example, chromium-containing laterites, formed by weathering of ultrabasic rocks, represent an interest in chromium production (Savvidis, S., Cargiotis, E., 1997.). Exploitation of this kind of rocks is cost-effective. The mineral processing ability of laterites is facilitated by the differences established in the grindability and magnetic properties of the constituting minerals.

Chromium containing laterites from the Philippines were investigated, with the aim to check the opportunity of application of magnetic methods in production of chromite concentrate. Preliminary studies of magnetic properties of the minerals contained in the ore were the reasoning of the present studies.

METHODS AND EQUIPMENT

Concomitant minerals, such as magnetite, silicate minerals, etc., have been found in the larger fractions of the ground material, which do not contain limonite aggregates. It has been established that their magnetic properties differ from those of chromite and they could be processed by magnetic separation.

Different vein minerals, accreted with the chromite grains are uncovered by selective grinding. Those which could not be separated, are, in most cases, strongly magnetized. In order to achieve high degree of mineral processing of the chromite concentrate, the accreted grains containing low percentage of chromite, should be separated by magnetic methods.

Franz-isodynamic separator was used for that purpose. To estimate the feasibility of the separation results in semi-industrial scale a “Jones separator” and a “cross band separator” were used.

The samples were dried at a temperature of 50^{0}C. The parameters of the classifier were established preliminary.

The initial separation of the material was made in 20 mT magnetic induction. Further experiments were made in higher intensity of the magnetic field. The magnetic induction has been increased on discrete levels, starting from 20 mT to the uppermost level of 120 mT (fig 1).

MINERAL PROCESSING OF CHROMITE IN FRANZ-ISODYNAMIC CLASSIFIER

Preliminary experiments for magnetite separation

The fraction 100 μm was used for these experiments. The content and extraction of Cr_2O_3 and FeO in the magnetic material depend on induction. In 20 mT magnetic induction, the ferromagnetic, i.e. strongly magnetized minerals, are being separated. The content of FeO was 8.6%, in extraction rate 0.1%. The chromite content was represented mainly by incorporation of chromite ions in magnetite lattice and small proportion of accreted chromite.

In 40 mT magnetic induction (fig. 2), FeO content decreased to 68.3%, while the extraction was 4.9%. Contrary to this, Cr_2O_3 content increased to 20.3% and its extraction to 0.9 %. The grains were with magnetite or martitized magnetite. Mainly, strongly magnetized minerals accreted to chromite are being involved here.It was found in the material accreted together magnetite and martitized magnetite.

A decrease of FeO content, respectively an increase of Cr_2O_3 content, was observed in induction values between 60 and 80 mT. Yet, not accreted ferrimagnetic materials were not observed. It can be inferred from the metallic content of the products, that iron-rich accreted grains should be separated as a rock material. Therby small chromite loss could not be avoided.

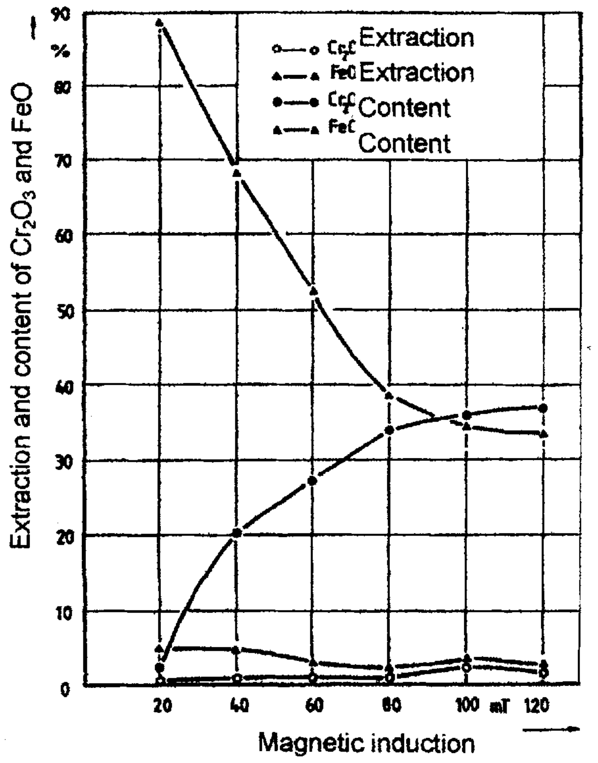

Figure 1. Extraction and content of Cr_2O_3 and Fe0 in the magnetic product of Franz-isodynamic separator in terms of magnetic induction

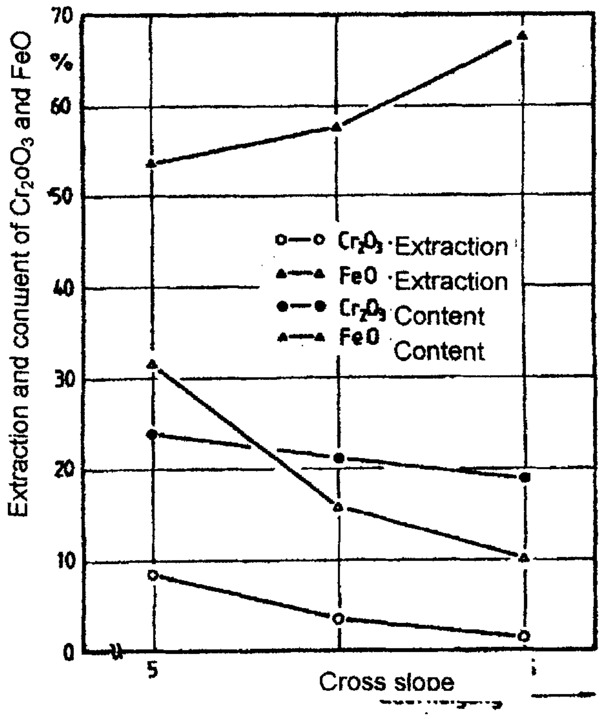

Figure2.. Extraction and content of Cr_2O_3 and FeO in the magnetic product in terms of the cross slope of the classifier at magnetic induction 40 mT

Cr_2O_3 content in the magnetic product increases significantly at more higher magnetic induction values. So, at 120 mT, Cr_2O_3 content was 38.3%, with extraction 1.7%, and Fe content in the raw material was 31.9%. Cr/Fe ratio was 1.06

CHROMITE SEPARATION BY DRY MAGNETIC METHOD

The fractions >100 μm and 100-163 mμ were used in the experiments of mineral processing of cbromite by the method of dry magnetic separation. Because the fraction 63-20 mμ consists mainly of limonite aggregates, it could not be processed by magnetic separation methods.

The separation of the raw material was implemented in two stages. Three products were obtained:

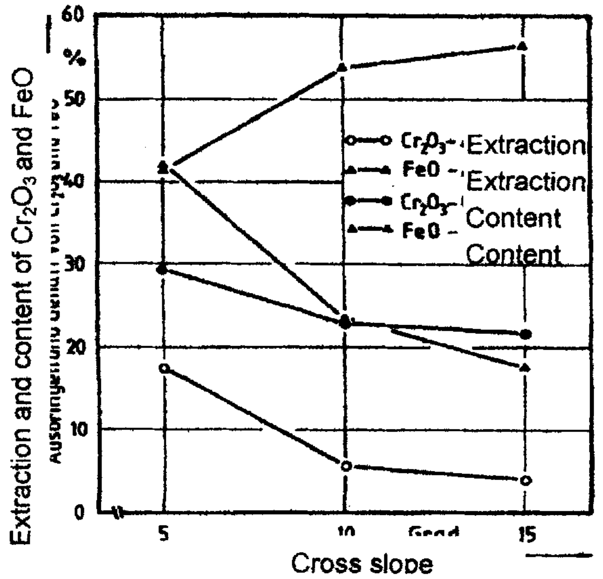

Figure 3. Extraction and content of Cr_2O_3 and FeO in the magnetic product in terms of the cross slope of the classifier at magnetic induction of 60 mT

iron rich product; chromite concentrate; and waste product. The magnetite and the grains strongly accreted with magnetite were separated at magnetic induction 480 mT. Table 1 shows the results of this separation.

The data from the separation of fraction >100μm are shown in Table 2. In increasing the time of grinding the amount of iron rich product decreases from 6,7 to 3,2%. In the same time the extraction of Cr_2O_3 decreases from 3,6 to 1,6%. The metallic contents show, that in these conditions part of the accreted with magnetite chromite grains have not been separated. So, for example, at milling time 20 min the content of Cr_2O_3 in metallic product was 18,2%, at extraction 1,6%. This amount of chromite should be separated from the iron concentrate. Thus the chromite concentrate was obtained, by separation of the iron rich product from the waste product.

The raw material, which was milled for 5 min exhibited high chromium extraction rate in the concentrate – 95,1%. The mineral processing of Cr_2O_3 got increased from 31,5% to 37,4%, but in general, stayed on a low level. The remaining limonite aggregates in the material were removed mainly together with the chromite. The content of FeO in the concentrare, therefore, was very high -29,4%.

Since for 10 min grinding, limonite aggregates were almost absent in the fraction >100μm, Cr_2O_3 content in the concentrate greatly increased in comparison to the product ground for less time. Cr_2O_3 content in the concentrateв was 42,9%, at extraction rate 96,2%.

In increasing the milling time, the result of the magnetic separation was further improved. In 15 мin milling time Cr_2O_3 content in в the concentrate was 44,5% at extraction rate 96,8%. In 24,1% FeO content, the ratio Cr/Fe was 1,62. The metallic contents show, that a part of this concentrate still contains chromite grains accreted to the iron minerals. An increase of the milling time to 20 min resulted in further increase of chromium content. Based on this result, one can conclude that for these milling conditions, the raw material should not be milled for more than 15 min, since great part of the chromite will go in the finer fraction.

In 480 mT induction, a small part of the chromite did not get magnetized, thus went into the waste product, together with the rock minerals. The chemical composition of these chromite spynels determines their magnetic properties. The content of FeO in the grains varied between 13,3 and 16,5%, while MgO content was between 14,3 and 17%.

Table 1. Weight distribution and distribution of the metal for laterite chromite ore of the magnetic products in different magnetization (ρ>4.1)

Magnetic induction [mT]	Weight [%]	Content[%]				Cr/Fe-Ratio	Cr_2O_3 - Extraction [%]
		Cr_2O_3	FeO	MnO	Al_3O_3		
-40	5.6	15.6	69.4	2.2	4.3	0.20	2.1
40-80	7.9	30.3	42.2	4.3	10.4	0.63	5.6
80-120	8.8	34.2	34.0	6.6	12.8	0.89	7.1
120-160	3.6	36.9	29.2	7.0	13.2	1.11	3.1
160-200	4.9	39.3	27.8	7.9	14.2	1.24	4.5
200-240	2.3	41.3	24.9	8.5	14.4	1.46	2.2
240-280	8.6	43.2	23.5	9.7	14.4	1.62	8.8
280-320	11.0	46.5	21.8	10.3	14.8	1.88	12.1
320-360	16.7	48.7	19.2	10.9	15.0	2.27	19.2
360-400	23.4	49.4	18.5	11.6	15.1	2.48	27.3
400-440	5.2	48.3	18.2	12.7	16.5	2.47	5.9
440-480	0.7	47.7	17.4	13.3	16.8	2.41	0.9
+480	1.3	39.2	18.0	14.5	15.3	2.03	1.2
	100.0	42.4	26.1	9.3	13.8	1.43	100.0

This shows that the ferromagnetic Fe^{2+} ions, have been replaced by paramagnetic Mg^{2+} ions. Since the magnetic permeability of these grains does not differ at all from iron containing silicate minerals, they could not be separated by magnetic method. The extraction of Cr_2O_3 in the waste product varied between 1.3 and 1.7%.

As it can be seen from Table 3 the separation of the iron rich product for the fraction 100-63μm showed almost the same tendency as the fraction >100μm. Since the magnetic separation of the products containing limonite aggregates was performed together with the chromite, Cr_2O_3 content in the concentrate did not reach high rates. In increasing the milling time, the content of Cr_2O_3 was increased from 31,1% to 38,2%. Due to the high content of FeO, Cr/Fe ratio varied between 0.86 and 1.29. This fraction should be processed by other sorting methods.

Influence of the cross slope of the classifier upon the separation.

The content of Cr_2O_3 in the magnetic concentrate of the fraction >100μт could not reach the values of the same product extracted from the primary ore. Part of the laterite concentrate consists of chromite grains having low value of Cr/Fe ratio. Since these grains get magnetized easier than those which have not accreted to chromite, they should be separated in order to achieve better mineral processing of chromium concentrate.

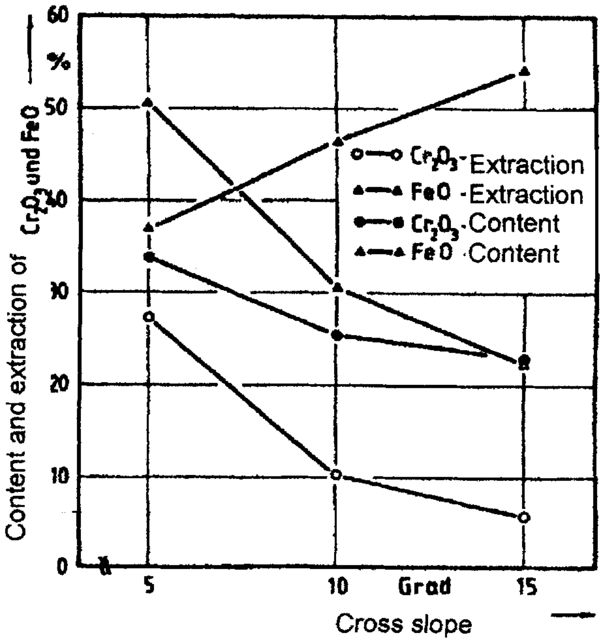

Figure 4. Extraction and content of Cr_2O_3 in the magnetic product in terms of cross slope of the classifier at magnetic induction 80 mT

According to the accretion the grains magnetize to a different degree, so they could be separated by increasing the magnetic induction, without formation of aggregates. Since the cost of magnetic separation in industrial scale is very high, this way for mineral processing of chromite is not used in practical cases.

Magnetic separation should be implemented in two stages. In the first stage should be separated the iron minerals, as well as the grains with low Cr/Fe ratio accreted to them. A high induction is necessary for that purpose. An increase in the magnetic field gradient leads to an increase of the magnetic force action between the grains. Magnetic aggregates are formed, in which could participate slightly magnetized grains.

Because of that, the classifier could chock with the aggregates formed. If the cross slope of the classifier decreases, the gravitational force F_eO, acting upon the grains decreases too. This means a relative increasing of the magnetic force F_M. In this way, aggregate formation could be diminished, from one side, and the separation of the material is improved, from the other side.

Table2. Results from the magnetic separation of the fraction >100 μm

Milling time			Content, %		Cr/Fe-	Cr_2O_3 -
[min]	Product	Weight, %	Cr_2O_3	FeO	Ratio	Extraction
5	Iron rich product	6.7	16.9	70.3	--	3.6
	Chromium concentrate	80.1	37.4	29.4	1.12	95.1
	Waste	13.2	3.2	4.2	--	1..3
	Total	100.0	31.5	28.8	--	100.0
10	Iron rich product	4.2	20.0	66.1	--	2.3
	Chromium concentrate	81.8	42.9	25.3	1.49	96.2
	Waste	14.0	3.9	3.8	--	1.5
	Total	100.0	36.5	24.0	--	100.0
15	Iron rich product	3.3	18.9	67.3	--	1.7
	Chromium concentrate	82.0	44.5	24.1	1.62	96.8
	Waste	14.7	3.8	3.6	--	1.5
	Total	100.0	37.7	22.5	--	100.0
20	Iron rich product	3.2	18.2	68.5	--	1.6
	Chromium concentrate	78.6	44.8	23.9	1.65	96.7
	Waste	18.2	3.4	2.9	--	1.7
	Total	100.0	36.4	21.7	--	100.0

The separation behavior of the raw material should be kept in terms of magnetic induction and cross slope. The cross slope of the classifier was changed to 5, 10 and 15 degrees. The fraction sized >100μm and milled for 15 minutes was sent to a magnetic classifier.

The first experiments were performed at magnetic induction 40 mT. Fig. 2 shows the extraction and the content of Cr_2O_3 and FeO of the magnetic product. At cross slope of 5^0, it was achieved high level of separation of FeO containing material. The content of FeO in the product obtained, amounted a 53.7% at extraction rate 31.3%; Cr_2O_3 content was 23.9% at extraction rate 8.3%. This separation result shows that, at relatively high degree of mineral processing of the chromium concentrate, an inevitable, high loss of chromium is observed.

Table 3. Results from the magnetic separation of the fraction 100- 63 μm.

Milling	Product	Weight, [%]	Content [%]		Cr/ Fe	Cr_2O_3
time min			Cr_2O_3	FeO	Ratio	Extraction
5	Iron rich product	6.6	15.8	69.5	--	3.8
	Chromium concentrate	83.2	31.1	31.7	0.86	94.2
	Waste	10.2	5.4	6.8	--	2.0
	Total	100.0	27.5	31.5	--	100.0
10	Iron rich product	4.1	16.9	68.3	--	2.3
	Chromium concentrate	83.7	34.5	28.9	1.05	95.4
	Waste	12.2	5.6	4.7	--	2.3
	Total	100.0	30.4	27.5	--	100.0
15	Iron rich product	2.9	18.4	67.2	--	1.7
	Chromium concentrate	82.5	37.0	27.2	1.20	95.8
	Waste	14.6	5.5	4.1	--	2.5
	Total	100.0	31.9	25.0	--	100.0
20	Iron rich product	2.5	19.2	66.1	--	1.5
	Chromium concentrate	82.2	38.2	26.0	1.29	95.7
	Waste	15.3	6.0	3.8	--	2.8
	Total	100.0	32.8	23.6	--	100.0

Chromium loss was diminished by increasing the cross slope. The decrease of FeO extraction was greater than that at 40 mT induction.

Due to magnetic aggregates formation however, magnetic induction should be limited up to 80 mT.

Chromium extraction diminished sharply at cross slope of 10^0; and FeO extraction rate was 15,8%.

In the next experiments the material was separated at 60 mT magnetic induction. Fig 3 shows that the weak induction increase leads to significant increase of the magnetic force which acts upon mineral grains. In cross slope of 5^0 FeO content was 41.7% in extraction rate 41.9%; Cr_2O_3 content was 29.4% at extraction rate 17.6%.

This result implies that, in increasing the magnetic induction, the cross slope of the classifier has more and more tangible effect upon the separation results. At cross section of 10^0 and 15^0, the extraction rate of Feo was lower, and FeO content was high: 53.8 and 56.5% respectively.

The final experiments were conducted at 80 mT magnetic induction. Fig 4 shows the results from the separation of the magnetic product. Magnetic aggregate formation occurred in this field intensity. This process increased chromium extraction in the magnetic product. Cr_2O_3 content was 33.9% at cross slope of 5^0, while the extraction was 27,4%. At 10^0 cross slope, the extraction of Cr_2O_3 was 10.2%, while the extraction of FeO was 30.6%. These results were not so good, in comparison to the other results, e.g. those at 40 mT induction and 5^0 cross slope.

For two stage processing of the chromite concentrate, a nonmagnetic material was transferred to the Franz – isodynamic classificatory. In this case the magnetic induction was 480 mT, and cross slope was 15^0. The results from this concentrate separation are shown on table 4. By separation of the silicate rock minerals, the material, whose iron rich grains were separated at 40 mT magnetic induction, was processed with a small Cr loss. Concentrate Cr_2O_3 content varied between 44.5 and 47.1%, and the extraction rate between 96,8 and 90,2%.

Table 4. Results from the magnetic separation for the fraction >100 μm, in different magnetic induction and different cross slope of the classifier

Magnetic induction	Cross slope	Weight	Content, %		Cr/Fe-	Cr_2O_3 -
mT	[°]	%	Cr_2O_3	FeO	Ratio	Extraction, %
40	5	72.2	47.1	21.6	1.92	90.2
	10	79.1	45.3	23.3	1.71	95.1
	15	82.0	44.5	24.1	1.62	96.8
60	5	62.7	48.6	20.0	2.14	80.9
	10	75.6	46.2	22.2	1.83	92.6
	15	78.3	45.5	23.0	1.74	94.5
80	5	54.8	48.8	19.5	2.21	71.2
	10	70.5	47.3	21.4	1.95	88.5
	15	75.7	46.1	22.2	1.82	92.6

The separation of the iron rich grains at 60 mT induction was accompanied with high Cr content in the concentrate. It reached 48.6% at cross slope of 5^0, at 80.9% extraction rate. In 20% FeO the Cr/Fe ratio of the concentrate was 2,15. This shows that the accreted to iron minerals chromite grains were separated almost completely.

The material from which the iron rich particles were separated at 80 mT magnetic induction and 5^0 cross slope, showed almost the same Cr_2O_3 content in the в concentrate as it was at 60 mT. And, chromium extraction decreased significantly and reached 71.2% value. At these separation parameters, the Cr rich grains were separated as magnetic material.

The separation results show that the two stage magnetic separation leads to high Cr_2O_3 in the concentrate. Furthermore, aggregate formation can be diminished. The least possible magnetic induction should be used for separation of the iron rich particles.

MINERAL PROCESSING OF CHROMITE BY FLAT JONES TYPE CLASSIFIER

The results from the Franz isodynamic classifier should be considered, thinking about practical application of magnetic separation in mineral processing of chromite from laterite ore. Dry Jones type classifier with strong field produced by Humboldt-Wedag company is widely used for separation of mineral raw materials. The above mentioned particle sizes of the material determine the width of the channel between the profiles of the plot. (Wenz, Aufbereitungs-Technik, S. 142/149 (1973) –f). The content of a solid substance in the pulp is 40 %. Magnetic induction varying between 0.10 and 0.25 T was applied in order to separate the iron rich mineral particles. The rotation speed of the rotor was 3.4 m/min. The magnetic material was moved upon the plot's surface by washing with water at 4 bar pressure. A sample of about 10 kg weight was used for each experiment. Fig. 5 shows the content and extraction rate of Cr_2O_3 and FeO. In this induction range, the material was separated without chocking of the channels.

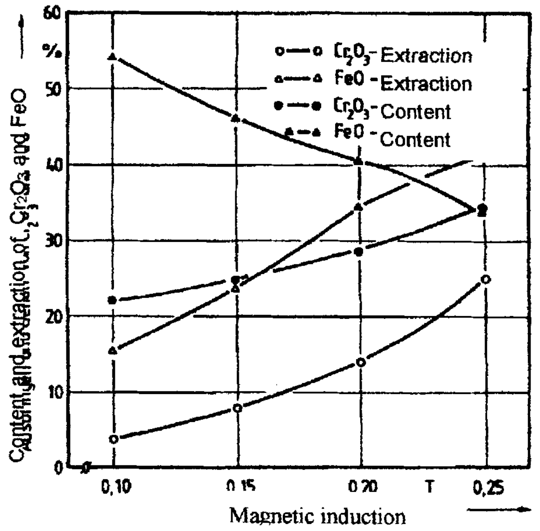

Figure 5. Extraction and content of Cr_2O_3 and FeO in the magnetic product, in terms of magnetic induction for the case of flat classifier.

It can be seen from the curves, that the separation of the iron rich grains was best implemented in the range of 1.10 – 0.20 T. The extraction of FeO increased from 15.5 to 34.6%, and the Cr_2O_3 extraction also increased from 3,8 to 14.4 %. Weakly magnetized iron containing silicates, such as enstatite and iron rich quartz, were found in the magnetic material, which was separated at 0.20T induction. In the separation zone, these light rock materials were kept in agglomerates consisting of strongly magnetized iron minerals. Due to this circumstance, the content of FeO decreased. At 0.25 induction rate, the extraction of Cr_2O_3 in the magnetic material increased strongly in comparison to the extraction of FeO. And, it was observed that, at this induction rate, the chromium rich grains separate like a magnetic material.

In comparison to the results obtained by Franz isodynamic classifier, a concluson can be drawn, that, at 0.20T induction rate, the separated nonmagnetic material is suitable for further mineral processing of the chromite The result obtained at this induction rate is shown on the table below:

Product	Yield %	Content %		Extraction%	
		Cr_2O_3	FeO	Cr_2O_3	FeO
M	19.2	28.2	40.5	14.4	34.6
NM	80.8	39.9	85.6	85.6	65.4
Total	100,0	37.7	100.0	100,0	100,0

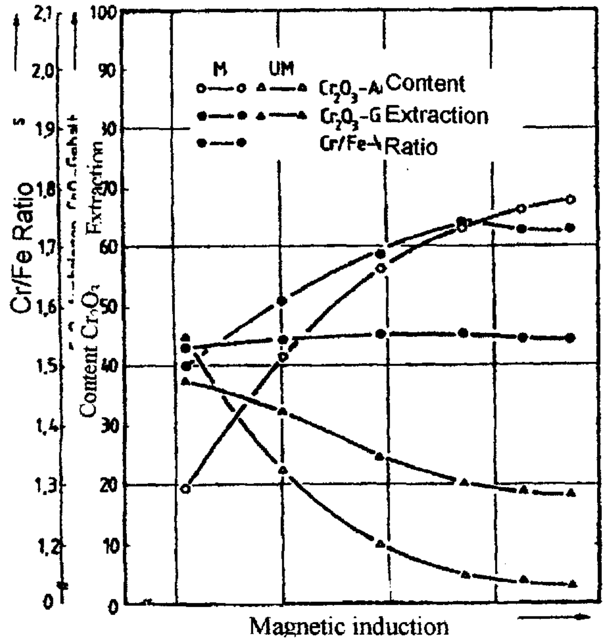

Figure 6. Extraction and content of Cr2O3 in the magnet magnetic product (M) and the nonmagnetic product (NM), and Cr/Fe ratio, in terms of magnetic induction for flat Jones type classifier

For the mineral processing of the chromite concentrate the magnetic induction values varied between 0.62 and 1.35T. Three products were obtained: magnetic product (concentrate); medium magnetic product (intermediate product); nonmagnetic product (waste product). Fig 6 shows the extraction rates and the contents of Cr2O3 of the magnetic and nonmagnetic product, as well as the Cr/Fe ratio. At 0.62T induction rate, only a small amount of the chromite in the concentrate was extracted. The content of Cr_2O_3 in the concentrate was 43.3% at extraction rate of 19.7%, and the process ran with a significantly higher induction, compared to that of the Franz isodynamic classifier. This shows that in the process of separation implemented with a flat Jones type classifier, with the same magnetic induction, the ratio between the gravitational and magnetic force is greater than the same ratio in Franz isodynamic classifier, so the iron poor chromite grains are extracted as nonmagnetic or medium magnetic raw material. And, the content of Cr_2O_3 in the nonmagnetic sample was 37.8% at induction rate of 44.4%. In magnetic induction 0.80T, the extraction of chromium in the concentrate increased sharply and reached a value of 41.7%. The Cr_2O_3 content in the sample, further, had a lower value of 44.5%. Still a considerable part of the chromite stayed in the waste product.

It was necessary to increase the magnetic induction rate, in order to magnetize the iron poor chromite, which has remained in medium product and in the waste product. The highest content of Cr_2O_3 in the concentrate was achieved at 1.14T induction; it reached 45.6% at extraction rate 63.4%. The Cr/Fe ratio was 1.74. A small part of the concentrate consisted of iron containing silicate rock materials, so despite the significant increase of the extraction rate, the chromite content did not reach high values. In further increase of the magnetic induction, it was increased both the Cr_2O_3 extraction and the incorporation of silicate rock materials in the concentrate. So, for example, at 1.35T induction, Cr_2O_3 content in the concentrate was 44.6%, and the extraction was increased to 68%.

In nonmagnetic sample the extraction of Cr_2O_3 showed very small value of 3.5%. This shows that in a flat Jones type classifier, for the iron-containing silicate minerals is true almost the same relation between the forces, as in the case of iron poor chromite grains , despite that the first ones have lower magnetic permeability than that of the chromite. It is due to density differences. The poor separation result could be improved by classification of the materials. For the laterite chromite as-applied method is not economically viable.

In increasing the induction, the extraction rate of FeO was increased from 25.3 to 49.7%, while the extraction rate of Cr_2O_3 was increased from 6.6 to 30.3%.

Induction rate of 0.2T targeted the achievement of very good result, which could be obtained in Franz- isodynamic classifier at 60mT induction and cross slope of 5^0.

The separation result is shown on the table below.

The separation of the rock minerals from the nonmagnetic product in the first stage of magnetic separation was performed at magnetic induction varying between 0.50 and 0.70 T. Fig 7 shows Cr_2O_3 content and the extraction of the concentrate and the waste product, as well as Cr/Fe ratio of the magnetic product in terms of the magnetic induction.

The low content of Cr_2O_3 in the concentrate –44.6% which came at 0.5T induction showed that one part of the chromium rich particles has not been magnetized and has gone to the waste product as nonmagnetic material. Thereby, the extraction of Cr_2O_3 reached the same low value – 58.2%.

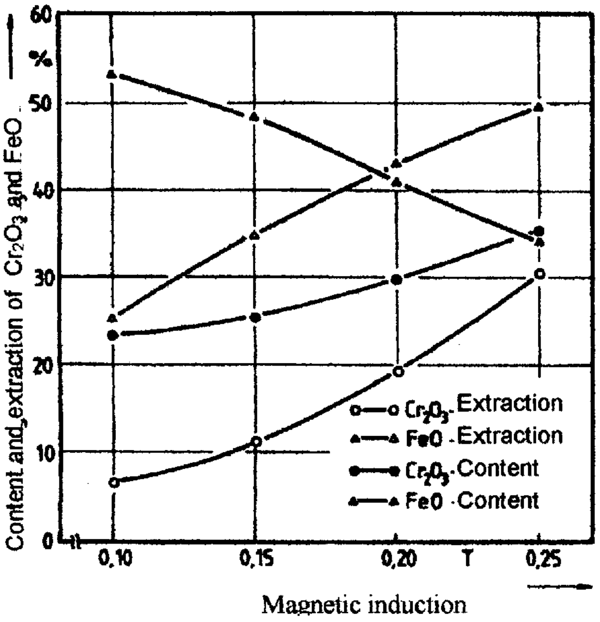

Figure 7. Extraction and content of Cr_2O_3 and FeO of magnetic product in terms of magnetic induction for cross band classifier.

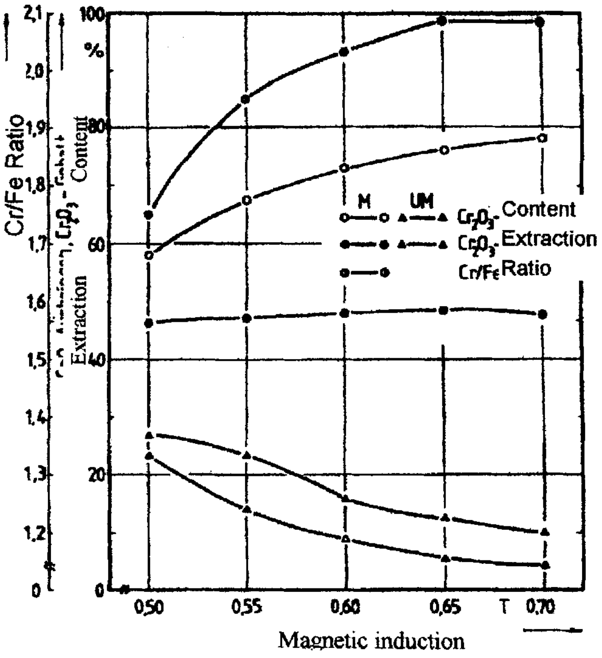

Figure 8. Content and extraction of Cr_2O_3 *in magnetic product (M) and nonmagnetic product (NM), Cr/Fe ratio of M in terms of induction for cross band separator. NM was separated at 0.2T magnetic induction*

Product	Mass %	Content %		Extraction%	
		Cr_2O_3	FeO	Cr_2O_3	FeO
M	23,7	29,6	40,9	18,6	43,1
NM	76,3	40,2	16,8	81,4	56,9
Total	100,0	37,7	22,5	100,0	100,0

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MINERAL PROCESSING OF CHROMITE BY CROSS BAND CLASSIFIER

Further, an attempt was made to check if the results obtained by means of Franz-isodynamic classifier could be transferred in an industrial scale in case of dry magnetic separation. Cross band classifier was used for these experiments. The classifier operated according to the following specifications:

Magnetic induction: 0.10-0.25 and 0.50-0.70 T	
Velocity of the main band:	0.36m/sec
Velocity of the cross band:	0.50m/sec
Sample amount:	10 kg

Fig 8 shows the content and the extraction rate of the magnetic product. In comparison to the results obtained by flat Jones type classifier, much more extraction rate of Cr and Fe was achieved for each of the induction values. This difference in the extraction shows that in the case of cross band classifier the magnetic force is greater than that in flat Jones type classifier. Therefore, in this case was achieved better separation of the iron rich grains. In increasing the induction, the chromium content in the magnetic concentrate was achieved. At 0.60T induction Cr_2O_3 induction was 47.9% at extraction rate 72.8% and Cr/Fe ratio 2.03. At 0.65T induction it was achieved the most higher Cr content in the concentrate – 48.2% at extraction rate 76.3%. At FeO content of 20.3%, Cr/Fe ratio in the concentrate was 2.08. And there was a loss of Cr_2O_3 in amount of 5.1%. This loss can be diminished by induction increase. At 0.70T induction the extraction of Cr_2O_3 was 3.8%. Despite that iron-containing silicate minerals were magnetized and have been extracted as magnetic product, Cr_2O_3 content in the concentrate decreased. The values were 47.8% at extraction rate 77.6%. And, the content of FeO decreased too, so the ratio stayed 2.08.

CONCLUSION

The investigations performed in this studies have shown that the difference in the magnetic properties of the minerals which are constituents of chromium containing laterites can be used for production of chromite concentrate.

The investigations, performed in a laboratory and semi-industrial scale have verified this.

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MAGNETIC PROPERTIES OF CHROMIUM-CONTAINING LATERITES

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ABSTRACT

Magnetic properties of chromium-containing laterites from the Philippines and Vourinos deposit, Greece, were investigated. Magnetic properties of the main minerals in the ore, chromite and limonite, were investigated by means of laboratory Franz – isodynamic magnetizer. Differential thermoanalysis at different temperaturesand magnetic induction was used, as well as infrared spectroscopy at different wavelengths. Moessbauer spectroscopy was used for determination the ratio of different iron forms in the minerals. The different magnetic permeability of the different minerals in the sample is shown.

The established difference in the magnetic properties of chromium-containing minerals and limonite shows that the ore can be processed by magnetic separators for mechanical separation of the minerals; in suitable magnetic field strength, after selective grinding.

INTRODUCTION

Geological and mineralogical investigations implemented so far have shown that Philippine's laterites, due to their large reserves would be of great importance for the future chromium production (1-5). However, the processing of this kind of ore by mineral processing methods is complicated due to their peculiarities and complex mineral composition. Laterite processability depends mainly on the establishment of the differences in physical and chemical characteristics of the constituted minerals. The difference in the magnetic properties has a great significance.

So far, there are not many investigations on magnetic separation of laterite chromium, because it should be studied the dependence between the magnetic properties and the structure of the minerals; respectively their chemical composition and their behavior in magnetic field

The present study shows the results from the investigations of the magnetic properties of laterite minerals. These results could be useful in magnetic processing of the ore.

METHODS AND EQUIPMENT

To investigate the magnetic properties of the ore a laboratory Franz-isodynamic magnetizer was used. Magnetic permeability of the ore minerals was investigated. The limonite aggregates, obtained atdifferent magnetic induction, were analyzed by means of differential thermoanalysis. Their infrared spectrum was studied too. Moessbauer spectroscopy was applied for the estimation of Fe^{2+} /Fe^{3+} ratio in iron minerals

Equipment used in the experiments

Fig.1 shows the equipment used. This is a laboratory Franz-isodynamic-magnetizer, in which the magnetic induction can be determined without levels up to 2 tesla (T). It is used for an investigation of the magnetic properties of the minerals. The separation is performed in a vibrating channel which the length and cross-section have been established preliminary.

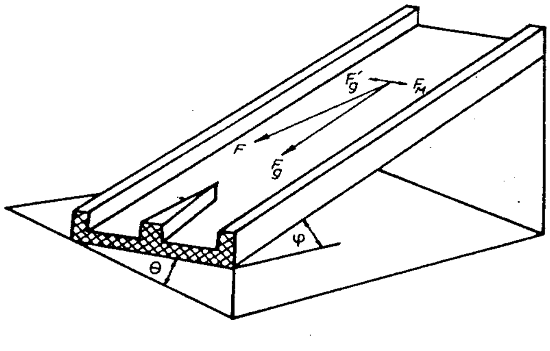

Figure 1. Presentation of the forces acting in the classifier

Two forces act in the sorting channel: magnetic force and gravitational force. The magnetic force Fm for a particle with a mass *m* and magnetic permeability
$\chi = \kappa/Qq$ acts decreasingly upon the axis of the channel.
It can be expressed by the formula:

$$F_M = \mu_0 . \chi . m . H \text{ grad } H, \quad [N], \qquad (1)$$

Where *m* is the mass [кg]; *H* is the field strength,

[A m^{-1}].

Simultaneously acts the friction force F'_g:

$$F'g = m.g.\sin\theta, \text{[N]} \qquad (2)$$

Where *g* is gravitational constant, g = 9,81 [m.s^{-2}]; θ - is the angle of the slope of the channel.

In the case of equilibrium of the forces it is fulfilled:

$$F_M = F'g$$

and $$\chi = g \sin\theta \frac{1}{HGradH^2 \mu_0} \qquad (3)$$

By this formula one can determine magnetic permeability of the mineral grains. Transverse slope θ = 15^0, while longitudinal φ = 30^0. The initial size of the raw materials was 100 – 200 μm. The determination of the materials as magnetic ones was made by microscopic observations.

Magnetic properties of the minerals

Magnetic permeability of the most important minerals

If we place a particle in a magnetic field, the elementary magnets in the substance get magnetized due to the action of the external magnetic field. External magnetic field acts upon the substances placed in it with different force H and proportional magnetization M.

This magnetization can be defined as induced magnetic moment per unit volume. Proportionality constant is determined as magnetic permeability and participates in the formula:

$$M = \kappa.\mu_0.H, \qquad (4)$$

where μ_0 is induction constant ($\mu_0 = \pi\ 10^{-7}$ Vs/Am).

The quantity k can be defined as a parameter characterizing the magnetic properties of the substances. For different substances it depends on the flux density or the field strength. It can be expressed in terms of:

$$\mu_r = 1+\kappa \qquad (5)$$

Depending on the value of the magnetic permeability the substances can be classified as diamagnetic, paramagnetic and ferromagnetic. It is the difference in the permeability which is used in the process of sorting in magnetic field.

The magnetic permeability of the minerals should be averaged in order to influence crucially the magnetic force of the field. The most suitable magnetic field force for separation of chromite from the vein minerals can be determined on the basis of these results.

MEASUREMENT RESULTS

Fig. 2 displays average magnetic permeability of the major minerals. Magnetite permeability varies within 1.280.000 до 25.990.10^{-9} м^3/кg. The permeability of partially magnetized magnetites and partially martitized grains is within the same limits.

While needle-shaped ferric goetite and lepidocrite are the main constituents of limonite, showing thus weak paramagnetic behavior and low permeability, the limonite aggregates from laterite areas vary widely and possess relatively high permeability. It can be concluded thereby, that, there are ferromagnetic and ferrimagnetic substances in strongly magnetized limonite aggregates. Hematite possesses relatively high magnetic permeability in comparison to chromite. Accreted to hematite chromite grains have slightly higher magnetization and their separation behavior during classification is very alike.

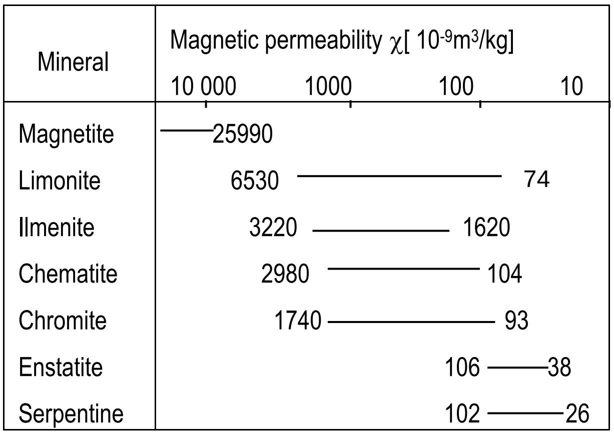

Figure 2. Total magnetic permeability of major minerals

Magnetic permeability of ilmenite grains varies widely. It depends on the content of Fe_3O_4 and Fe_2O_3.

The silicates with less iron content such as enstatite and serpentine have lower permeability compared to paramagnetic oxides; iron content in these samples is less than 10 %.

Because vein minerals, such as gypsite and montmorilonite, possess lower permeability than the other minerals, they also do not initiate problems in the process of separation.

Magnetic permeabilility of sulphidic nickel-base minerals, rutile and forms of quartz have been very rarely reviewed.

Magnetic properties of chromite

Chromite mingled crystal, like magnetite, is categorized as ferrimagnetic substance.

Feromagnetic behavior of such ferrimagnetic minerals is exhibited by weak spontaneous magnetization. Chromite contains in larger extent different ions, which are either chemically different or have physically different crystal lattices. Such kind of lattice is presented on fig. 3. The spinel structure forms a dense cubic cell of O^2 ions in whose octaedric and thetraedric sites adhere cations. Different metallic ions interchange their places due to crystallization difference, so chromite allows the existence of many substituted crystals.

Thirty two oxygen and 24 metallic atoms participate in one elementary chromite cell. For one single junction it is allowed 16 trivalent ions, as Cr^{3+}, Al^{3+} and Fe^{3+} in two different places. Eight atoms are tetraedric of type A, and the remaining eight atoms, such as Fe, Mn and Mg are of type B. The dipoles of these 16 trivalent ions compensate their distribution in the crystal. Eight divalent ions, such as Fe^{2+}, Mn^{2+} and Mg^{2+} occupy the remaining sites of B type and they contribute for the magnetization of chromite spinels. Such orientation of magnetic moment in solids is determined as antiferromagnetism.

The spontaneous magnetic moment of chromite can be described by its own from the divalent metallic ions. As a rule, metallic atoms ordered in antiparallel way exhibit paramagnetic behavior in magnetic field.

Based on these theoretical observations, magnetic properties of chromite vary depending on the mineral structure and the chemical composition.

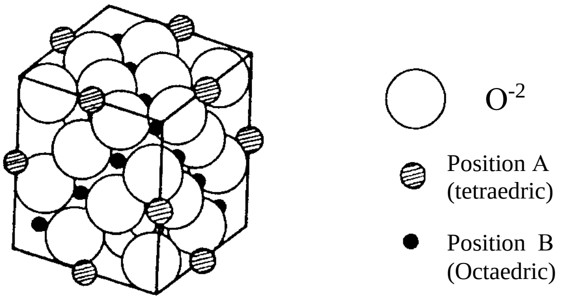

Figure 3. Perspective drawing of spinel structure

Microscopic study shows that chromite grains are frequently accreted with vein minerals. Because the vein mineral in most of the cases have high iron content, they can influence the magnetic properties of chromite grains. Mass distribution of some minerals in magnetization depends on the magnetic induction. As-used laterite and primary chromite ores originate from alike deposits. Their heavy mineral concentrates were processed by sorting in classifier. During the separation, the cross slope of the classifier was 15^0 and longitudinal slope 30^0. Table 1 shows that the observed laterite chromites are more strongly magnetized in comparison to the primary ores. In magnetic induction of 240 mT the magnetization of the laterite ore is around 33.11 %, while the magnetization of the primary chromites is only 4.4 %. The primary ore is magnetically separated mainly in the 329-480 mT limit.

Table 1. Magnetically separated rudimentary and laterite chromite, limonite aggregates and silicates, depending on magnetic induction

Magnetic induction, mT	Primary chromite	Weight part,%		
		Laterite chromite	Limonite aggregates	Silicates
80	0.2	13.5	2.5	--
80-160	0.6	12.4	17.6	--
160-240	3.6	7.2	29.3	--
240-320	5.4	19.6	33.7	--
320-400	59.8	40.1	15.6	--
400-480	29.1	6.7	1.2	0.2
480	1.3	0.5	0.1	99.8
	100	100	100	100

The different magnetized areas of the laterite chromites (ρ> 4,19 g/cm^3) were analyzed chemically (table 2 and 3). It was found that the increasing magnetic induction of FeO decreases significantly, while the contents of Cr_2O_3, Al_2O_3 and MgO increase. In magnetic induction of 480 mT, iron-containing silicates separate, thus Cr_2O_3 content decrease.

It is found from the results that the laterite mass of weakly magnetized chromites has accreted to strongly magnetized minerals, such as magnetite, maghemite and other unknown minerals, which could not be identified by means of microscope. In order to determine the influence of the chemical composition upon magnetic properties of chromite, chemical experiments with short induction intervals of 15 mT were conducted. In increasing magnetic induction FeO content decreases in general,while MgO content increases. Furthermore, oxide content, such as Cr_2O_3 and Al_2O_3, varies widely in all classes. This means that these paramagnetic components of the substance contribute in a low degree to the magnetic moment, therefore, their influence upon magnetization is not significant.

It is known that the spontaneous atomic magnetic moment depends on the number of electrons in 3d and 4f layers. Manganese which might have 4 or 5 electrones in its d layer could contribute crucially for the overall magnetization. Since MnO content is very low in all classes, varying between 0.06 and 0.1 %, manganese magnetic moment is irrelevant to the overall magnetization of chromite. Four electrons in d layer in iron are crucial for the magnetic moment. Elements like titanium do not influence the overall magnetization.

Magnetic properties of the limonite aggregates

Most of the mineralogical studies upon mineral processing of natural iron oxide, respectively iron hydroxide have been made by means of x-ray diffraction analysis, and differential thermoanalasysis (DTA). They show, that the ore contains almost all, so far known crystallographic, iron oxide-base and iron hydroxide-base minerals. There are even oxides without OH-group (α - Fe_2O_3), hematite, and maghemite (γ - Fe_2O_3) as well as oxides which contain OH-group, such as goetite (α - FeOOH) and_lepidocrite (γ - FeOOH). The remaining part of the oxides is x-ray amorphous.

The conditions of ore formation, such as climate, Eh and Ph values, primary rocks, are factors, on which depend the type of bond in iron oxides, respectively hydroxides. The limonite aggregates shown on fig. 2, consisting mainly of iron hydroxides, exhibit widely varying magnetic permeability in magnetic field.. This hinders the application of magnetization in mineral processing of chromite from laterite soils.

Different metals could be found in the limonite aggregates. At first, it was analyzed the chemical composition of limonite aggregates, magnetized in a different degree. The contents of Fe, Cr, Mn, Ni and Co, which influence the magnetization of the aggregates were measured (table 4).

It could not be proved, that there is a connection between the magnetization, and Ni and Co content which would lead to ferromagnetic properties of the substances. Ni content varies between 0.3 and 0.6 %, while Co content between 0.02 and 0.05 %.

The different content of chromium and manganese does not affect the overall magnetic moment. Cr content varies between 0.8 and 1.2%, while Mn content between 0.2 and 0.4 %.

There is dependence between magnetization and iron content. In increasing magnetic induction of separation, iron content decreases from 57.4 to 39.2 %. This shows possible presence of iron minerals (magnetite, maghemite) in strongly magnetized limonite aggregates. In strongly magnetized aggregates, separated in magnetic induction varying between 80-95 and 160-175 mT, magnetite could not be identified by means of microscope.

Table 2. Weight distribution and distribution of the metal for laterite chromite ore of the magnetic products in different magnetization (ρ>4.1)

Magnetic induction mT	Weight %	Content,%				Ratio Cr/Fe	Cr_2O_3 - Extraction %
		Cr_2O_3	FeO	MnO	Al_3O_3		
-40	5.6	15.6	69.4	2.2	4.3	0.20	2.1
40-80	7.9	30.3	42.2	4.3	10.4	0.63	5.6
80-120	8.8	34.2	34.0	6.6	12.8	0.89	7.1
120-160	3.6	36.9	29.2	7.0	13.2	1.11	3.1
160-200	4.9	39.3	27.8	7.9	14.2	1.24	4.5
200-240	2.3	41.3	24.9	8.5	14.4	1.46	2.2
240-280	8.6	43.2	23.5	9.7	14.4	1.62	8.8
280-320	11.0	46.5	21.8	10.3	14.8	1.88	12.1
320-360	16.7	48.7	19.2	10.9	15.0	2.27	19.2
360-400	23.4	49.4	18.5	11.6	15.1	2.48	27.3
400-440	5.2	48.3	18.2	12.7	16.5	2.47	5.9
440-480	0.7	47.7	17.4	13.3	16.8	2.41	0.9
+480	1.3	39.2	18.0	14.5	15.3	2.03	1.2
	100.0	42.4	26.1	9.3	13.8	1.43	100.0

Table 3. Chemical composition of laterite chromite for specific magnetic products

Magnetic induction mT	Content, %				
	Cr_2O_3	FeO	MnO	Mg	Al_3O_3
160-175	47.5/53.3	23.0/23.7	0.09/0.10	7.6/8.2	15.7/21.
240-255	41.1/58.5	21.1/21.6	0.06/0.08	9.5/10.1	11.1/27.
320-335	44.0/56.8	18.6/19.3	0.06/0.07	11.8/12.3	12.0/25.
400-415	39.4/60.3	17.0/17.5	0.06/0.10	13.4/13.8	8.8/30.
480-495	40.6/59.0	14.0/16.5	0.07/0.09	14.3/16.9	9.4/29.

Table 4 Chemical composition of the limonite aggregates in different magnetic products

Magnetic induction mT	Content, %				
	Cr	Fe	Mn	Ni	Co
80-95	0.9	57.4	0.2	0.5	0.04
160-175	1.2	53.8	0.2	0.6	0.03
240-255	1.1	51.2	0.3	0.3	0.05
320-335	1.0	47.7	0.2	0.6	0.02
400-415	0.8	45.4	0.4	0.4	0.04
480-495	0.8	39.2	0.2	0.3	0.03

The raw material was investigated for maghemite also. The creation of magnetism can be attributed to oxidation of magnets, heating of lepidocrites or other iron trioxides, such as goetite. All these ways of creation could be observed in the nature. Since maghemite shows exothermic reaction in differential thermoanalysis (DTA), this mineral can be easily distinguished from the other iron minerals.

Differential thermoanalysis

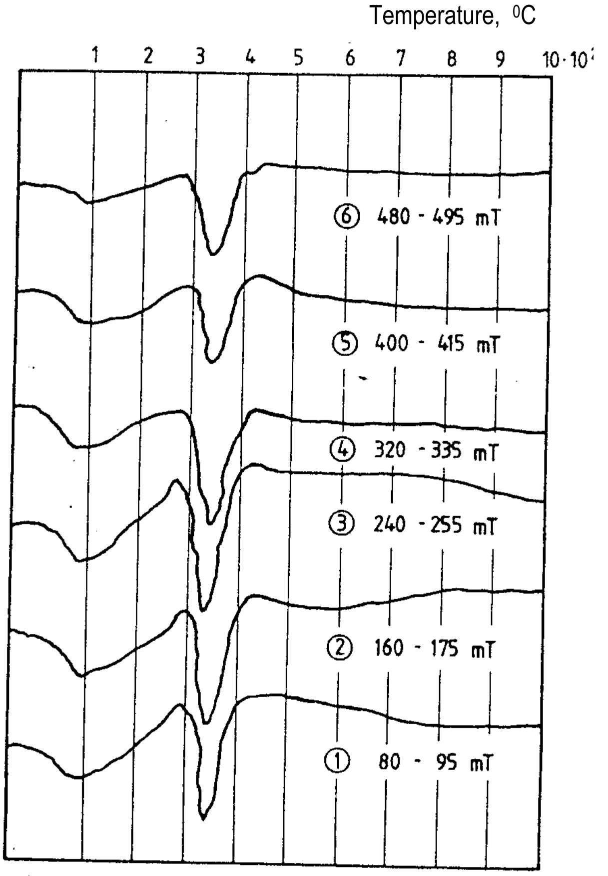

Figure 4. Differential thermoanalysis of different limonite aggregates, separated at different magnetic induction

Chemically analyzed material was used for this study. Fig. 4 shows DTA curves. It was found that two different endothermic peaks occur in the low temperature region – at 90⁰ C and at 340⁰C. The first one expresses the release of absorption water, while the second one – the formation of crystalline water and OH-groups in goetite, as well as their transformation to hematite. According to Geit, the exothermic reaction of maghemite occurs in degree of crystallization between 350 and 600⁰C. The expected exothermic reaction was not found in this temperature interval. This reaction was not observed in higher temperature intervals too.

Infrared spectroscopy was applied to study further the minerals (fig 5). For that purpose, the same material which has been used for DTA, was used. In each of the curves, shown in Fig. 5, one can found infrared absorption of goetite and lepidocrite (fig. 5). The characteristic wave number of goetite – around 904 and 803 cm^{-1} is measured precisely in each sample. At around 1028 cm-1 wavelength, there is weak infrared absorption, typical for lepidocrite. The characteristic lines of infrared absorption of magnetite and maghemite can not be traced in these spectra. Peculiarity of curves 3-5 are the slightly sharp peaks between 3700 and 3400 cm^{-1}. In wave frequency 1600 cm^{-1} the absorption could not be unambiguously determined, because different hydroxide minerals are absorbed in this region.

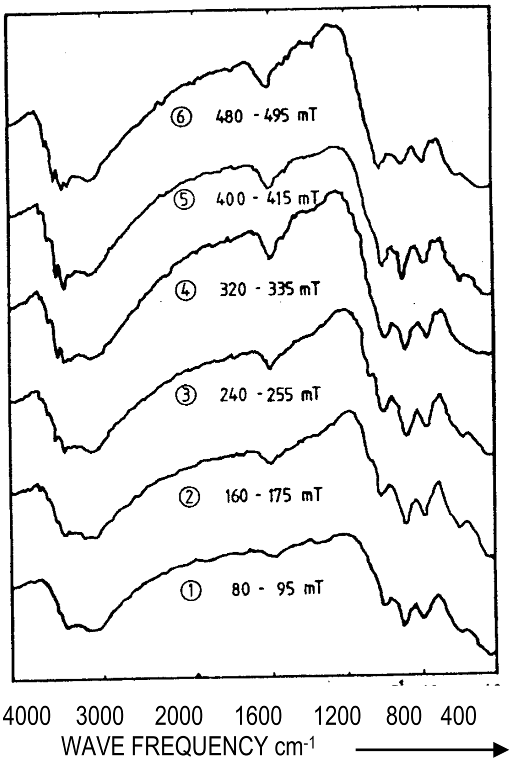

Figure 5. Infrared spectra of different limonite aggregates, separated in different magnetic induction

The results of DTA and infrared analysis show, that the limonite aggregates consists mainly of goetite.

Finally a Moessbauer spectroscopy was applied, to measure Fe^{2+}/Fe^{3+} ratio in the iron minerals. In changing the γ - source speed, each sample showed different isometric deviation and different radiation adsorption. The six lines spectrum, necessary for estimation of Fe^{2+}/Fe^{3+} ratio could not be observed, meaning that this spectroscopy method is not suitable for determination of minerals in this case.

CONCLUSIONS

The present studies of magnetic properties of chromium-containing laterites, incorporating modern and effective methods, show that there is a difference in magnetic properties of chromite and the other basic mineral – limonite.

In suitable magnetic induction, within 320-480 mT, a good separation of these two minerals could be achieved.

The chromite product obtained reaches over 40 % Cr_2O_3 content, at FeO content around 17 %. These results could be a base for future research aimed at obtaining a chromite concentrate.

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TECHNOLOGICAL POSSIBILITIES FOR PULP DENSITY ALTERATION AT ELATZITE FLOTATION MILL

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Bulgaria

ABSTRACT
The pulp density expressed in percent solids is an important technological factor, depended upon the mineralogical-technological characteristics of the treated ore, the type of the flotation cells employed and the quality characteristics required for the products obtained. During several years the Elatzite flotation mill has been operating at 32 % pulp density for rougher flotation. The lab and industrial scale investigations performed have provided an opportunity to raise this parameter up to 42 % at a concomitant technological values increase.

INTRODUCTION

The ore from Elatzite deposit is known as gold bearing copper-pyrite ore, having copper content about 0.4 % and 0.5 % sulphur. Chalcopyrite, bornite, chalcozine and coveline are the principal copper minerals. The amount of oxidised copper minerals does not exceeds 6-7 %. Very unevenly distributed molibdenite is met in the ore with mean concentration ca 0.004 % Mo. Gold is present both in metallic form, finely dispersed inside copper minerals and quartz, as well as an inclusions inside copper sulphides and pyrite crystal lattices. Metallic gold is from 1 to 5 μm in size. It is liberated during fine grinding. The liberated particles of metallic gold either sticks onto larger mineral particles or floats in thickeners overflow waters. Gold is either recovered in the collective flotation circuit or is inevitably lost in the tailings with the intergrowths. Fine clay or iron hydroxides slime fractions are rarely met only in limited sections of the deposit.

The described peculiarities for the mineralogical and technological characteristic of the ore provide a challenging avenue for testing the possibilities for pulp density increase in rougher flotation. The flotation cells employed at present in the mill are of Denver 500 D-R type. They offer possibilities for maintaining higher pulp density. Moreover, various companies around the world treating copper sulphide ores with the same cell types sustain pulp solids of 40 % and higher (Pima, Pallabora, Betlehen, Sperita etc.). Our objective at first instance, was to study the influence of pulp density under lab and industrial scale upon grade and recovery of copper in the copper concentrates.

EXPERIMENTAL

The study has been performed under lab and industrial scale. The laboratory experiments have been carried out by the help of Denver lab machine with cell volume 8 L and impeller speed of 1500 min^{-1}. In order to figure out precisely the pulp density influence, the laboratory tests were performed under different flotation regimes. The flowsheets used copy part of the existing in the mill flowsheet. Four tests with different respective densities of 17.85, 33.03, 42.52 and 51.90 % solids, were performed following the flowsheet described at Figure 1. At Figure 2 the relationships between pulp density and Cu/S ratio in concentrate I and II, the recovery of copper in concentrate I and copper losses in the tailings are studied.

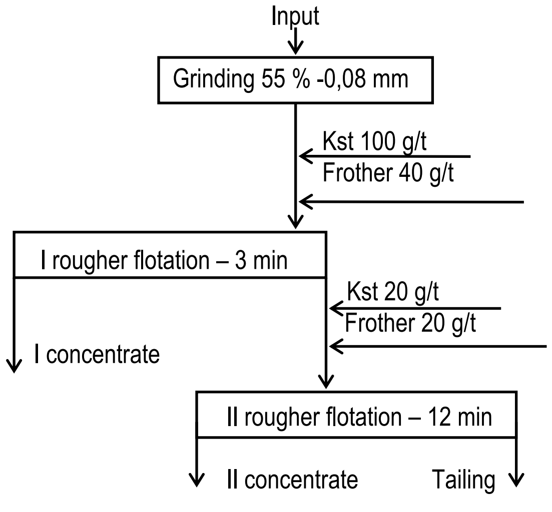

Figure 1. Flowsheet for investigation influence of the pulp density upon technological results

The relationships shown at Figure 2 suggest that the optimal value for pulp density concerning the technological results is shifted from 32 % (the density under which the mill operates) to 42 %. Moreover, this density increase will lead to increase in grinding mills capacity at no sacrifice in technological quality, since maintaining an increased density promotes coarser mineral grains to float in the concentrate.

Table 1. Technological results (flow sheet fig. 1)

Input I rougher flotation, solid, %	Products	Yield %	Containse, % Cu	S	Recovery, % Cu	S
17,85	I c-te	1,48	24,8	28,9	74,84	68,73
	II c-te	1,27	1,27	8,43	10,249	17,204
	Tailing	97,25	0,08	0,09	15,697	14,064
	Ore	100,00	0,495	0,62	100,00	100,00
33,03	I c-te	5,50	9,19	9,01	86,46	84,15
	II c-te	2,96	0,51	0,68	2,58	3,42
	Tailing	91,54	0,07	0,08	10,96	12,43
	Ore	100,00	0,5846	0,5889	100,00	100,00
42,52	I c-te	4,64	10,10	9,90	88,24	92,30
	II c-te	8,34	0,54	0,25	8,48	4,20
	Tailing	87,0	0,02	0,02	3,28	3,50
	Ore	100,00	0,531	0,4976	100,00	100,00
51,90	I c-te	7,602	5,86	4,78	83,60	83,44
	II c-te	5,384	0,65	0,37	6,60	4,57
	Tailing	87,014	0,06	0,06	9,80	11,95
	Ore	100,00	0,5327	0,4385	100,00	100,00

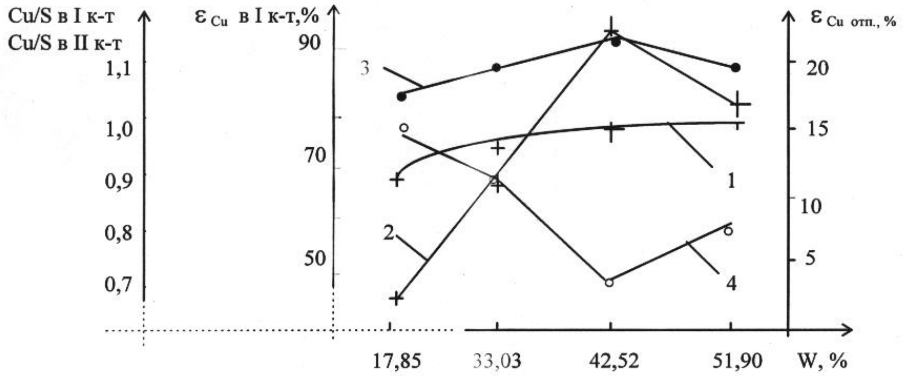

Figure 2. Influence of the pulp density (W, %) on the ratio Cu/S in: I concentrate (1); II concentrate (2); recovery of the Cu in concentrate (3); losses Cu in tailing (4)

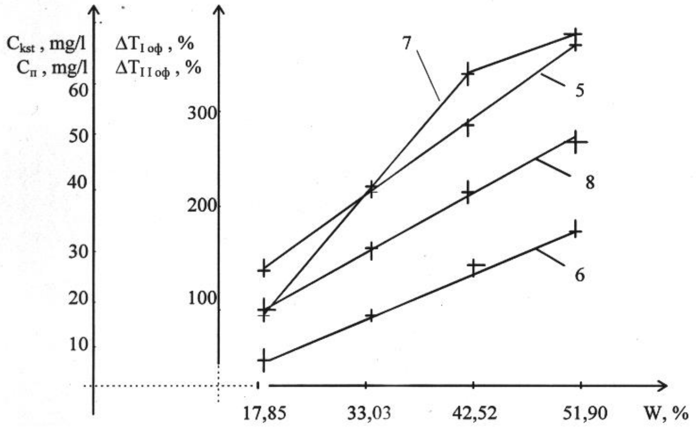

Figure 3. Influence of the input pulp density on: concentration of the Kst, mg/l (5); floter, mg/l (6); flotation time in I rougher flotation, min (7); flotation time in II rougher flotation, min (8)

When the pulp throughput remains the same, the increased density is leading to reagent savings at increased flotation time. The later fact with no doubts is leading to higher recovery of the principal components. However, the increase in pulp density for copper rougher is leading to lower copper content in the rougher concentrate. Owing to the specific flowsheet employed in the mill, an objective was set up to study how the increased density influence further upgrading and cleaning of rougher concentrate, provided it is not subjected to regrinding. Laboratory tests following the flowsheet shown at Figure 4 were performed.

The results obtained are presented in Table 2. They indicate, that the intergrowths which usually are recovered in first rougher flotation and are leading to lower grade of the concentrate, could be successfully directed in the first rougher tail and further on subjected to regrind together with the concentrate coming from second rougher flotation.

The final evaluation concerning the pulp density influence upon the flotation performance and for choosing the correct density value has been accomplished following the flowsheet shown at Figure 6.

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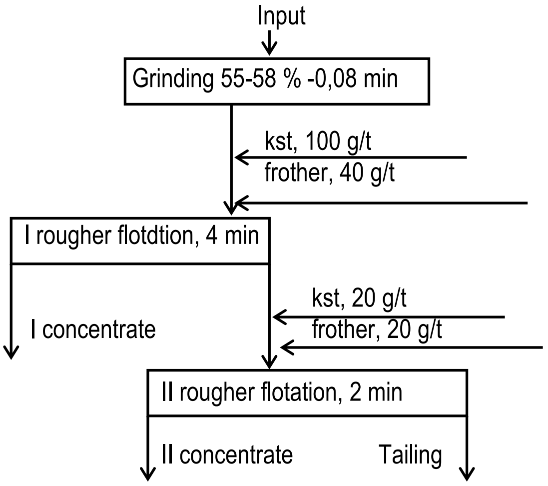

Figure 4. Flowsheet in open cicuite

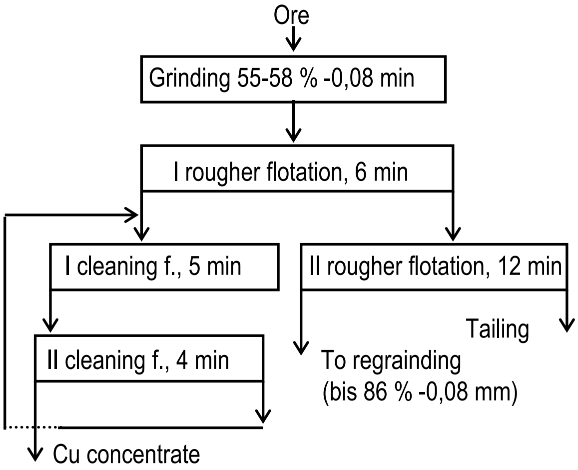

Figure 5. Flowsheet for investigation the influence of the grate on to recovery in I rougher flotation

Table 2. Technological results (flowsheet fig. 5)

Solid in I rougher flotation, %	Products	Yield, %	Contains, %		Recovery, %	
			Cu	S	Cu	S
32,22	Cu c-te	1,64	25,60	24,60	81,64	77,41
	Product for regrinding	7,73	0,64	0,70	9,55	10,39
	Tailing	90,63	0,05	0,07	8,81	12,17
	Ore	100,00	0,51	0,52	100,00	100,00
49,84	Cu c-te	1,96	24,40	24,70	81,64	77,41
	Product for regrinding	14,29	0,50	0,57	9,55	10,39
	Tailing	82,75	0,05	0,06	8,81	12,17
	Ore	100,00	0,58	0,61	100,00	78,66
40,00	Cu c-te	2,07	18,60	22,06	86,64	84,27
	Product for regrinding	5,07	0,62	0,94	7,09	8,88
	Tailing	92,86	0,03	0,04	6,27	6,85
	Ore	100,00	0,44	0,54	100,00	100,00

Table 3. Technological results (flow sheet fig. 6)

Solid in input in rougher flotation %	Products	Yield %	Contains, %		Recovery, %	
			Cu	S	Cu	S
32	Cu c-te	1,92	23,75	23,18	88,97	85,13
	Tailing	98,09	0,057	0,079	11,03	14,87
	Ore	100,00	100,00	100,00	100,00	100,00
40	Cu c-te	2,27	19,41	23,45	94,75	91,80
	Tailing	97,83	0,025	0,048	5,25	8,20
	Ore	100,00	0,466	0,58	100,00	100,00
51	Cu c-te	3,24	12,80	15,50	90,06	88,12
	Tailing	96,76	0,047	0,054	9,94	9,18
	Ore	100,00	0,46	0,57	100,00	100,00

Table 4. Technological results with high density pulp in plait conditions

Solid in input in rougher flotation, %	Cu in ore, %	Cu in concentrate, %	Cu recovery in concentrate, %
41,08	0,491	24,07	86,67
41,57	0,408	26,25	88,15
42,39	0,440	27,73	89,39
43,17	0,419	26,32	87,36
43,32	0,414	25,65	86,36
average 42,16	average 0,440	average 26,42	average 87,30
average 32.00	average 0,410	average 24,70	average 86,80

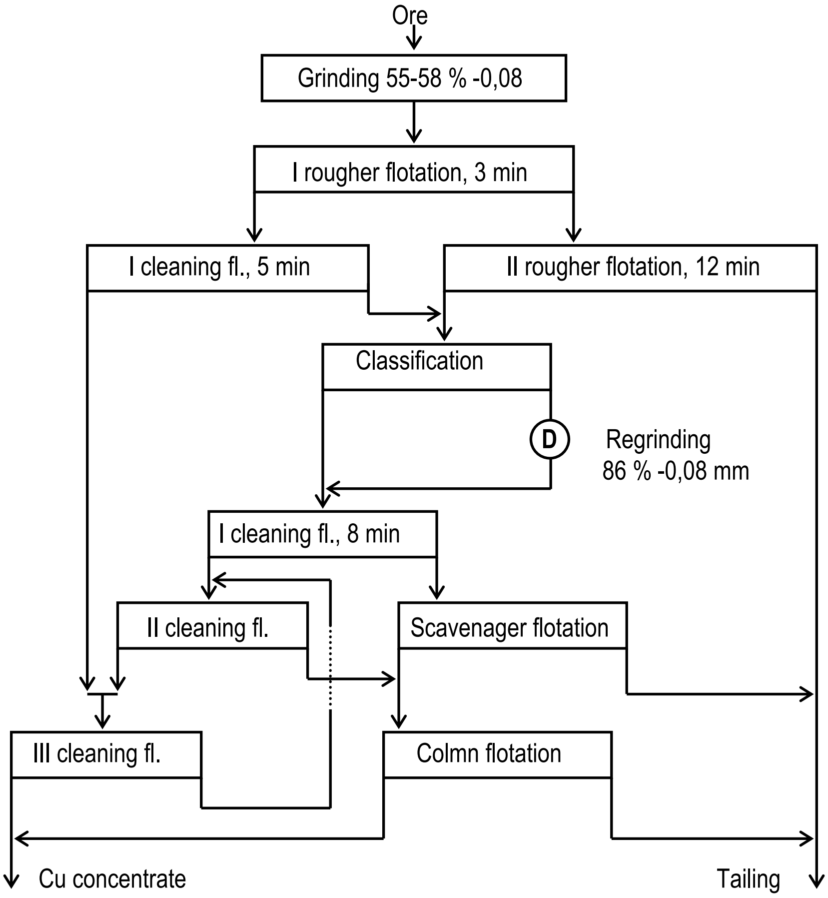

Figure 6. Flowsheet with colmn flotation

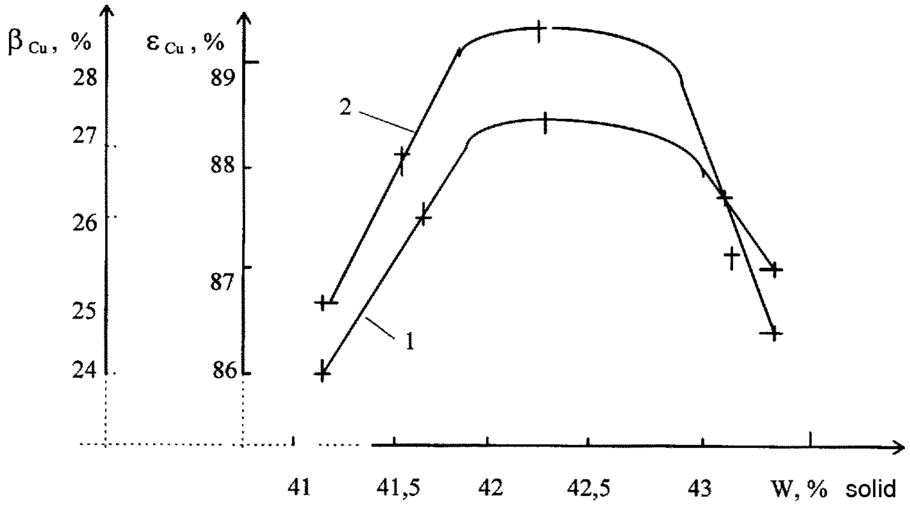

Figure 7. Influence of pulp density (W, % solid) on quality of concentrate (β_{Cu}, %) – 1 and recovery Cu (ε_{Cu}, %) - 2

The results obtained are presented in Table 2. They indicate, that the intergrowths which usually are recovered in first rougher flotation and are leading to lower grade of the concentrate, could be successfully directed in the first rougher tail and further on subjected to regrind together with the concentrate coming from second rougher flotation.

The final evaluation concerning the pulp density influence upon the flotation performance and for choosing the correct density value has been accomplished following the flowsheet shown at Figure 6. The obtained results are shown in Table 3. They suggest that 42 % pulp density seems to be the optimal one for Elatzite ore flotation.

Industrial tests were performed at mill site in order to confirm the above findings. The results are presented in Table 4, while the mill operates under the flowsheet shown at Figure 6 without column flotation stage.

Figure 7 presents the relationships between pulp density [W, % solids] for rougher flotation and copper grade (β_{Cu}, %) and recovery (ε_{Cu}, %) in the final concentrate. Industrial results have confirmed the findings deriving form the lab scale tests that the optimal pulp density is 42 %.

CONCLUSIONS

The performed laboratory investigations, which have been validated at industrial scale indicate that the increase in pulp density from 32 % to 42 % could lead to the following:

1. Copper recovery increase, most probably due to the intergrowths recovered during rougher flotation stage, which are subjected to regrinding and thus are leading to copper recovery increase without decrease in concentrate grade;
2. The increased rougher flotation pulp density offers the possibility for increase in grinding mills capacity and for reagents savings;
3. The fact that there is no need to finely regrind the whole ore, but the intergrowths are subjected to fine regrinding only is leading to energy saving during mineral liberation;
4. Further studies are warrant in direction of gold recovery, which is anticipated to benefit from the suggested approach as well.

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NEW SELECTIVE COLECTOR FOR FLOTATION OF SULFIDE ORES

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ABSTRACT
A purposefully synthesized reagent was applied as an additional collector to the flotation of integral sulfide ores. Investigations were carried out with real ore under laboratory conditions in an open and closed cycle. Technological properties of the new reagent were studied for different slurry density and different mode of grinding. It was established that use of an additional reagent collector, supplied into the grinding process allows significant enhancement of gold recovery from collective copper-pyrite concentrate.
Key words: flotation, gold, collector

INTRODUCTION

General technology for flotation of sulfide auriferous ores employs xanthogenate as a main collector. Pyrite for this type or ores is depressed with significant quantities of lime. As it is known, large quantities of calcium oxide, available in the flotation slurry depress the elementary gold and reduce its recovery in copper pyrite concentrates (*Boteva, 1992*). Use of additional collectors for enhancing gold recovery in sulfide concentrates is rarely practiced. Gold recovery is low under these conditions. The high rate of lime consumption depresses it, and xanthogenates are insufficiently effective gold collectors, especially in the cases, when particles of elementary gold are covered with iron hydroxide.

A new reagent collector is synthesized for avoiding the above disadvantages in the industrial technology for selective, gold-containing ores. Synthesis is performed on the basis of cheep chemicals, large quantities of which are produced by chemical industry. The reagent is water-soluble and most probably contains two functional groups. The two functional groups provide high rate of gold recovery in sulfide concentrates, forming most probably, a hepatic ring with the metallic catione. Rate of gold recovery is not accompanied with reduction of copper sulfide recovery. Technological properties of the new collector were studied under laboratory conditions with tests in the open cycle.

SETTING OF THE EXPERIMENT

The synthesized new reagent – collector is analyzed by infrared spectroscopic methods (fig. 1). It is subjected to analysis in its natural type. It is studied in the domain from 5 to 40x100 cm^{-1}. This is the field, where C=S, C-S, SH, N-C, N-C-O connections will be revealed.

Laboratory investigations for technological properties of newly synthesized reagent-collector are carried out with real ore under conditions of open cycle according to the schemes sin figures 2 - 4.

Three types of ore are investigated: from the Elatsite, Chelopech and Asarel, respectively.

Mineralogical characteristic of the assay from Elatsite deposit

A total of 61 minerals are established in the ores of the Elatsite deposit, including 48 ore minerals and 13 non-ore minerals. They are subdivided into major, secondary and rare. Major ore minerals are chalcopyrite and pyrite, secondary minerals are bornite, molybdenite, native gold, electrum, hematite etc., non-ore minerals are presented as quartz, potassium feldspar, biotite etc.

Ores in the Elatsite depsoit are divided into three sorts: sulfide copper ores - not more than 10 %, mixed ores – oxide copper from 10 to 30 % and oxides with oxide copper more than 30 % Average copper content indifferent sorts of copper is the following:

Sulfide ores in granodiorite rocks:	0.43%
Sulfide ores in schistous rocks:	0.38%
Mixed ores in granodiorite rocks:	0.32%
Mixed ores in sschistous rocks:	0.32%

Major source of copper in the sulfide ores is the chalcopyrite – nearly 78%, then follows the bornite – 22%.
Content of gold is as follows:

Economic sulfide ores:	0.14 g/t
Economic mixed ores:	0.13 g/t
Non-economic oxide ores:	0.18 g/t

Content of sulfur and pyrite varies from 0.1 to 2.3%.

Mineralogical characteristic of the assay from the Chelopech deposit

The most important economic value of the deposit is determined by the mineral association of copper-arsenic-gold. It is characterized with the high concentration of sulfosalts. The major minerals are: pyrite, enargite, bornite, tenantite, chalcopyrite, accompanied by gold and gold-containing minerals. Pyrite is the mostly available mineral. It is represented by fine granular aggregate, and pyrite crystals are rarely available. The sphalerite is available as isolated injections in altered tuffs and compact masses, together with other minerals, as well. The galena is available at periphery of the ore body, where it is incorporated in lead-zinc deposits together with pyrite and sphalerite. The tenantite is bound in a pyrite-bornite-chalcopyrite association and contains not only copper, arsenic and sulfur but also tellurium and tellurium-containing sulfosalts. This association is the main carrier of gold.

Most important rock-forming minerals are quartz and barite. The quartz forms granular aggregates of grain size of several microns. The barite is distributed as natural, coarse granular, almost mono-mineral deposits, formed in the marginal parts and above the ore bodies.

Mineralogical characteristic of the assay from the Asarel deposit

The deposit is of porphyry copper type. Ore reserves are calculated in three sorts: oxides, mixed sulfide-oxide and primarily – sulfide. Other copper minerals are bornite, chalcopyrite, covelline, copper oxides and sulfates. Copper is the major economic component of the deposit. There are several parageneses at the deposit. Major minerals at the feldspar – biotite – magnetite parageneses are potassium feldspar, biotite and magentite, and the secondary are epidote, aduare, chlorite, specularite, quartz. Pyrite is the only ore mineral in the quartz-sericite-pyrite paragenesis. It is available in fine veinlets or accumulations. Major minerals in the quartz-pyrite-chalcopyrite paragenesis are pyrite, chalcopyrite and quartz and secondary are molybdenite, tenantite, tetrahedrite etc.

The major primary ore mineral in the deposit chalcopyrite. It is totally available and appears as veinlet injections in both sericite rocks and slightly changed propilitized diorite porphyrites.

Major secondary ore mineral is the chalcosine, pyrite also has economic importance. The chalcosine is the most widely distributed mineral in the mixed sulfide-oxide ores. Furthermore, in the deposit there are bornite, coveline, malachite, azurite, natural copper and natural gold.

Technical characteristics

Flotation tests are carried out in a Denver flotation cell, 1500 revolutions/min with a cell capacity of 4 liters for the rough and 2 liters for the scavenge flotation.

Slurry density is different according to type of material and particular flotation conditions. Grinding is performed in a ball mill of 105 revolutions/min. The solid – liquid ratio is 1:1 in its volume. Mill loading with balls is as follows:

Table 1. Granular composition of mill loading with balls

Diameter of balls, mm	**8**	**8÷17**	**17÷20**	**20÷28**
Quantity, кг	1	2.2	2	0.8
yield, %	17	36.6	33	13.1

The reason for testing with three types of sulfide ores – from the deposits of Elatsite, Chelopech and Asarel, respectively is observing the behaviour of newly synthesized reagent for different mineralogical composition of the ore.

RESULTS FROM EXPERIMENTS

A new compound characterized by the following infrared spectrum is synthesized on the basis of several initial substances (figure1).

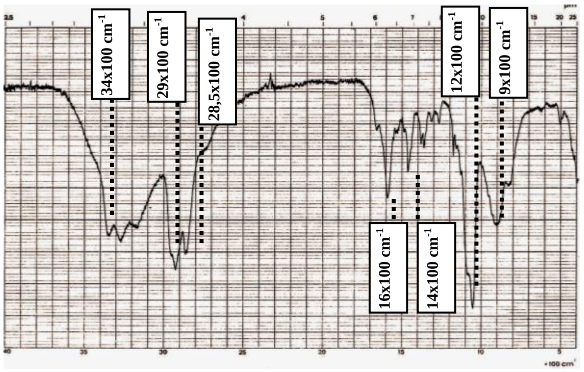

Figure 1. Infra-red spectrum of newly synthesized reagent – collector.

The new compound is water-soluble, crystallizing in regular rhombohedral, transparent, light yellow crystals. The infra red spectra show availability of S=C, -S-H, CH_2 – S - CH_2, HO-CH_2 links. The availability of these links suggests availability of two functional groups, fastened to a common hydrocarbonic - radical. The last suggests good technical behaviour for flotation of sulfide copper gold-containing ores, especially for gold metallic cations, which are expected to form hepatic rings. Investigations for establishing of technological characteristics of the reagent are carried out with ores from the Chelopech, Elatsite and Asarel deposit, respectively, for the above-mentioned reason.

Experiments on ore from the Elatsite deposit

Experiments on assays from the Elatsite deposit are carried out according to the flowsheet in fig. 2. Results are represented in table 2 and graphically shown in fig. 5. They reveal rate in gold recovery without disturbing the recovery of copper for consumption 15 g/ton, fed into grinding. Deterioration of output for consumption higher than 15 g/ton is most probably caused by the formation of poly-layered coating of the new collector.

Experiments on ore from thee Chelopech deposit

Objective of experiment is improving the recovery of gold and copper in the collective concentrate by the use of additional reagent-collector. Tests are carried out according to the scheme in fig. 3 and results are represented in table 3 and figure 6. The best results for gold and copper are obtained for consumption of newly synthesized reagent of 20g/ton.

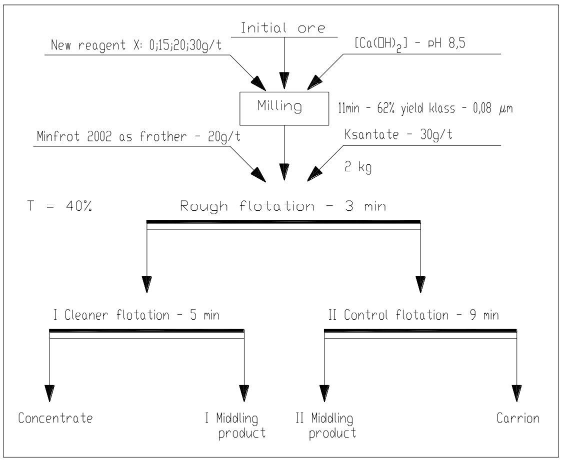

Figure 2. Flowsheet for ore from the Elatsite deposit

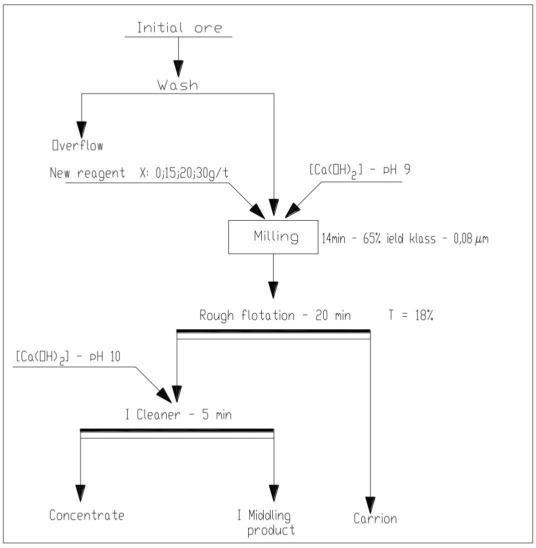

Figure 3. Flowsheet for ore from the Chelopech deposit

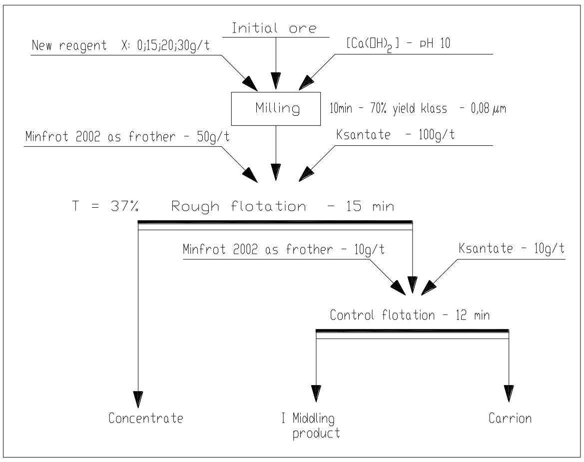

Figure 4. Flowsheet for ore from the Asarel deposit

Experiments on ore from the Asarel deposit

Experiments are carried out according to the flowsheet in figure 4. Results are shown in table 4 and figure 4. The best results for recovery of gold and copper are obtained for consumption of the newly synthesized reagent of 20 g/ton.

Table 2. Results from flotation tests on ores from the Elatsite deposit for different consumption of newly synthesized reagent

Addition of collector	Products	yield γ %	Content β,%			Recovery ε, %		
			Au	Cu	S	Au	Cu	S
			g/t	%	%	g/t	%	%
0 g/t	concentrate.	2,67	5,65	16,9	21,97	50,66	67,12	61,36
	I middle product.	2,86	0,86	1,86	2,80	8,25	7,90	8,36
	II middle product..	5,03	0,68	1,26	2,20	11,48	9,42	11,57
	waste	63,00	0,14	0,166	0,284	29,59	15,54	18,69
15 g/t	concentrate.	3,09	5,82	14,35	18,5	83,33	73,85	71,16
	I middle product.	2,70	0,16	1,43	2,02	1,99	6,42	6,78
	II middle product..	3,70	0,35	1,06	1,35	5,99	6,52	6,20
	waste	62,50	0,03	0,127	0,204	8,67	13,20	15,84
20 g/t	concentrate.	2,225	5,25	13,57	16,85	70,44	60,01	67,83
	I middle product.	2,90	0,24	1,88	2,35	4,19	10,83	12,33
	II middle product..	3,75	0,55	1,39	2,00	12,43	10,36	13,56
	waste	63,00	0,034	0,15	0,055	12,91	18,78	6,26
30 g/t	concentrate.	2,10	5,87	16,5	20,8	77,20	79,37	88,40
	I middle product.	2,65	0,24	0,94	1,40	3,98	5,70	7,50
	II middle product..	2,925	0,35	0,15	0,37	6,41	1,00	2,19
	waste	66,00	0,03	0,09	0,01	12,40	13,91	1,89

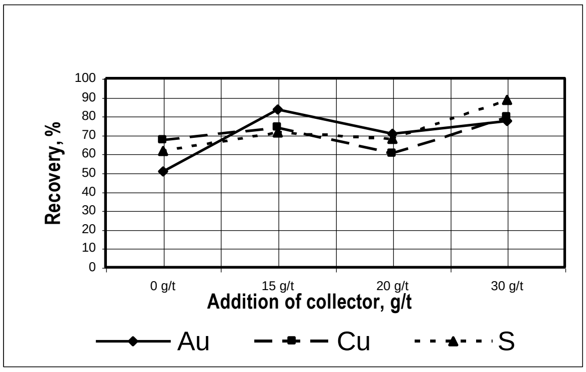

Figure. 5. Recovery of Au, Cu and S as a funtion of new collector addition - "Elazite" mine

CONCLUSIONS AND DISCUSSION OF RESULTS

Experiments with the three types of ore revealed:

1. The new reagent enhances recovery of gold and much less recovery of copper, without deteriorating the quality of concentrates.

2. The three rounds of experiments show an optimum for rate of consumption. Rate of consumption is higher for ores of higher content of sulfide minerals (Chelopech) or availability of very fine slimes that increase adsorption of collector, due to its larger relative surface. This confirms the suggestion for poly-layered adsorption of additional collector.

3. It may be suggested that for a certain rate of collector consumption the availability of more than one functional group changes the structure of adsorption layers and brings to hydrophilizatoin of gold particles.

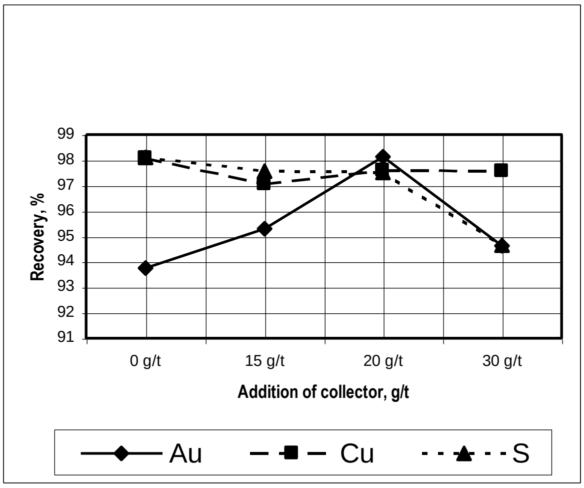

Figure. 6. Recovery of Au, Cu and S as a funtion of new collector addition - "Chelopech" mine

Table 3. Results after flotation experiments with ore from “Chelopech” mine by using of diferent addition of a new reagent”

Addition of collector	Products	yield γ %	Content β,%			Recovery ε, %		
			Au	Cu	S	Au	Cu	S
			g/t	%	%	g/t	%	%
0 g/t	concent rate	48,93	9,03	9,14	46,2	93,74	98,08	98,10
	Middle product	9,36	1,99	0,56	4,62	3,95	1,14	1,87
	waste	41,71	0,26	0,08	0,01	2,30	0,76	0,02
15 g/t	concent rate	51,14	9,40	4,14	21,77	95,28	97,03	97,57
	Middle product	9,09	1,17	0,33	2,97	2,10	1,37	2,36
	waste	39,77	0,33	0,087	0,01	2,60	1,58	0,06
20 g/t	concent rate	51,57	9,7	3,61	19,62	98,12	97,58	97,51
	Middle product	5,66	1,2	0,46	3,67	1,33	1,36	2,00
	waste	42,77	0,06	0,047	0,11	0,54	1,05	0,47
30 g/t	concent rate	50,30	10,04	4,08	21,5	94,62	97,56	94,65
	Middle product	5,99	2,89	0,38	4,07	3,24	1,08	2,13
	waste	43,71	0,26	0,065	0,84	2,12	1,35	3,21

Table 4. Results after flotation experiments with ore from “Asarel” mine by using of diferent addition of a new reagent.

Addition of collector	Products	yield γ %	Content β,%			Recovery ε, %		
			Au	Cu	S	Au	Cu	S
			g/t	%	%	g/t	%	%
0 g/t	concentrate	6,324	0,590	3,480	24,380	47,119	78,504	90,534
	middle product.	7,601	0,030	0,170	0,830	2,880	4,609	3,705
	waste	86,073	0,046	0,055	0,114	50,001	16,887	5,762
	overflow	21,769	0,139	0,250	1,060	38,215	19,414	13,550
15 g/t	concentrate	6,870	0,787	3,570	25,170	65,941	84,104	92,679
	middle product.	6,870	0,030	0,110	0,570	2,514	2,591	2,099
	waste	86,218	0,030	0,045	0,113	31,545	0,292	5,222
	overflow	26,981	0,031	0,260	1,080	10,213	23,692	15,619
20 g/t	concentrate	7,292	0,920	3,670	25,980	71,911	84,668	92,608
	middle product.	8,036	0,010	0,150	0,670	0,861	3,814	2,632
	waste	84,670	0,030	0,043	0,115	27,228	11,519	4,760
	overflow	24,500	0,030	0,300	1,110	7,885	23,255	13,292
30 g/t	concentrate	6,430	1,315	3,850	27,980	33,464	76,678	85,531
	middle product.	3,890	1,556	0,230	1,140	23,955	2,771	2,108
	waste	89,660	0,120	0,074	0,290	42,581	20,551	12,361
	overflow	23,390	0,109	0,270	1,150	10,093	19,564	12,788

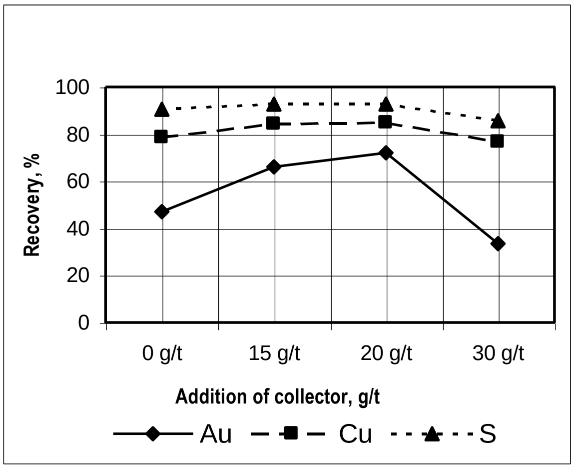

Figure. 7. Recovery of Au, Cu and S as a funtion of new collector addition - "Asarel" mine

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PRELIMINARY TREATMENT OF THE COPPER SLAGS

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ABSTRACT

It is examine preliminary treatment of the copper slag's, product obtained in process of black lead copper cleaning. The slag's are separated in two products - one rich with lead, and the other with copper. Thesis products can treated directly in lead and accordingly copper smelting. By that the lead recovery in lead smelting goes up, the NaOH consummation goes down and furnace productivity increases too.

INTRODUCTION

Pyrometallurgy is the main metallurgical method for lead concentrates treatment. It is obtained black lead with As, Sb, Sn, In, Zn and Cu like impurities. The first stage of cleaning is to remove copper in copper slag's. In relationship with composition of the input lead concentrates and treatment parameters, the copper slag's contains: 45-47 % Pb; 10-20 % Cu; to 7 % - Sn, Se, Te, In and precious metals to 0,12 %. In copper slag's transmit 11 % from black lead. In directly metallurgical treatment it is obtained like middling "stain" and "shpaza" which go to metallurgical treatment. The booth products are rich of copper, but contain some amount of lead which goes out of lead smelting. The but of present investigation is to check possibilities for copper slag's separation before metallurgical treatment in two products - one rich to lead and the other rich to copper. Each of them can treated more effectively, than lick copper slag's.

CHARACTERIZATION OF THE SAMPL AND METHODS

It was investigated two samples from copper slag's. The contains of the main components and sizometrical analyze are given in table 1.

The carried out mineral and chemical analyzes showed that the samples are very similar. They are heterogeneous mixture from powder and granule material. The granule material is from metal grains containing metal lead or hard solution between copper and lead. The powder material is presented with complicated substances from Cu, As, Te and S. The phase analyses have shown that 80 % input lead is in metal form. The rest part is PbS and small part CuS. To 80 % from Cu is lick substances with As and Sb (Cu_3As, Cu_3Sb), ore in halkozin and bornite. The small part of copper is in metal form.

In relationship with conditions of the lead solidifying the surfaces of the sulfides are oxides in different stage. Fe is in from of the chemical substance with As ore $FeSO_4$. Gold is lick substance with Pb and Cu. Ag is in hard solution with Pb. The amount of the rock minerals is very little.

The fraction analyze of the copper slag's was made by the havy liquids ($CaCl_2$, Fe_2Si_3) at density 2,5 g/cm^3; 3,0 g/cm^3; 3,5 g/cm^3. The obtained results are given in table 2 and table 3.

The milling properties of the copper slag's were investigated by relative production of the class -0,068 mm in t/m^3 for rod grinding, ball grinding, semiautogenous grinding and fullatogenous grinding (fig. 1).

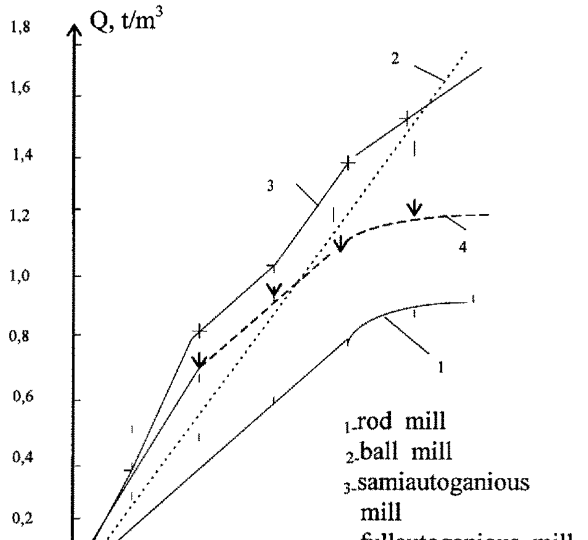

Fig.1. Influence of the milling time (t, min) on the relative productivity (Q, t/m^3) in class –0,068 mm

The rod grinding was investigated by laboratory mill L = 40 cm and D = 20 cm, with rodds ф 20 mm, φ = 36 %.

The ball grinding was investigated by laboratory mill L = 30 cm, D = 35 cm, with balls ф 16 mm, φ = 42 %.

The semiautogenous grinding was investigated by laboratory mill L = 25 cm, D = 40 cm, 10 % balls ф 16 mm.

The fullautogenous grinding was investigated in mill L = 25 cm and D = 40 cm.

The input in all tastes was 500 g copper slag's; W: S 1 : 1.

The obtained results are given in table 4.

Table 1. Characterization of the samples from copper slag's

№ of the sample	Size-mm; γ , %						Chemical contains, %			
	+3,0;	+1,0;	+0,25;	+0,12;	+0,063;	0,063;	Pb	Cu	Sb	As
I	38,68	57,85	68,29	83,79	94,99	100,00	62,74	16,89	3,56	2,43
II	41,20	59,83	69,04	85, 77	95,45	100,00	53,75	19,38	4,71	3,20

Table 2. Fraction analyze with recovery of the metals in fractions

Density of the have liquid g/cm³	Size, +3,0mm Recovery,		Size, -3,0 +1,0mm Recovery,		Size, -1,0+0,25 mm Recovery,		Size, -0,25 +0,12mm Recovery,		Size, -0,12 +0,063mm Recovery,		Size, -0,063mm Recovery,	
	Cu,%	Pb,%	Cu,%	Pb,%	Cu,%	Pb,%	Cu,%	Pb,%	Cu,%	Pb,%	Cu,%	Pb,%
2,5; floated	3,75	0,30	7,19	0,76	2,52	3,25	8,88	0,80	9,38	9,38	52,49	58,22
3,0; floated	8,55	3,88	29,01	13,87	24,69	17,12	52,52	30,44	43,92	34,94	25,66	20,81
3,5; floated	24,10	17,44	31,17	30,76	46,91	47,88	32,12	35,29	42,21	42,19	1,83	6,84
3,5; settled	63,30	78,38	32,68	54,61	25,88	32,35	7,26	33,47	13,49	13,44	14,02	14,13
Input sample	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0

Table 3. Fraction analyze with metal contains in fractions

Density of the have liquid, g/cm³	Size, +3,0 mm Contain,		Size, -3,0 + 1,0mm Contain,		Size, -1,0 +0,25mm Contain,		Size, -0,25 +0,12mm Contain,		Size, -0,12 +0,063mm Contain,		Size, -,063 mm Contain,	
	Cu,%	Pb,%	Cu,%	Pb,%	Cu,%	Pb, %	Cu,%	Pb,%	Cu,%	Pb,%	Cu, %	Pb, %
2,5; floated	24,17	6,20	12,12	7,80	8,63	30,10	5,60	8,88	24,40	3,10	19,21	32,75
3,0; floated	31,33	45,00	27,71	35,65	11,09	78,81	46,28	52,52	16,14	35,80	27,30	34,00
3,5; floated	26,30	60,20	10,11	60,17	7,12	77,20	42,10	32,12	12,11	33,10	27,35	36,65
3,5; settled	20,20	73,10	8,10	82,60	6,15	81,70	7,26	79,79	16,15	61,60	27,30	41,79

Table 4. Pb and Cu contains in class -0,068 mm at different tips millings.

Milling time, min	Rod mill Contain, %		Ball mill Contain, %		Semiautogenious milling (10 % balls) Contain, %		Fullautogenious milling Contain, %	
	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu
10	20,2	24,2	19,8	26,2	18,3	28,6	18,1	29,2
15	21,6	25,6	20,6	25,5	20,6	26,2	21,4	28,1
20	23,5	19,4	24,7	24,2	24,3	25,9	22,6	26,2
25	26,7	21,5	30,9	19,5	30,6	25,6	28,3	24,3
30	30,1	16,2	36,8	20,5	32,4	24,2	30,1	20,6

RESULTS AND DISCUTION

Analyze of the obtained results from chemical and gravity investigations show:

1. The main part of the copper slag's is in grains with size up to 0,25 mm.
2. The rich lead containing grains are with average size up to 0,25 mm and relative density up to 7,0 g/cm³.
3. The rich copper containing grains are with down to 0,25 mm and density down to 7,0 g/ cm³.
4. Increasing of the grinding time goes to increasing the yield the grains down to 0, 068 mm with increasing the contains of the lead and copper in.
5. The relative production of the mills is highest by ball grinding, but selectivity of the autogenous grinding is better.

On base of results of the carried out investigations we created flowshit for copper slag's treatment (fig.2). The obtained results are given an fig. 2 too.

The lead rich product was treated by smelting with 15 % lead concentrate, 6 % NaOH and 4 % coke in laboratory furnace. The obtained metal lead contains 97,60 % Pb; 1,03 % Cu; with 96,62 % recovery of the lead and 9,62 % recovery of the copper.

The copper rich product was treated with 22 % lead concerted, 10 % NaOH $^{-}$ and 94,97 % Pb and 2,98 % Cu with 87,3 % recovery of the lead and 2,98 % recovery of the copper.

The suggested flowshit for copper of lead to rest in lead smelting and only little part goes to copper smelting. In results the recovery of the lead goes up and consummation of NaOH goes down.

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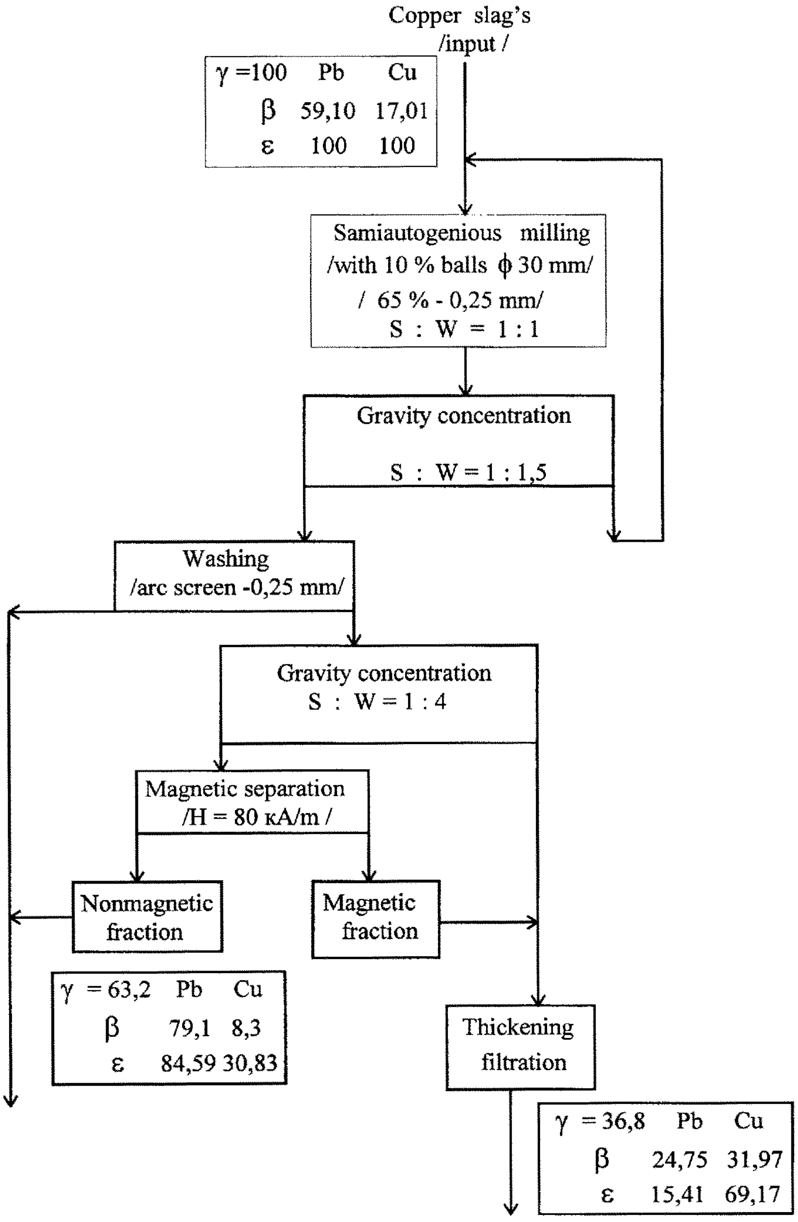

Fig.2. Flow shit in closed circuit for copper slag's treatment

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RESEARCH WORK OF THE IMPACT OF THE PULP AGITATION FLOATATION SPEED AT DIFFERENT DENSITY ON ADSORPTION OF SULPHO HYDRILLIC COLLECTORS

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ABSTRACT
Xanthate with different length of hydrocarbonaceous radical is the main collector used in selective floatation of sulfide minerals. Basic interaction of sulfide minerals with collector takes place in a process of agitation of the stirring agitators. This interaction basically depends on the density of floatation pulp. This research work is devoted namely to this problem.

Key words: floatation, xanthate, pulpdensity, stirring velocity.

INTRODUCTION

Selective floatation of the mineral grains runs effectively under strictly determined pulp density. This density provides several principle conditions for normal flowing of mineral floatation, as well as the appropriate selectivity of the process. High content of hard phase in the floatation pulp ensures necessary probability for meeting the mineral with air bubbles, however it hinders saturation of the pulp with air bubbles. Low content of hard material in the pulp allows high airing of the pulp but intensifies all oxidizing processes. Thus the content of the hard phase in the floating pulp is an optimal quantity, which leads to the achievement of utmost technological results. Its determination more often is performed in experimental way and depends on:

1. mineral content of the floating raw material;
2. required extent for grinding;
3. Relative density of minerals
4. Availability of initial middling slimes in the ore;
5. Used floatation reagents;
6. Accepted technological scheme;
7. Constructive specification of used machines;

This research work has the limited task to verify the possibilities for improving selectivity of division of materials at high content of hard phase in the floatation, pulp as the main obstacle of the dense pulp is diminished selectivity in division of materials through floatation. Usually the pulp density during the process of selective floatation is identical to the pulp density in the process of agitation, or more properly, the pulp density in agitation of mineral grains with floatation reagents are determined by the required density for successful realization of selective floatation of minerals. In certain technological cases successful selective floatation can be realized only if the agitation with floatation reagents has run at certain density. This is the case with the selection of mica and fluorite (50% hard content during agitation) while cleaning the feldspar (60-70% hard content during agitation) etc.) In dense pulp physically adsorbate reagents on certain minerals are rubbing around and the reagent is concentrated on the minerals where setting firmly of the reagent is hemi-absorbent. This increases the difference between floatation capacity of the two divided minerals. After agitation the pulp is diluted and floatation is carried out at lower content of hard phase in the pulp. All this leads to the necessity of independent study of the possibilities for agitation in dense pulp and particularly the speed of agitation of mineral particles in a dense pulp on the selectivity of consequent process of floatation of the mineral grains.

By increasing agitation velocity the quantity of drained in air through the open surface inevitably grows. Around the shaft of the propeller for stirring the pulp due to the rotation of the shaft and the movement of the layers of fluids a cone is set up which is as big as the bigger is the stirring of the shaft velocity and lower is the pulp density. Thus the bigger is the stirring velocity the higher is quantity of existing oxygen contained in pulp with certain density as a component of the air.

This explains the direct dependency of the speed of pulp agitation at certain level of hard content on the oxidizing processes, which are taking place in it.

Methods of research performance

We have studied through residual concentration of xanthate in the liquid phase of pulp measured in UV area at 301 nm the intensity of oxidizing at different agitation velocity and different pulp density. The velocity of rotation and percentage of hard content in the pulp have been changed. The density of the pulp expressed in percentage of the hard phase was provided through ground quartz, class – 0,2 + 0,04 mm. A sample of double purified through spirit solution isobutylene xanthate was used as xanthate is used at concentration of 100 mg/l. Calibrated curve line of the xanthate concentration in mg/l and the extinction of UV peak at the ray length of 300nm.

..Apart from oxidizing processes velocity of agitation of minerals with floating reagents has impact also on the rubbing of the surfaces of the minerals attached by adhesion to the mineral surfaces reagents, products of the oxidizing processes and middling slime particles. To find out the essence of these processes three sets of tests have been carried out. First series of test accounts for the possibility at high content of hard phase in the pulp and high agitation velocity to get removed from the mineral surface physically adsorbed floatation reagents. To this end it was chosen pure chalcopyrite and de-xanthate.

Quantity of desorbed xanthate was measured in mg/l through UV spectroscopy at 280 nm. To this end a calibrated curve was preliminary constructed between the concentration and the extinction of de-xanthate, received through electric oxidizing of isobutylene xanthate.

Achieved results and discussion

Results of performed tests of the study of impact of the density of floatation pulp and the agitation velocity on the oxidation of the xanthate at its agitation with mineral suspension are shown on figures from 1 to 6. Results of the tests for finding the role of stirring velocity at the agitation on desorption of the xanthate from mineral surface are shown on figures from 7 to 9. Quoted results displays as follows:

1) By increasing time of agitation desorption grows.
2) By accelerating agitation velocity desorption grows.
3) At equal time and velocity of agitation increased density accelerates desorption by 50% and after that level it practically does not have any effect. This is due most probably to the balance of accelerating and retarding factors of desorption. When the pulp density is increased the number of blows between the particles for a unit time grows and thus desorption of collector is accelerated. At the same time at equal velocity of pulp agitation less quantity of oxygen is dissolved calculated per 1 cm^2 division surface and therefore the oxidizing processes on the mineral surface are delayed. Bigger mineral division surface per volume unit of floatation pulp leads to more intensive oxidizing of the surface of sulfide minerals and this helps building up more reducing environment.

Balancing the running velocity of all these processes leads to certain buffering of the system, which is reflected in studied dependence.

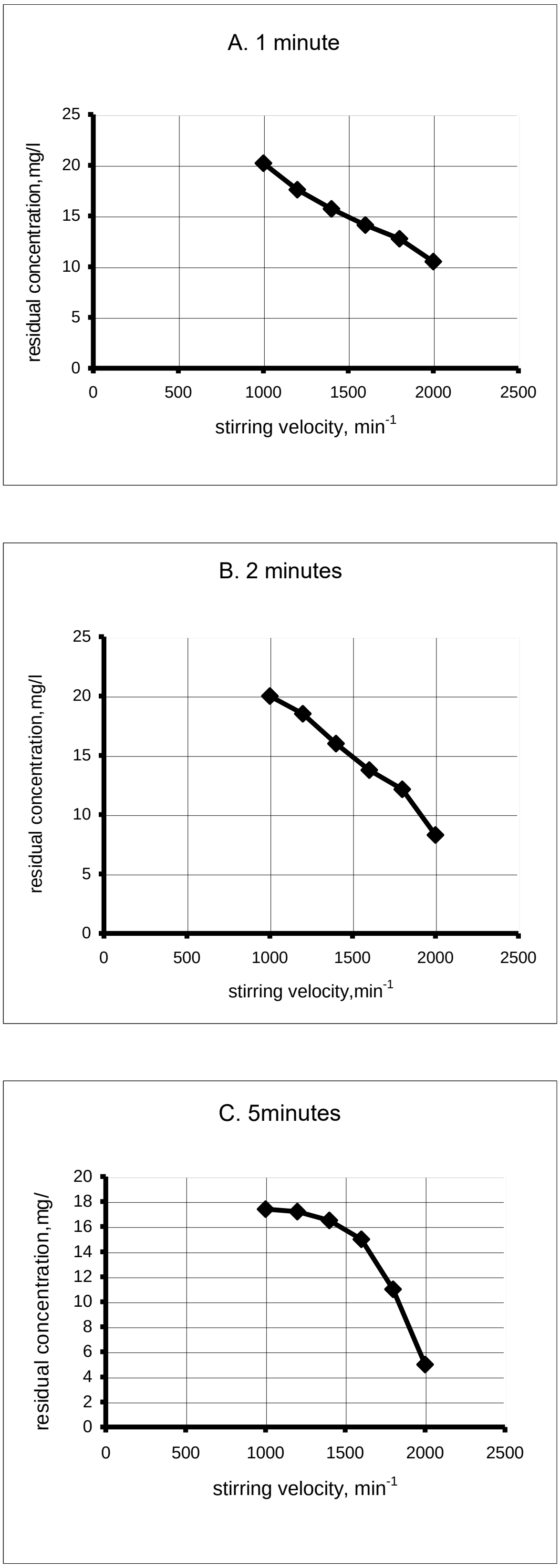


Figure 1. Influence of the stirring velocity on the oxidizing processes in the floatation pulp at density of the pulp 10%.

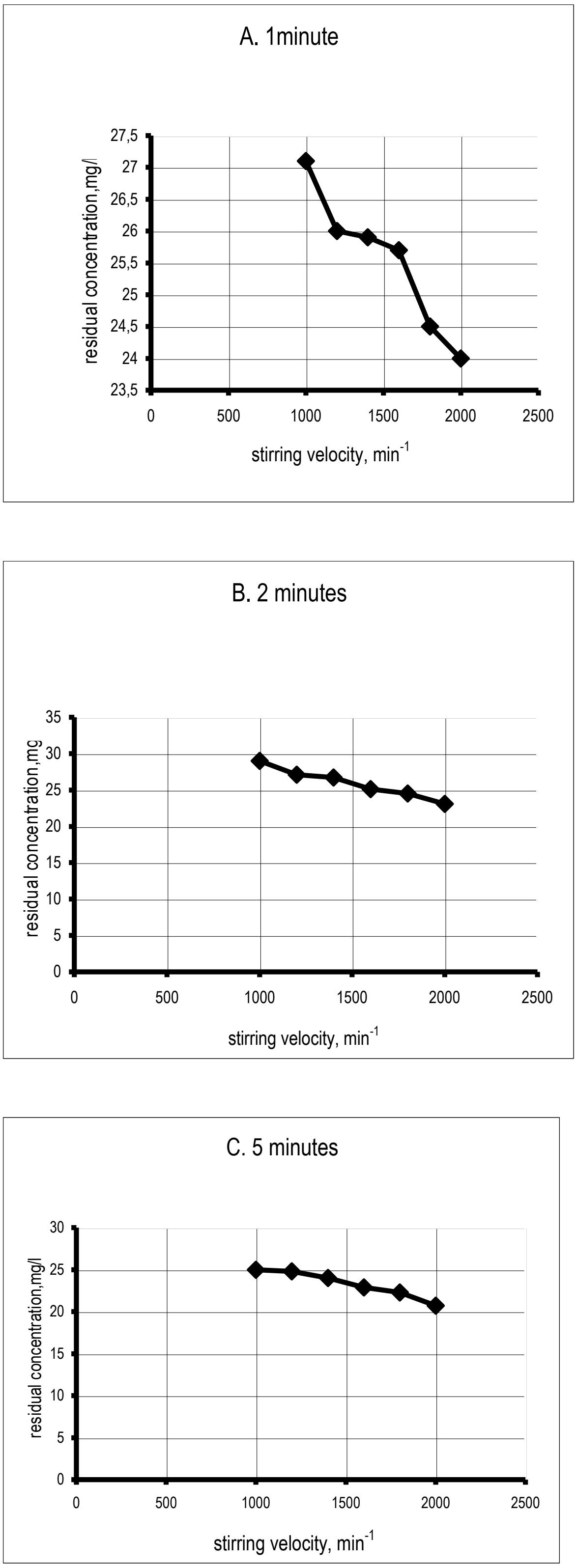


Figure 2. Influence of the stirring velocity on the oxidizing processes in the floatation pulp at density of the pulp 20%

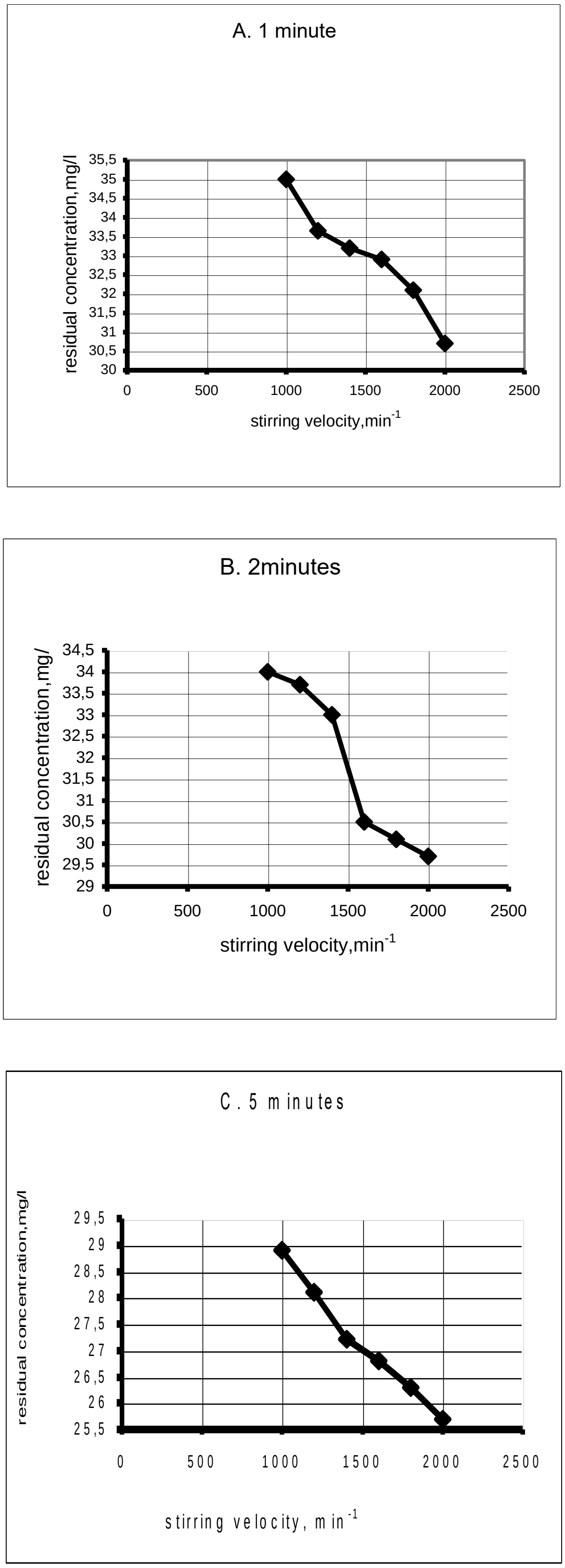


Figure 3. Influence of the stirring velocity on the oxidizing processes in the floatation pulp at density of the pulp 30%

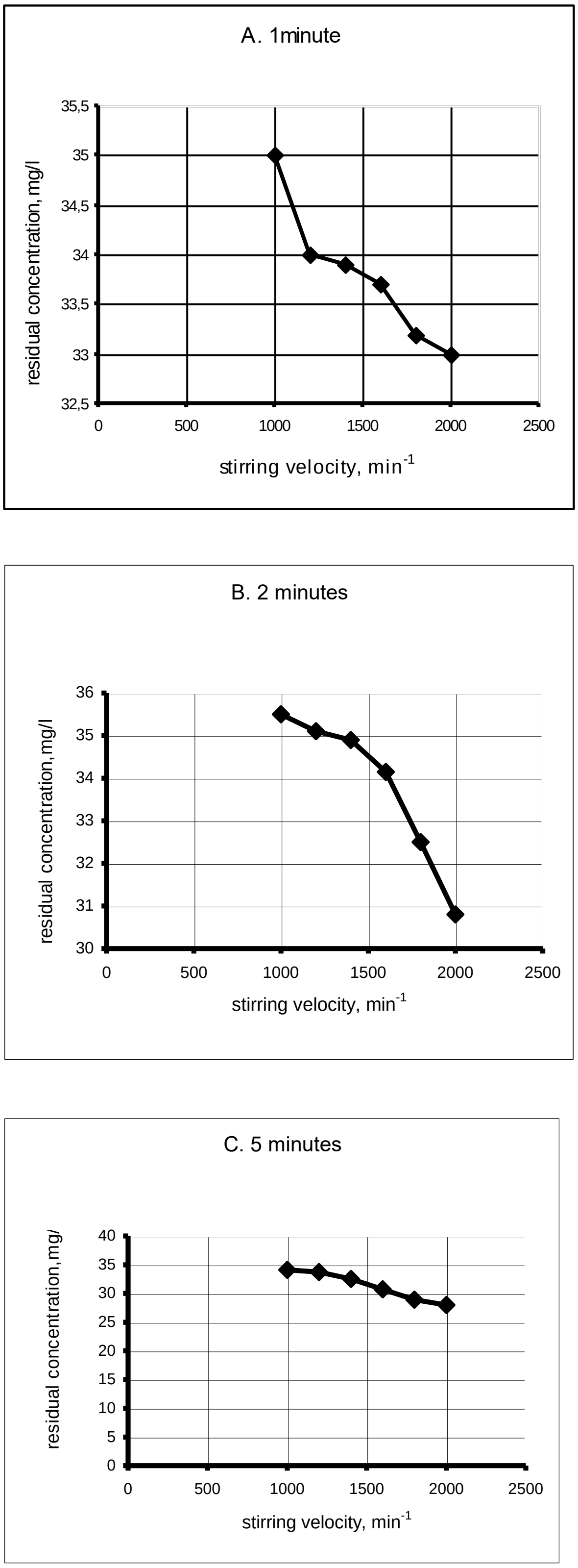


Figure 4. Influence of the stirring velocity on the oxidizing processes in the floatation pulp at density of the pulp 40%

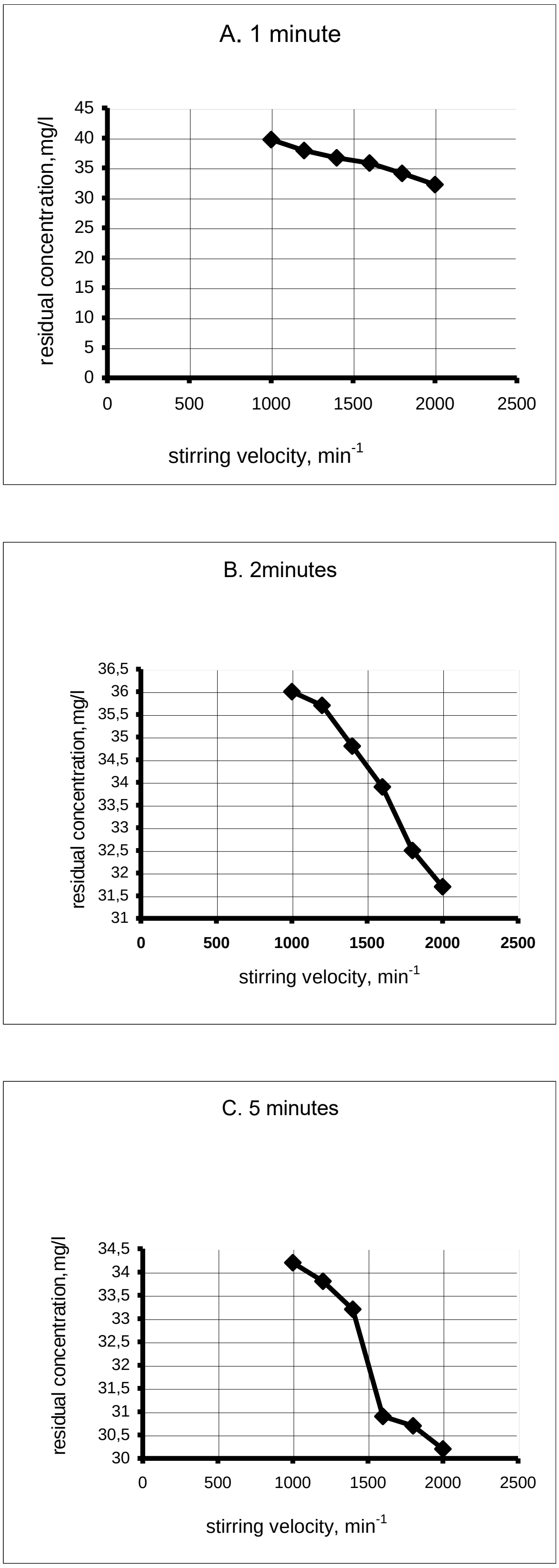


Figure 5. Influence of the stirring velocity on the oxidizing processes in the floatation pulp at density of the pulp 50%

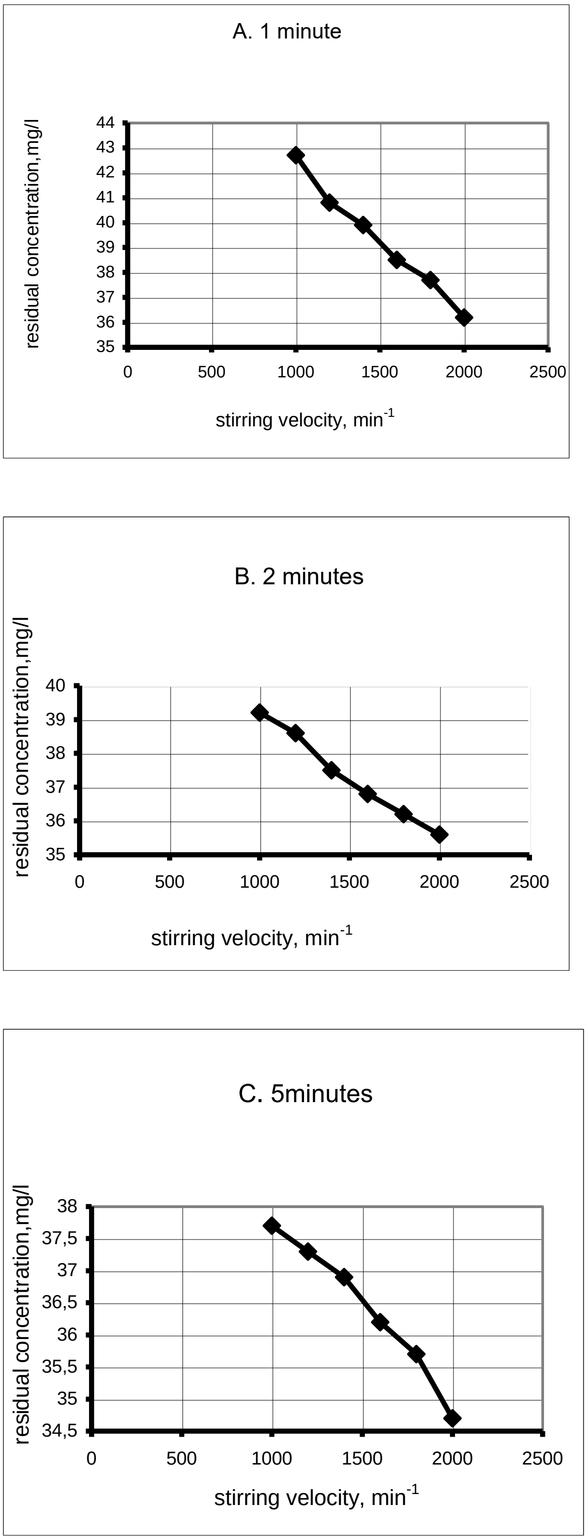


Figure 6. Influence of the stirring velocity on the oxidizing processes in the floatation pulp at density of the pulp 60%

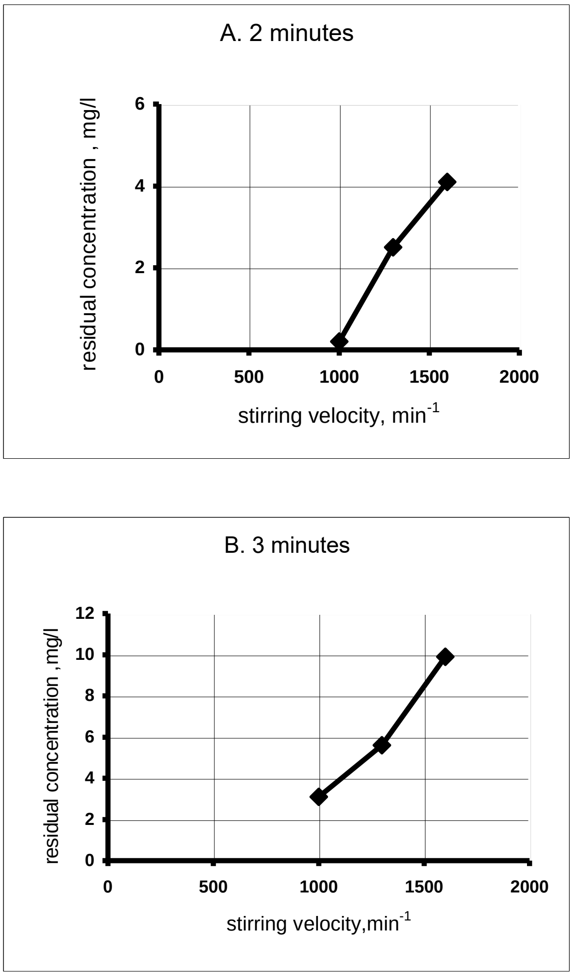
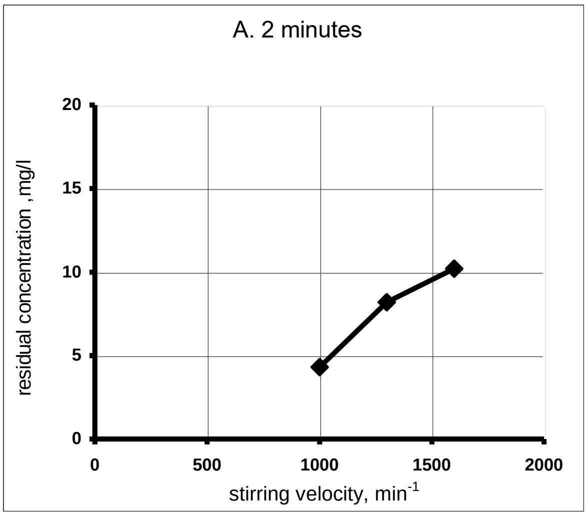


Figure 7. Desorption of the de-xanthate from the mineral surface in conditions of the density pulp with increased stirring velocity at density of the pulp 40%



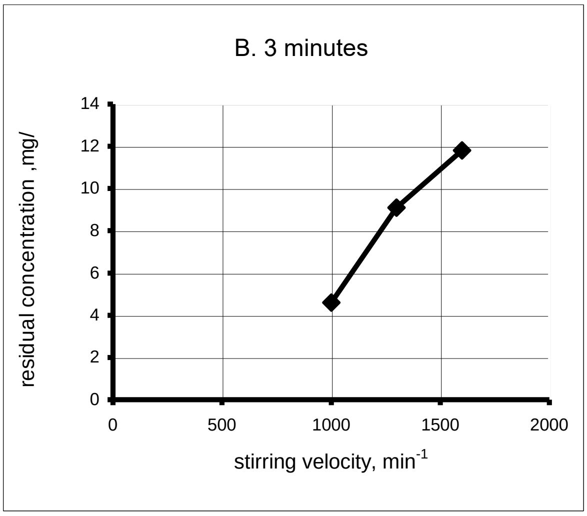


Figure 8. Desorption of the de-xanthate from the mineral surface in conditions of the density pulp with increased stirring velocity at dencity of the pulp 50%

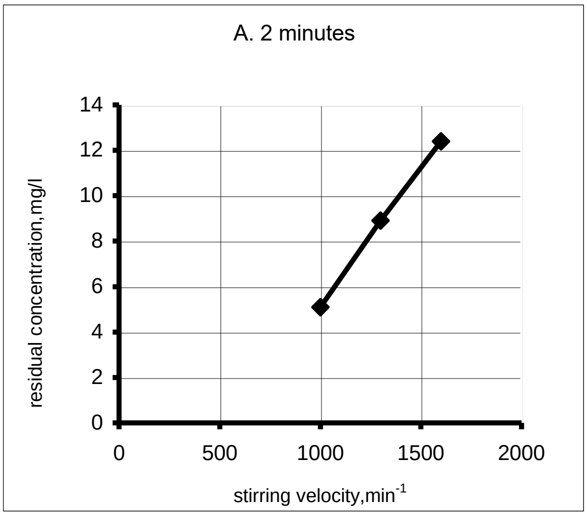


Figure 9. Desorption of the de-xanthate from the mineral surface in conditions of the density pulp with increased stirring velocity at density of the pulp 60%

Final conclusions

1) Stirring velocity of material in the period of its agitation with floatation reagents before entering the floatation machines is an essential factor influencing both effectiveness and selectivity of the next floatation process.

2) In case of low density of the pulp (up to 30% content of hard phase) acceleration of stirring velocity mainly leads to intensification of oxidizing processes. At pulp density over 30% hard content the process of mutual rubbing of mineral grains of one another is starting to play the dominant role.

3) In case of low density of the pulp over 40% hard content and velocity of 1600 min^{-1} desorption of attached by adhesion on the mineral surfaces oily reagents is possible.

4) Agitation at high velocity and pulp density is one of the ways for improving selectivity of the floatation process through reduction of the quantity of physically adsorbed collector on the less hydrophobic mineral.

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RESEARCH WORK OF THE FOAM REGULATION MECHANISM IN FLOATATION OF CASSITERITE WITH OXYHYDRILLIC COLLECTORS

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ABSTRACT
Effective floatation dressing of cassiterite ore is yet an unsolved problem in the world practice. The main reason for it lies in the low selectivity of division of the cassiterite ore from the rock forming minerals. One of the ways to improve the division of casseterite from the rock forming minerals is the use of froth extinguishers. This article is devoted namely to this problem.

KEY WORDS: Froth regulators, froth extinguishers, slime waters, two-phase and three- phase froth, surface active substance (SAS), adsorption, coalescence.

INTRODUCTION

Traditionally cassiterite is floatated with oxyhydrillic collectors in acid floatation pulp (pH 2,5-3). Main obstacle for its effective selection from the remaining oxides and silicones is the abundant froth output, according to L.O.FILIPOV (1997, 2000). It carries away into three phase froth a number of rock forming minerals. Traditional drainage of slime waters in three phase froth is not sufficient to ensure selection of the minerals, according to A.BOTEVA (1992). In order to improve secondary floatation in a three phase froth layer, during performed research work the collector Aerosol 22 was used in a combination with silicone froth extinguisher. Achieved results under item (5) that while using oxyhydrillic collector containing sulphonate and carbonic functional groups (Aerosol 22) the most appropriate froth extinguisher is the silicone type.

An attempt is being made in this research work to draw up hypothesis, explaining the froth-depressing role of the silicone polymers.

RESEARCH METHODS

The following methods have been employed in the research work:
1) determining the angle of watering;
2)determining inter-phase pressure of the borderlines oil-water and oil-oil;
3)measuring time of destruction and the thickness of the froth layer in a two-phase froth.

Research is carried out on clean cassiterite as mineral sample. As oils are used: Aerosol 22, Sodium oleate, Bisilon AC 3099, Bisilon E Froth Depressor 7800, Froth Depressor DNE which represent mixtures of carbonyl acids and Hydrocarbons, and Bisilon E and Bisilon AC3099 are present on silicon base.

In measuring angle of watering θ the method of catching bubbles is employed. Surface pressure is measured by the method of the ring and the faculties of the two phase froth through barbotage with a certain amount of air to a water column with dissolved reagent in a glass cylinder.

RESEARCH RESULTS

As yet mentioned above the surface pressure along the borderlines of water-oil and collector-froth regulator (oil-oil) is measured by the ring method. Mutual penetration of oil phases in one another is appraised according to the (5) on inequalities.

$E = \sigma_F + \sigma_{EF} - \sigma_E > 0$; (1)
$S = \sigma_F - \sigma_{EF} - \sigma_E > 0$; (2)

where σ_F - surface pressure along the borderline water – froth output;
σ_E – surface pressure along the borderline water – froth regulator;
σ_{EF} - surface pressure along the borderline froth output – froth regulator;
E – rate of mutual penetration of the froth output and froth regulator;
S – rate of mutual mixing (spread out) of the froth output and froth regulator.

Measured parameters and calculated on their base values of E and S are matching those quoted in (5) values.

It has been interesting and rewarding to examine the impact of the two types of froth regulators – those based on organic silicone compounds and the others based on carbonic acids on the height of froth layer. It is characteristic for the two types of reagents that when its concentration in water solution grows the surface pressure along the borderlines oil-water falls down as at 10 mg /1 it reaches saturation and then remains unchanged. However, the impact of the two types on the height of the froth layer is fundamentally different.

With regard to the organic silicone compounds the height of the froth layer falls dramatically with the increase of its concentration. Concerning the froth regulators based on carbonic acids the growth of its concentration almost does not affect the thickness of the froth layer. This very important fact shows difference in the mechanism of interaction of used collector Aerosol 22 with the two types of compounds and the fact that the surface pressure is not the determining factor influencing the froth regulators regarding the structure of the two phase froth.

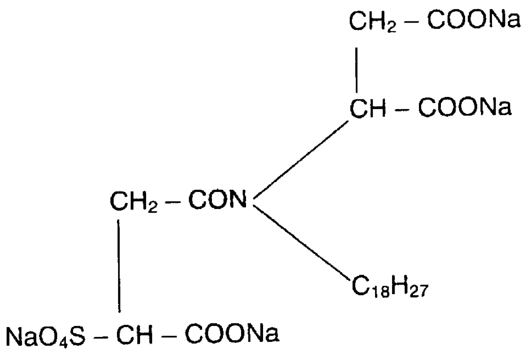
As the measurements of the surface pressure answer the question about the interaction of the froth regulators and the collector Aerosol 22 along the boardeline water-air, as the angle of watering θ shows us the degree of absorption of considered surface active substances (SAS) along the borderline mineral-liquid phase. The angle of watering has been measured at pH2,5 (traditional, according to R.P.Allen and C.J.Vial (1988) pH for floatation of cassiterite with oxyhydrillic collectors), while using the natural cassiterite crystal. After each measurement the surface has been refreshed by polishing with chrome oxide and tenth times washing with distilled water. Under concentration 65 mg/1 of the Aerosol 22 the angle of watering θ reaches the maximum value of 71,5°. Additives of organic silicone froth regulators do not affect the angle of watering θ as for those based on carbonic acids.

It rises to 80°. It shows that organic silicone compounds cannot be absorbed on mineral surface, as in the case with carbonic acids and hydrocarbons there appears adsorption.

COMMENTS ON ACHIEVED RESULTS AND CONCLUSIONS

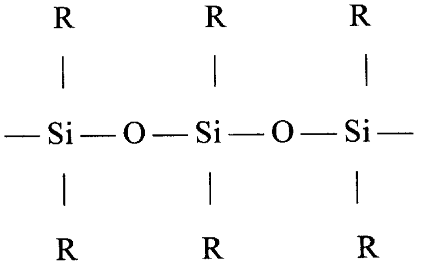
On the basis of achieved results regarding the synergy between the oxyhydrillic collectors and used reagents-froth regulators, one may come to the main conclusions, as follows:

1. Froth regulation role of the reagents is determined by the structure of the oxyhydrillic collector and the froth regulator. Oxyhydrillic collector as a strong SAS apart from the borderline mineral-water actively adsorbs also along the borderline air-water and forms with the collector associative groups tearing the link between the molecules of the collector and actively acts as froth depressor. In this case air bubbles easily coalesced and disrupted. When used froth regulator coalesces the molecules of the collector in an unbroken range the froth is stabilized and this reagent cannot act as a froth depressor.
2. The collector Aerosol 22 has the following structure [1]:



[1]

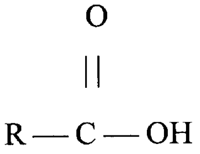
The froth depressors, which are silicone polymers, have the following structure [2]:



$$-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-$$

[2]

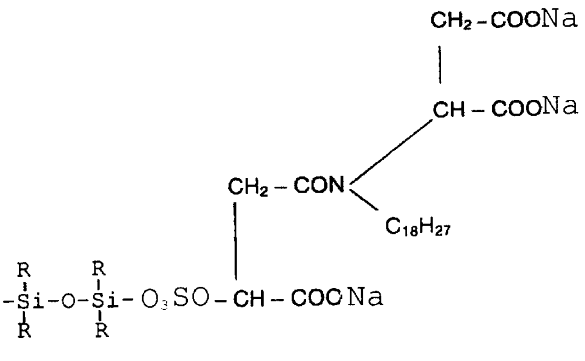
Froth depressors set up on the basis of highly molecule carbonic acids have the common
Formula (3):



$$R-\overset{O}{\overset{\|}{C}}-OH$$

[3]

In this way carbonic acids at pH2,5 coalesce in unbroken associates through hydrogen links the molecules of the carbon-sulpfonates and harden them probably through the following mechanism:



Hardening of the collector adsorbed along the borderline of liquid-gas-waters until easy disruption of the slime seams between the air bubbles, coalescence of the latter and disruption of the froth.

3. Easier separation of the slime liquid in a three phase froth leads to improvement of the selectivity. In this way carbonic acids at pH 2,5 coalesce in unbroken associates through hydrogen of floatation of the oxide with oxyhydrillic collectors.

4. In formation of a three phase perimeter of watering most probably the froth regulator which is adsorbed at the top of the mineral surface is sliding on the surface of the bubbles and thus additionally stabilizes the froth.

5. The chemical compounds used as froth stabilizers should meet the following criteria::

- To serve as a link between the molecules of the collector;
- Not to be adsorbed along the borderline liquid-mineral;
- Value of rate R does not affect considerably the work of froth depressors.

The value of rate S is of essential importance for the work of froth depressors.

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VIBRATORY COLUMN FLOTATION MACHINE – VIBRATORY – ACOUSTIC AND TECHNOLOGICAL RESEARCHES

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ABSTRACT

A laboratory model of column flotation machine with height 2000 mm and diameter 50 mm with vibratory – acoustic powder disperser of gas phase is presented. A module principle, which gives an opportunity for determination an optimum height of the supply device is used, regulation without rate at the level of pulp and precisely determination of the necessary quantity of additional water which is need for irrigation of the foam layer. Research of effect of frequency and amplitude of vibrations on precipitation of mineral granules with different density are done.

Key words:column flotation, vibratory – acoustic powder disperser of gas phase

INTRODUCTION

The flotation technique and technology developments are closely connected with the improvement of the flotation machines design. The main road solving the task for flotation process intensification is the creation of high – productive flotation machines.

The contemporary requirements in the field of pulp aeration and bubble mineralization theories impose the design of pneumatic flotation machines of column type that find application at the flotation of ores of non-ferous , noble, rare and ferrous metals, coal and other mineral resources as well as wide use at purification of waste water from different productions. (Черных, 1996)

The column flotation machine wide practical introduction appears to be an important achievement during the last decade in the field of flotation concentration. The advantages of the column flotation machine in comparison with the mechanical and pneumomechanical are the following: increased productivity improved hydrodynamics, of concentrate with the required quality at minimal quantity purifying and control operations, production area decrease and economy of electric power.

The movement nature of the particle and the bubble is an important factor, which determines the probability of flotation complex formation, mineralization rate, flotation speed and the process power consumption. (Черных, 1996) The inertial forces which destroy the particle – bubbles complex in column are insignificant. This is connected with the absence of a stirring device and the pulp flow low turbulence.

The increase of the air bubbles flotation activity is connected with the increase of their conditioning time, i.e. the interval between the formation moment and the bubble mineralization. In consequence of the column considerable height the sojourn duration of the air bubbles in it is not longer than 20s, i.e. a mineralization process at optimal flotation activity of the bubbles is realized. (Рубинщайн, 1989).

Here should be mentioned the increased flotation selectivity in he column devices due to acceleration of the processes of the secondary concentration, which is going in the purification zone of the froth layer, where fresh water is supplied. This affords an opportunity for high-quality concentrates obtaining and simplifies the technological scheme.

The basic research field in column devices is the fine-grained pulp flotation. The absence of intensive pulp mixing, product purification zone, high position of the feeding level, and the thick froth layer contribute to the obtaining of concentrate of better quality in comparison with the impellers. .(Рубинщайн, 1989).

There is a bigger probability of capture and withstanding of the coarse particle to the bubble so in some cases the column flotation machine use could turn out to be expedient for coarse – grained material flotation, as well. (Foot, 1986)

The flotation machines work effectiveness depends on the conditions of the air dispersion. The aerators must provide a maximum gas content at an optimal average massiveness of the bubbles. The following claims are demanded to the aerators: providing for such a bubbles size that assures the flotation complex emerging, minimal pulp macrocirculation in the chamber, stable aeration characteristic.

The aerators designs developed in accordance with the requirements could be combined by the action principle as follows: pneumatic, hydraulic (swift – flowing) and pneumohydraulic.

The perforated pipes or plates through which the compressed air passes are assigned to the most widespread pneumatic aerators. Textile aerators are also used at the column flotation machine. Their advantages are the low price and restoration after concentration while the unsteady aeration, the coarse bubbles (up to 3 mm) appearance and the possibility of liquid fall into the airway are considered to be disadvantages. (Finch, 1990) The textile aerators are in shape of disk frame, jacket, perforated pipes, lattice, etc. Aerators differently shaped as air distributive lattices are used as well.

Aerators made from Teflon, porous and metal ceramics are out of use because of the great value, holes blocking by particles and complicated regeneration. (Рубинщайн, 1989)

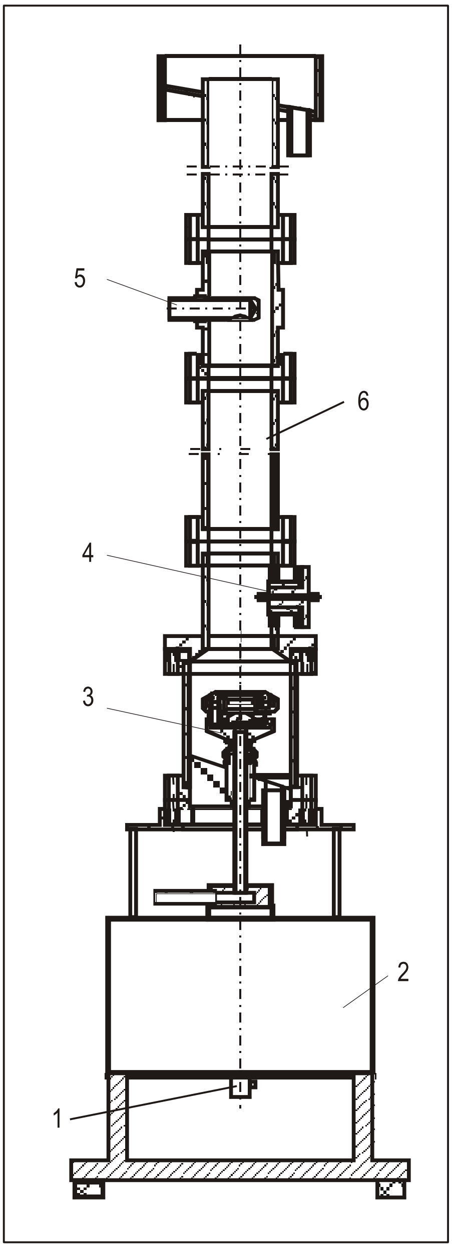

Figure 1. Vibratory column flotation machine – scheme of principle

The basic aerator type in the column flotation machine is the pipe device. An aerator representing a set of tightens in group hollow rings from porous (wool or porous polyethylene) or elastic (raw rubber) material is proposed for the aeration characteristics improvement. Changing the group tightening extent regulates the bubbles dispersive composition. The pulley aerator design is analogous. The ring pivot is vertically situated and the diameter increases from top to bottom. The diameter and the height of the pulley aerator АШ - 15 for air feeding up to 15 m^3/h with compression of 0,15 MPa are respectively 14 cm and 13,5 cm. (Рубинщайн, 1989)

As a separate tendency the vibrating pneumatic flotation machines design should be mentioned. Their action principle is based on air dispersion by vibrations at its feeding to the aeration chamber. The pulp vibrating turbulent movement creation reinforces at the liquid flow through special lattices.

VIBRATORY COLUMN FLOTATION MACHINE

A laboratory model of a vibratory column flotation machine – 2000 mm in height with diameter 50 mm and gas phase vibrating disperser is developed at the laboratory of “Vibroacoustic Intensification of the Technological Processes” at the department of “Mineral Technologies” of the University of Mining and Geology “St. Ivan Rilski”. It is realized on a modular principle, which provides a possibility for determination of the feeding device optimal height infinitely – variable regulation of the pulp level and precise determination of the necessary quantity of extra water for the froth layer irrigation. The vibratory column flotation machine basic elements are sensor (fig. 1-1), vibrator (fig. 1-2), air disperser (fig. 1-3), module for creation of single gas bubbles (fig. 1-4), feeding device (fig. 1-5), machine chamber (fig. 1-6).

The vibratory disperser provides the opportunity of certain technological parameters research: gas bubble size change, change of the gas bubbles emerging speed and solid phase sedimentation speed, the influence on the opportunity of mineral particles attachment to the air bubbles, purifying of the froth layer from rock particles.

The vibrator is electrodynamic type, power 40 W and a possibility of a wide range frequency and amplitude change, overlapping the supposed range of vibratory parameters, required by the research.

Two modifications of the air- dispersing unit were constructed- for vertical and horizontal vibrations. The air-dispersing unit for vertical vibrations (fig.2-1-air) disperses air by its transition through an annular slot, which allows rate regulation within certain range and production of gas bubbles of certain size by regulation of vibrations frequency and amplitude. Simultaneously, with the bubbles production, the vertical oscillations create a vibroacoustic field, which is distributed along the column height.

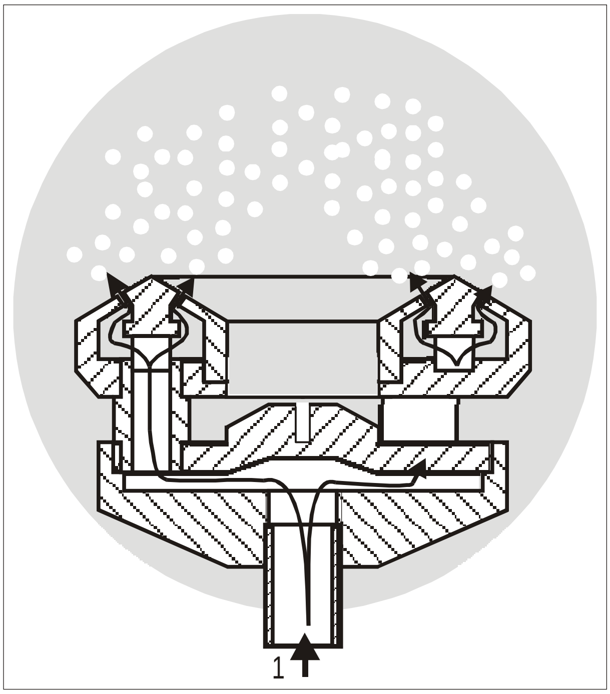

Figure 2. The air-dispersing unit for vertical vibrations

The air-dispersing unit for horizontal vibrations (fig.3-1-air) produces gas bubbles through round holes, perpendicular to the direction of the vibratory field vector.

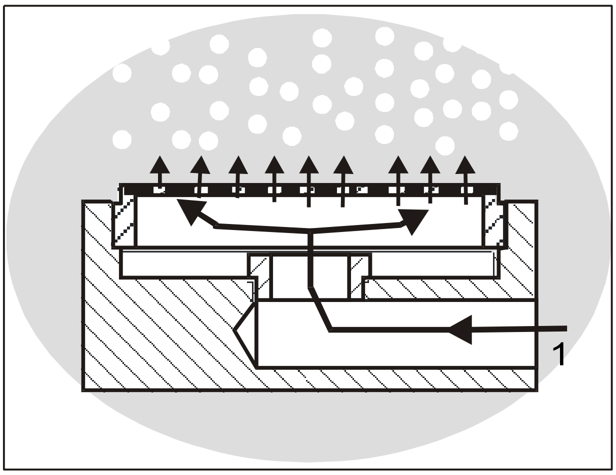

Figure 3. The air-dispersing unit for horizontal vibrations

The feeding modulus allows pulp supply into the flotation machine and even distribution of pulp along the column section as well as filling with water for vibroacoustic measurements.

The module for gas bubbles production provides the opportunity of air micrometric supply through changeable air nozzles of certain initial diameter. The pulp level is infinitely – variable regulated by the communicating vessels method. . Fig 4 shows the air disperser 1, apart of the machine chamber 2 and a vibrator 3. The chamber product is removed by a pipeline and valve 4 to the tank 5 for the coarse fraction and the fine fraction is collected in an extra vessel. The spillway movement in vertical direction provides the required pulp level in the column.

Figure 4. Vibratory column flotation machine – basic parts

THE VIBRATIONS INFLUENCE ON THE SOLID PHASE

Researches were carried out for the effect of frequency and amplitude of vibrations on speed of precipitation of mineral grains of different density. It was known that speed of precipitation decreases with the increase of intensity of oscillating, however the question of effect of diameter and relative weight of particles was still open. For that purpose a series of experiments were carried out with single mineral grains of a diameter from 0,09 to 0,155 and densities of different grains 2,65; 5,1 and 7,6 g/cm3. Frequency of oscillation changes from 20 to 70 Hz, and amplitude – from 1,5 to 3,0 mm. Average results of experiments were presented in tables 1. Experimental researches involved the conclusion that vibrating media provided additional force of resistance, applied to the mineral particle, which provoked decrease of the speed of falling down. This force is a function not only of frequency of applied vibrations – fig. 5, where experimental values showed decrease of speed depending on density of particles. It was visually observed that when the particle did not reduce significantly its speed /for certain vibration parameters/, its amplitude of oscillation is approximately equal to the amplitude of oscillation of the liquid. When speed of a particle reduces significantly its amplitude increases visibly.

This dependency between speed of falling down of mineral grains into a liquid vibrating medium and parameters of vibrating field may be explained as an interaction between two oscillation motions – motion of mineral grains and motion of applied vibrations.

Table 1. Decrease of the speed of precipitation in dependence of density of particles

Frequency f [Hz]	Amplitude 2 mm, d=0.12 mm		
	Reduction of V [%] for density g/cm3		
	2.65	5.1	7.8
	%	%	%
20	1.54		
30	3.39	5.38	4.1
40	1.34	7.6	9.73
50	4.54	6.59	7.68
60	5.6	6	8.77
70	4.22	9.6	12.16

For lower frequencies of vibration reduction of speed is lower due to lower vibration speed. For particles of higher density reduction is higher due to higher speed, with which they meet the pulsing medium.

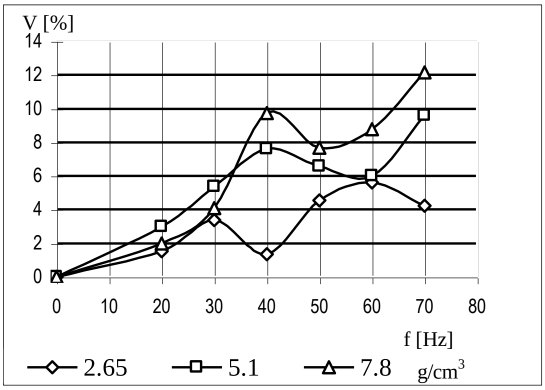

Figure 5. Decrease of speed of precipitation in dependence of frequency of vibrations and density of particles

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NEW FERRO-MAGNETIC HEAVY MEDIA FOR SUSPENSIONAL DRESSING OF COALS

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ABSTRACT
There is offered a new heavy media, like substitute of magnetite. There are shown grain-size and magnetic characteristics of new ferro-magnetic heavy media. The priorities of heavy media are proved. It is cheap, with suitable grain-size; high content of magnetic fractions, low residual and it is easy to downward magnetization. It is established that containing under 60% iron, it can make divided density of the suspension 1800 kg/m^3, by bulk content of ferro-magnetic oxides under 30%.

Traditional ferro-magnetic heavy media for suspensional dressing of coals is magnetite. In Bulgaria for dressing coals from Central Dressing Factory “Pernik” and Central Dressing factory “Bobov dol” for a long time was using ferro concentrate from Dresssing Factory “Martinovo”. After closing that factory, coal-dressing factories in Pernik and Bobov dol have serious problems, because of lack of magnetite’s heavy media. The schemes of regeneration for both gravitational factories use magnetic separation and can`t use non-magnetic heavy media (for example baryte).

Using of foreign magnetite`s concentrates for heavy media is making problems and uncertainty with supplying of production and heavy media is becoming more expensive. We import ferro-magnetic heavy media from Ukraine and Macedonia. Some of them are nonstandard by size of grains and need to be grinded. That makes difficult additionally factories, because demand construction of installation for grinding, classification and compressing of heavy media till suitable density for suspension.

The problem of supplying our factories, which are dressing energetic coals in heavy suspensions, with suitable heavy media – Bulgarian production is very topical and urgent.

In laboratory for magnetic methods in University of Mining and Geology were made trials of ferro-magnetic heavy media, imported from Ukraine and Macedonia and were compared with new ferro-magnetic heavy media, produced from the scrap of Bulgarian dressing factory. Ferro-magnetic concentrate was separated from the scrap with original magnetic separator (patent application № 104941/3.11.2000), which makes suitable magnetic fields with definite intensity (H = 55 кA/m), succession and duration of the impulses.

The scheme of dressing included one basic and one refining technological operations, with desliming of magnetic concentrate, which is quickly getting compressed, by sedimenting till 75 – 80% hard. A part of the concentrate was drown and was divided by classes. It was definited by density, containing of commonly iron and was researched for magnetic hysteresis characteristics of heavy media. The last part of the suspension was standardizing by density and was used for suspensional separation of energetic coals. In table 1 and 2 are shown characteristics of the grain-size, composition and density of suggested and already used heavy medias.

If we compare data of tables 1 and 2 for different heavy medias we will establish, that the sample of Macedonian coarse - grained concentrate doesn`t reply on requirements for grain-sizes, because content of class + 150 μm is over 10%, and weight of class + 1 mm, without extra grinding range from 6 to 16% and contain 81% magnetic fractions. The high content of magnetic fractions in the class – 1 + 0,16 mm (till 94 – 95%) can be used, but it need to be extra grinded, about the standard of coarse (under 0,15 mm). The class – 0,16 mm contains 90% magnetic fractions. After extra grinding of the sample, the average content of magnetic fractions is becoming about 92%, so it is replying of the requirement to be over 86%.

The content of magnetic and commonly iron is the highest in Ukrainian magnetite`s concentrate, which has the highest density too. The problem is that Central Dressing factory “Pernik” use only 3000 t concentrate for an year, and Ucraina is not interested in deals for quantity less than 15000 – 20000 t and is making deals only with serious consumers.

For using of coarse-grained concentrate, coal-dressing factory need to have grinders, classifiers and magnetic deslimators, that confuses the scheme of the factory.

The researched sample about magnetic heavy media is fine-grained and has high contents of magnetic fractions, for average content of commonly iron and acceptable density. It does not require extra grinding.

A part of researched product was separated, drown and was subjected to magnetic researches.

Table 1. Characteristic of grain-size of concentrates, used for heavy medias in Central Dressing factory "Pernik"

Classes μm	Summary weight, %		
	Ucrainian concentrate	Macedonian coarse-grained c-te	Offered heavy media
+ 150	3,00	34,00	1,22
- 150 + 80	29,00	50,00	10,72
- 80 + 40	69,50	69,00	24,30
- 40 + 20	81,50	82,00	48,00
- 20 + 10	90,00	90,00	82,50
- 10	100,00	100,00	100,00

Table 2. Phase, chemical composition and density of heavy medias

Indicators	Summary weight, %		
	Ucrainian concentrate	Macedonian coarse-grained c-te	Offered heavy media
Content of magnetic fractions %	94	92	92,5
Content of commonly iron %	68,2	61	49,3
Density кg/m^3	4200	3850	3770

Hysteresis properties were researched by method of Ghuie. It was measured variation of magnetic force of drawing long rode-like body from the sample, formed in long glasses test-tube, hanged so it as one end hang in solenoidal, controlled for intensity magnetic field. In the area of hanging, intensity of field is equal to zero.

The magnetic force was valuated, by measuring variation of the mass of rode-like body, which contains ferro-magnetic phases, under influence of intensity of gradiented magnetic field.

The intensity of magnetization of the sample and it magnetic susceptibility were definited by known formulas.

CONCLUSIONS

1. Magnetic phases in researched product possess hysteresis properties, similar to natural and unnatural magnetite and they can be dressed in weak magnetic fields.
2. The resistance force of the researched magnetic phases (H = 2,5 кA/m) is closer to magnetite (H = 3,2 кA/m), than to magnetic hematite (H = 9,2 кA/m).
3. The residual intensity of magnetization of researched magnetic phases (J = 3 kA/m) is seven times lower than this of magnetite (J = 20 kA/m) and fourteen times lower than this of magnetic hematite (J = 42 kA/m).
4. The intensity of magnetization by saturation of experimented magnetic phases is J = 36 kA/m and it is 5,4 times lower than this of natural magnetite (J = 196 kA/m) and 3,3 times lower than this of magnetic hematite (J = 120 kA/m).
5. The magnetic susceptibility of researched phases is 5,5 times lower than magnetite and 3,9 times lower than magnetic hematite.

Table 3. Data for hysteresis and magnetic susceptibility of magnetic phases in the sample

Electricity	Intensity of the field	Variation of the mass ΔP	Intensity of magnetization		Magnetic susceptibility	
A	A/m	g	relative	volumetric	relative	volumetric
0,5	4400	0,008	0,476	1,80	1082	0,408
1,0	8800	0,039	1,150	4,34	1307	0,493
2,0	17600	0,193	2,872	10,83	1632	0,615
4,0	35200	0,694	5,163	19,46	1467	0,553
8,0	70400	2,402	8,935	33,68	1269	0,478
14,0	140800	5,132	9,545	35,98	678	0,256
8,0	70400	2,596	9.657	36,41	1372	0,517
4,0	35200	0,988	7,350	27,71	2088	0,787
2,0	17600	0,387	5,758	21,71	3271	1,233
1,0	8800	0,111	3,310	12,48	3761	1,418
0,5	4400	0,039	2,030	7,65	4614	1,739
-0,5	-4400	0,025	-1,502	-5,66	3414	1,287
-1,0	-8800	0,087	-2,589	-9,76	2942	1,109
-2,0	-17600	0,234	-3,482	-13,13	1978	0,746
-4,0	-35200	0,736	-5,476	-20,64	1556	0,587
-8,0	-70400	2,396	-8,913	-33,60	1266	0,477
-14,0	-140800	5,172	-9,620	-36,27	683	0,257

Consequently researched magnetic phases can be characterized like low residual, weakly flocculated and easy lose of magnetization. This magnetic properties favour technology of magnetic separation for receiving of pure concentrates.

Lower magnetic susceptibility and intensity of magnetization probably are obliged to silicon, included in crystal lattice of magnetic phases. Lower magnetic properties in wet magnetic separation will reflect on the recovering and it will require magnetic fields with higher intensity or closing of magnetic particles to magnetic poles to be holder there.

In laboratorial attempts for suspensional dressing of energetic coals from Central Dressing factory "Pernik", with new heavy media was established, that dividing density of 1800 kg/m^3 is received at 29 volumetric per cents of heavy media, which is in rates (25 – 30 volumetric per cents).

The regeneration of heavy media, by magnetic separation doesn`t require downward magnetization. That lightens technology and suspensional density become stable.

At the moment we develop industrial models of separator. Then we are going to test technology of dressing in industrial conditions.

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INVESTIGATION THE ADSORPTION PROPERTIES OF THE NATURAL ADSORBENTS ZEOLITE AND BENTONITE TOWARDS COPPER IONS

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ABSTRACT

The possibilities for using Bulgarian natural adsorbents bentonite and zeolite is have been investigated for purification of model solution of Cu^{2+} at correlation of liquid to solid phase, v:m=100:1. It has been found out, that the specific surface of the both minerals takes leading part at the adsorption of Cu^{2+} from model solutions with concentration higher than 70 mg/dm^3. The cation adsorption capacity is highest at size of the particles of both adsorbents –0,071+0 mm. The thermodynamics of adsorption has been described with the most appropriate isotherms of uptake of Cu^{2+} from different particle sizes adsorbents. It has been reported, that the two natural adsorbents can be used to remove Cu^{2+} from model solutions with concentrations not higher than 10-20 mg/dm^3 with one stage of purification at adsorption time 5 min for reaching the Bulgarian standards for drinking waters. Under t these conditions the optimum values of pH for the zeolite are in a wider interval from 4,6 to 8 and for the bentonite 4,6.

Key words: zeolite, bentonite, adsorption of copper ions, adsorption isotherms

INTRODUCTION

In world-wide scale the volume of waste water reaches about 440 km^3/year. Due to that purification is one of the most wide spread technological processes. A perspective method for purification of waste water is adsorption. Using this method the adsorbents have to answer to number of requirements to be active, stable, accessible, cheap, easy to regenerate and most important is that the exchange ions should be harmless and should not provoke secondary water pollution. The natural minerals zeolite and bentonite respond to these requirements.

The big deposits of zeolite and bentonite near the town of Kurdjali, their low self value and their unique ion exchange and adsorption properties, make them attractive for purification of wastewater from ions of heavy metals.

Considerable amounts of mine and drain waters from the copper mines and mineral dressing enterprises “Asarel-Medet” and “Elazite-Med” contain mainly copper ions as well as iron, zinc, aluminium and other ions in lower quantities.

Due to that the aim of the research is: a) to compare the adsorption properties of both natural minerals depending on the size of their particles; b) to find the most appropriate equation describing the thermodynamics of the adsorption; c) to investigate the kinetics of adsorption under the same conditions for both minerals; d) to examine the influence of pH of the solutions on the adsorption of Cu ions from model solutions.

PHYSICOCHEMICAL CHARACTERISTICS OF ZEOLITE AND BENTONITE

Zeolite

The clinoptilolite zeolites are most wide-spread in NE Rodopi. The mian mineral is a clinoptilolite and its amount reaches up to 90% from the composition of the rock. The size of its grains vary from a thousand part of the millimeter up to 0.05-0.08 mm. The zeolites are built from (AlO_4) and (SiO_4) tetrahedrons, which alternate in grainy three-dimensional structure. The tetrahedrons can be connected in different ways, unified by common tops. Complex crystal structures with situated in determinate order micro-pores and canals with diameter in molecular order are formed in this way. The structural formula of cliniptilolite is $Na_6[(AlO_2)_6(SiO_2)_{30}].24H_2O$ and the number of the tetrahedrons in the ring is 8 according to Andronikashvili, Kirov “et al.” (1985). The high selection of zeolite with respect to metal cations with large dimensions is due to the existence in the structure of eight numerical siliceousoxygen rings. The clinoptilolite possess the following more important physicochemical characteristics: good mechanical strength (3,3-4 by Moos), density 2,16 g/cm^3, ion exchange capacity $\approx$2.16 mgeq/g.

The adsorption ability of the zeolite is different in comparison with the ions of the heavy metals. According to Obal, Rozman “et al.” (1991) the adsorption order with respect to the counted metals is following: Pb>Cu>Zn>Ni>Fe>Cr. The selectivity order of the same ions for the clinoptilotite can be also observed in the work of Chelischev, Bernshtein “et al.” (1977): $Pb^{2+}>Cd^{2+}>Cu^{2+}>Zn^{2+}>>Na^{+}$. The exposed data show that the clinoptilolite zeolite reveal good selectivity with respect to the copper ions.

Bentonite

The bentonite deposits mainly are concentrated around Kardjali town. The bentonite is clay in which basic clay mineral is the montmorilonite. The crystal structure of montmorilonite is determinated by two layers of siliceous tetrahedrons with an inserted layer of aluminium octahedrons between them, i.e. the bentonite is also aluminium silicate but in contrast to zeolite possesses bedded structure. In the montmorilonite crystal different exchangeable cations take part - monovalence (Na^+, K^+, H^+) and divalence (Ca^{2+}и Mg^{2+}). The exchanging ability of the bentonite is determinated not only by the kind and the quantity of these ions, but also by the stirred crystal lattice of montmorilonite. The ideal chemical formula of montmorilonite is $[Si_8(Al_{3,34}Mg_{0,66})O_{20}(OH)_4]M_{0,66}.H_2O$, where M-ions of Na, Ca, H and Mg according to Pironcov, Stoev “et al.”(1991). The behavior of bentonite depends very much on the predominate exchange ion, for example, if we put Na –bentonite in water it increases his volume up to 14 times, while Ca-bentonite practically does not swell. In comparison to Na-bentonite the Ca-bentonite has better adsorption and discolouring properties. The bentonite can be used for removing Pb, Cd, Cu and Zn ions from water solutions according to Bereket, Aroguz “et al.” (1997).

EXPERIMENTAL STUDIES

Materials and methods

The natural clinoptilolite is from a big deposit “Beli Past” in NE Rodopi. The chemical composition by weight % is: SiO_2-66,16%, Al_2O_3-11,41%, Fe_2O_3-0,8%, TiO_2,-0,15%, MgO—0,06%, CaO-2,8%, Na_2O-0,22%, K_2O-2,9%. The content of clinoptilolite is≈70%, and the full exchange capacity is minimum100mgeq/100g. The correlation of Si:Al is 5, i.e. the zeolite is highly siliceous and is very stable to acid and basic solutions.

The natural bentonite is from deposit “Encher” near the town of Kardjali. The chemical composition of average probe by weight % is the folowing: SiO_2-52,7%, Al_2O_3-15,9%, Fe_2O_3-4,5%, MgO-3,5%, CaO-4,3%, Na_2O-0,9%, K_2O-1,1%. The content of CaO and MgO is respectively more than 1% and 2,5% and the correlation Na_2O:CaO is very little. This shows that the swelling property of bentonite in water will not be demonstrated. The density of bentonite is experimentally determined and it is 2,03 $g/cm^{3.}$

Three classes of natural minerals have been used for the accomplishment of the experiments: for zeolite -2,0+1,0; -1,0+0,071; –0,071+0 mm; and for the bentonite: +0,315; -0,315+0,071; –0,071+0 mm. The experiments have been carried out with model solutions of $CuSO_4.5H_2O$. The necessary concentrations of Cu ions are obtained by dilution with distillated water. The contact between the natural adsorbents and the solutions is realized in static conditions with the help of shaking machine CITRON, 150 min^{-1}, in correlation liquid:solid, v:m=100:1 for all experiments.

The cation adsorption capacity (CAC) for three classes adsorbents towards Cu ions was determinated during 24 hours, while in the first two hours a shaking machine is used.

The computer program “CURVE FIT 424” was used giving possibilities from 24 types equations to choose the best model describing the adsorption isotherms of Cu^{2+} for the three classes of adsorbents. The experiments were realized at the temperature of 17 °C. The pH values of the solutions were determinated with Metrohm E588 pH-mV meter and were modeled with solutions of H_2SO_4 and NaOH. The concentration of Cu ion in solutions was determinated by ICP-AES analysis.

CAC of the natural adsorbents towards Cu ions was calculated using the formula:

$$CAC = \left(\frac{c_1 - c_2}{m \cdot 1000}\right) \cdot V \quad or \quad CAC = \frac{c}{m} \cdot \frac{V}{1000}$$

where, c_1 is the concentration of the element in initial solution, mg/dm^3; c_2 is the equilibrium concentration of the element in solution, mg/dm^3; c is the quantity adsorbed substance, mg/dm^3; V is the volume of investigated solution, dm^3; m is the weight of dry sorbent, g; CAC is cation exchange capacity, mgelm/g sorbent.

RESULTS AND DISCUSSION

Influence of the adsorbents particle size upon their CAC towards Cu

The value of CAC shows the influence of the bentonite and zeolite particle size upon the adsorption of Cu ions, reached during the time of contact 24 hours. It is considered, that during that time full equilibrium between the solid and the liquid phases is reached. For this purpose 1g from three different classes of zeolite and bentonite contact with 100 cm^3 model solution of $CuSO_4.5H_2O$ with different concentration of Cu^{2+}.

The influence of the bentonite particle sizes is showed in fig.1 and of the zeolite in fig.2 on CAC depending on the concentration of Cu ions in the initial solutions. Fig.1 and fig.2 show that at the lower contents of Cu ions in the initial solutions (up to 72,6 mg/dm^3) the size of adsorbent particles does not influence essentially on CAC. But, with raise of the content of Cu ions in the initial solutions, CAC of both minerals raises with decreasing their particle sizes, i.e. with increasing their specific surface.

Comparing the dates from the figures of both minerals one can observe higher CAC of the zeolite towards the bentonite for the three classes at concentrations of Cu ions higher than 72,6 mg/dm^3. At the initial concentrations of Cu^{2+} in the solutions up to 10-20 mg/dm^3, after adsorption are obtained remaining concentrations of the same ions <0,2 mg/dm^3. That shows, that both minerals can be used for purification of waters, containing this quantity Cu^{2+} with one stage of purification. Moreover, the standards of Cu content are achieved in waste waters (<0,2 mg/dm^3), at which they can be released into rivers and into open-air reservoirs.

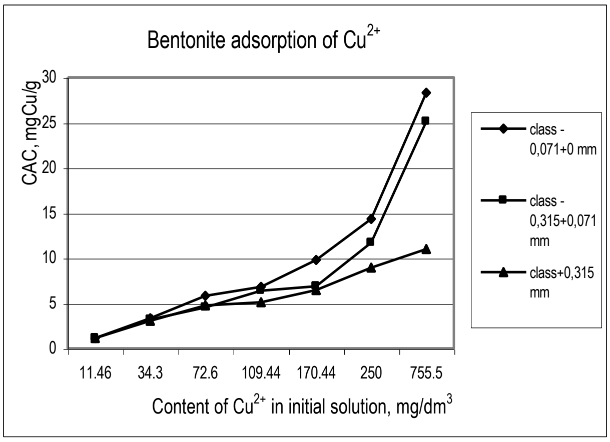

Figure 1. Influence of bentonite particles size on CAC towards Cu^{2+} from model solutions of $CuSO_45H_2O$

Thermodynamics of the copper adsorption from the natural adsorbents bentonite and zeolite

The adsorption such as desorption depends mainly on the thermodynamic parameters, temperature and concentration of adsorbtive and on the condition of the adsorbent surface. The quantity of strongly adsorbed adsorbate depends only on the concentration of adsorbtive, at certain temperature and established adsorption equilibrium. This dependence between the quantity adsorbed substance and the concentration of adsorptive is expressed by the adsorption isotherm. The adsorption isotherms of Cu^{2+} uptake from natural adsorbents were obtained with the help of computer program "CURVE FIT-424" at temperature 17 ^0C. From 24 types of equations the most suitable were chosen, describing the Cu^{2+} adsorption from different classes of bentonite and zeolite. The chosen equations give highest coefficient of correlation (r) of the dependence: $y=f(c_2)$,
where y is the quantity adsorbed substance (c) related to 1g bentonite or zeolite for contact time 24 hours, mgCu/g
$y=c/m$;
c_2 is equilibrium Cu^{2+} concentration, reached after 24 hours, mg/dm^3.

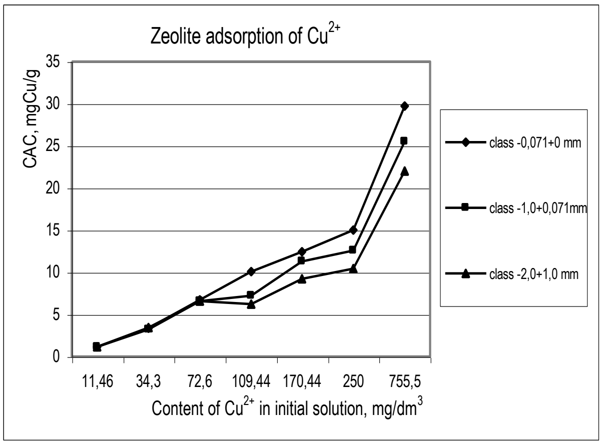

Figure 2. Influence of zeolite particles size on CAC towards Cu^{2+} from model solutions of $CuSO_45H_2O$.

Adsorption isotherms of Cu^{2+} uptake of bentonite:

for class –0,071+0 mm

$$y=\frac{c}{m}=2{,}5378+0{,}1204.c_2-1{,}3929.10^{-4}c_2^2;$$

$$(r=0{,}9941)$$

or

$$y=\frac{c}{m}=2{,}2839.1{,}0009^{c_2}.c_2^{0{,}3386};$$

$$(r=0{,}9922)$$

for class –0,315+0,071 mm

$$y=\frac{c}{m}=3{,}7899+4{,}2935.10^{-2}.c_2-\frac{0{,}1069}{c_2^2};$$

$$(r=0{,}9902)$$

or

$$y=\frac{c}{m}=1{,}9826.1{,}0016^{c_2}.c_2^{0{,}2775};$$

$$(r=0{,}9896)$$

for class +0,315 mm

$$y=\frac{c}{m}=1{,}9928.0{,}9999^{c_2}.c_2^{0{,}2671};$$

$$(r=0{,}9826)$$

or

$$y=\frac{c}{m}=1{,}9936.c_2^{0{,}2664};$$

$$(r=0{,}9826)$$

Adsorption isotherms of Cu^{2+} uptake of zeolite:
for class –0,071+0 mm

$$y=\frac{c}{m}=\exp\left[1{,}4841-\frac{0{,}1769}{c_2}+0{,}2958\ln\left(c_2\right)\right],$$

$$(r=0{,}9845)$$

or

$$y=3{,}0068.c_2^{0{,}3882};$$

$$(r=0{,}9745)$$

for class –1,0+0,071 mm

$$y=\frac{c}{m}=2{,}4115.c_2^{0{,}3706};$$

$$(r=0{,}9827)$$

or

$$y=\frac{c}{m}=2{,}4170.1{,}00007^{c_2}\,c_2^{0{,}3672};$$

$$(r=0{,}9844)$$

for class –2,0+1,0 mm

$$y=3{,}0191.1{,}00096^{c_2}.c_2^{0{,}2307};$$

$$(r=0{,}9840)$$

or

$$y=\frac{c}{m}=6{,}0039+2{,}9925.10^{-2}.c_2-\frac{0{,}1490}{c_2^2};$$

$$(r=0{,}9907)$$

Kinetics of Cu^{2+} adsorption by the natural adsorbents bentonite and zeolite

Class –0,071+0 mm for both adsorbents was chosen for studing the kinetics of Cu^{2+} adsorption. The concentration of Cu^{2+} in the initial model solutions is 11,46 mg/dm^3. The experiments were carried out at temperature 17 ^0C and pH of the solutions 4,62. The contact time between the solid and the liquid phases is accordingly: 5, 10, 25, 40 and 60 min at shaking with 150 min^{-1}. The selection of the content of Cu^{2+} in the initial solutions is based on the achieved remaining concentration <0,2 $mgCu/dm^3$ for all treated solutions with one stage of purification for both adsorbents. The achieved remaining concentration (<0,02 $mgCu/dm^3$) responds to the requirements of Bulgarian standards for potable waters (<0,05 $mgCu/dm^3$) and releasing of waste waters from mines and mineral dressing enterprises into rivers and into open-air reservoirs (<0,2 $mgCu/dm^3$).

The kinetics of Cu^{2+} adsorption is shown in fig.3, as relation between remaining concentration and contact time.

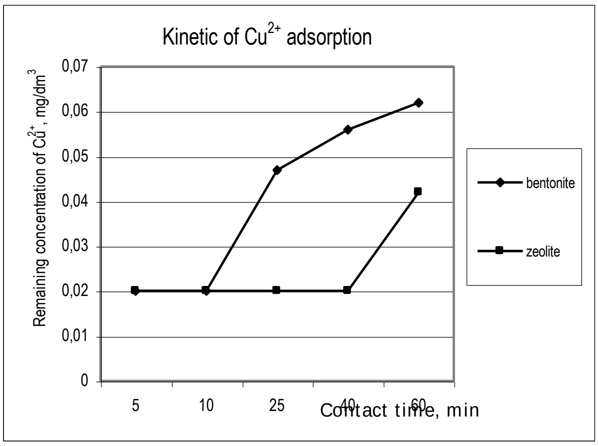

Figure 3. Kinetics of Cu^{2+} adsorption by bentonite and zeolite.

As we see in the figure, the kinetics of Cu^{2+} adsorption is very fast for both minerals and 5 min are sufficient for reaching the remaining concentration <0,02 mg/dm^3. An insignificant desorption of the copper ions from the bentonite were observed after the 10th min and form the zeolite after the 40th min. A conclusion can be made, that the Cu^{2+} adsorption is stable for both minerals under the indicated conditions.

Influence of pH of solution on the Cu^{2+} adsorption from bentonite and zeolite

The experiments were realized at the following conditions: temperature 17 ^0C; initial concentration of Cu^{2+} in the solutions 11,46 mg/dm^3; pH- 2, 4, 4,62, 6, 8, 10; contact time 5 min and size of the bentonite and zeolite particles –0,071+0 mm.

The low values of pH are reached by acidification with H_2SO_4 solution and the higher than 4,62 with a solution from NaOH. The influence of pH of the solutions upon the adsorption of Cu^{2+} is indicated in fig. 4. The change of the remaining concentrations of Cu^{2+} in function from pH of the solutions has been followed. It can be seen from the figure, that the remaining concentration begins to decrease, increasing the pH of the solutions after the process of adsorption. For the zeolite it is lowest at pH from 4,62 to 8 (c_2<0,02 mg/dm^3) and for the bentonite from 4,62 to 6 (c_2 from 0,02 to 0,13 mg/dm^3). It is due to the fact, that besides the process of adsorption there also runs precipitation of Cu^{2+} at pH>5 as a result of the removal of the reaction equilibrium to the right:

$$Cu^{2+}+2H_2O \leftrightarrow Cu(OH)_2+2H^+$$

$$\longrightarrow$$

An increase of the Cu^{2+} remaining concentration at pH >8 for both adsorbents was observed, which was probably due to their partial desorption from the adsorbents and the presence of unadsorbed $Cu(OH)_2\downarrow$ in solution.

The optimum pH value of the solutions at Cu^{2+} adsorption for zeolite is in wider range from 4,62 to 8 and for bentonite it is in more narrow range from 4,62 to 6. The results show that the zeolite has better adsorption qualities then bentonite.

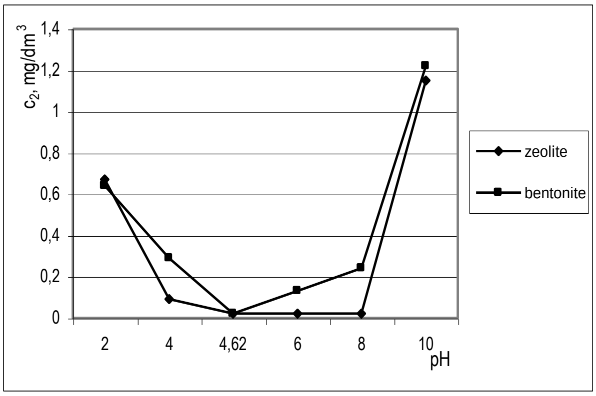

Figure 4. Influence of pH of the solutions on the Cu^{2+}adsorption.

CONCLUSION

1. The Bulgarian natural adsorbents zeolite and bentonite can be used for recovering Cu^{2+} with concentration between 10-20 mg/dm^3 in waste water, completing in one stage of purification by correlation liquid:solid=100:1. Both natural minerals have good adsorption properties towards Cu^{2+} with little superiority of zeolite.

2. The specific surface of the natural adsorbents does not play a significant role on the adsorption at concentrations of Cu^{2+} in the solutions up to 70 mg/dm^3. At higher concentrations the order of adsorption, according to the size of the particles of zeolite, is -0,071+0>+1,0-2,0>-1,0+2,0 mm and of bentonite is -0,071+0>+0,071-0,315>+0,315 mm.

3. The thermodynamics of the adsorption process at different sizes of the particles of both adsorbents was described by the most appropriate adsorption isotherms, obtained with the help of the computer program “CurveFit 424”.

4. The adsorption process at content of Cu^{2+} between 10-20 mg/dm^3 and pH of the solutions 4,6 is vary fast. The contact time is not more than 5 min for reaching the standard for potable waters, according to the content of Cu^{2+}, which is 0,05 mg/dm^3.

5. At adsorption with zeolite, the pH range of the waste waters containing Cu^{2+} between 10-20 mg/dm^3 is wide from 4,6

to 8, for reaching the standards of potable waters. The time of adsorption is 5 min for achieving remaining concentration of Cu^{2+} below 0,02 mg/dm^3. At adsorption with bentonite for the same contact time, the standards for potable waters are reached at pH 4,6. At pH value from 4,6 to 8 are reached the standards for releasing waste waters containing Cu^{2+} in rivers and open reservoirs.

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STUDIES THE IMPACT OF LOW-FREQUENCY ACOUSTIC FIELD UPON CATION EXCHANGE CAPACITY OF NATURAL ZEOLITE

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ABSTRACT
The work is dedicated to investigation of the influence of low-frequency acoustic treatment upon natural clinoptilolite. More precisely upon their sorbtion properties regarding some commonly meet heavy metal cations in the mine waste waters. A comparison is made between the cation exchange capacity, the coefficient of distribution and the recovery of no treated and treated with low-frequency sound zeolite towards the ions of Cu, Fe and Zn from model solutions in sulphate forms. The influence of the ions concentration upon the same indexes is investigated.

INTRODUCTION

Bulgaria is a country with limited availability of natural waters because of that with special stays a question for the water presrevation and conservation from different damaging effects. From the other hand, the water is the vulnerablest component towards contamination of environment and exerts strong influence on related flora and fauna. That’s why the preservation of the water supplies is connected besides with the rational usage but with purification of domestic waste waters and especially industrial waters before their over again using or joining with river courses.

One of the wide used methods for waste waters purification is adsorptional. In the last 10-15 years the interest in the zeolites as natural adsorbent for waste waters purification is exceptionally great. In this context they are a new raw material and the field of application for waste waters purification to a certain extent are unknown for technologists and

SUMMARY FOR THE ZEOLITES

1. Zeolite rocks

The zeolites today are accepted as main rock formed minerals in modified piroclastic sediments. Because of lack of unified system in the usage of names for one and the same rocks (Alexiev and Djourova, 1975) develop exemplary classification according which under zeolites rocks are marked all sediment rocks containing over 10% the zeolites. Until 1980 year 40 variety of natural and over 100 modified zeolites are established. A deposits with economically significant concentrations form eight zeolite minerals - clinoptilolite, shabazite, mordenite, filipsite, erionite (low interest because of cancer behavior), fererite and analcimite.

2. Chemical composition and property of the zeolites.

The zeolites represent crystal aluminium silicate minerals containing metal cations and water. The crystal lattice is composed of silicate and aluminate tetrahedryties bounded in between at different manner and united by common peaks. These tetrahedrites form three-dimensional complex crystal structures with disposed in fixed order microcavities and channels with dimensions from several to several of microns. The generalized formula of zeolite chemical composition is:

$$M_{2/n}O.Al_2O_3.xSiO_2.yH_2O$$

where: M is the cation of alkali or alkali-earth element with valence n, x vary between 2÷10, and y between 2÷7.

The alkali and alkali-earth cations are disposed in microcavities and are relatively low fixed to the lattice, that’s why they could be exchanged with others.

The zeolites are divided according to crystal pore size into wide-, middle- and narrow porosity i.e. “the free diameter” of the channels appears to be the basic controlling factor at entering of “outside” units. The commensurability of equivalent diameter of the zeolite crystal pores with dimension of series molecules define the ability for their selective adsorptions and with this property they are related to the group of the molecular sieves.

Based upon the correlation Si:Al the zeolites are divided into high-, middle- and less silica which determine their stability at different pH values.

They possess high termostability, like internal pore-cavity structure break over 1000^0 C.

The natural zeolites have high mechanical strength (3÷4.5 at Mos) and although behind quartz in this regard they may be successful utilized as filtration materials.

3. Occurrence of the zeolite rocks in our country.

Over 1000 deposit are known in different parts of the world-USA, Russia, Japan, Cuba, Romania, Italy, Mexico, Hungary, Bulgaria and etc.

In our country zeolite rocks are established for the first time eastern from Kardjali town, at railway station "Jelezni vrata". Now in this region are situated the considerablest deposits: "Jelezni vrata", "Beli plast", Beli bair", "Goloburdo", "Most", "Liaskovez" and "Perpelik". Clinoptilolite is a basic mineral in this deposits. Mordenite is found in regions around Malko Popovo village and filipsite around Obrochishte village.

4. Zeolite usage for industrial waste waters purification.

The purification of waste waters is one of the most widely distributed technological processes, that's way research interest is so big for the usage of natural zeolites as materials for filtration (Tarasevich, Kravchenko et al. 1985; Tarasevich et al. 1982), ion exchanging (Stoev, 1991; Poliakov et al. 1979), adsorption (Komarneni, 1985; Papachristou et al. 1993) and catalyzes (Xiao et al. 1998; Corma et al. 1994) materials.

The clinoptilolite shows high acid resistance and sufficient stability to the action of the basis (Poliakov et al. 1979; Barrer et al. 1964), from the other hand it softens the purified water Kovacheva et al. 1995).

During the last years for increasing of zeolite ion exchange capacity they are modified with solutions of different substances containing ions which settle in crystal pores and possess higher affinity to the waste water ions (Papachristou et al. 1993; Bowman et al. 1994).

It is getting clear that the usage of zeolite and the search of methods for increasing their sorbtional capacity is very actual direction for waste waters purification.

EXPERIMENTAL

The investigations are aiming to study the effect of physical impact upon the sorbtion properties of the zeolites and more precise low-frequency acoustic field with the objective to increase cation exchange capacity of natural zeolite.

1. Zeolite characterization and indexes.

For accomplishment of experiments was used a zeolite from enterprise "Bentonite"-Kardjali town with following characteristics:

1.1.Chemical composition - table 1

Table 1. Zeolite chemical composition.

Indexes	Average content, %
SiO_2	66.16
Al_2O_3	11.41
Fe_2O_3	0.80
TiO_2	0.15
MgO	0.85
MnO	0.06
CaO	2.81
Na_2O	0.22
K_2O	2.90
H_2O^+	7.49
P_2O_5	0.02

1.2. Content of impurity elements - table 2

Table 2. Impurity elements in the zeolites.

Elements	Contents, g/t
Pb	62÷102
As	6.0
Cd	2.0
Hg	0.2

1.3. Zeolite quantity indexes

a) Clinoptilolite content- 70%;

b) Sum of exchange ions K, Na, Ca, Mg (defined by NH_4 with usage of NH_4Cl), i.e. total exchange sorption capacity (TESC)- min 100 mgeq/100g;

c) Humidity- max 10%.

2. Determination of TESC as regard to Cu, Fe and Zn ions from model sulphate solutions

The sorptional indexes during achievement of total equilibrium between sorbent and the investigated elements from the solutions were determinated.

2.1. Methods of experiments. Three samples of 5g zeolite, class 0.8-2.5 mm are placed in Bunsen flask and each one of them is filled with model solution with concentration 1g/l of $CuSO_4$, $ZnSO_4$ and $FeSO_4$ in liquid:solid ratio 10:1. The contact between the solution and zeolite is realized through shaking machine CITRON at 150 min^{-1} during 1.5 h, after that the flasks are left for reaching equilibrium for 72 h.

The initial and remaining concentration of Cu, Fe and Zn ions from model solutions is determinated by spectrometer with inductive coupled plasma, ICP in mg/l.

2.2. Determination of TESC, recovery "ε" and coeficient of distribution "κ". The indicated sorbtional indexes are determined by the following formulaes:

$$\text{TESC} = \left(\frac{c_1 - c_2}{m \cdot 1000}\right).V \text{ ;}$$

$$\varepsilon = \left(\frac{c_1 - c_2}{c_1}\right).100,\% \text{ ; } \kappa = \left(\frac{c_1 - c_2}{c_1}\right).\frac{V}{m} \text{ ;}$$

where:

c_1- initial concentration of the element in solution, mg/l;

c_2- remaining concentration of the element in solution, mg/l;

V- volume of solution, ml;

m- weight of dry sorbent, g;

TESC- total exchange sorption capacity, mgelm/g sorbent;

ε- recovery of the element, %;

κ- distribution coefficient.

2.3. The obtained results. The obtained sorption indexes of zeolite regarding the investigated elements are shown at table 3.

Table 3. Zeolite sorptional indexes regarding Cu, Fe and Zn ions from model solutions.

Indexes	Elements		
	Cu	Zn	Fe
c_1, mg/l	245.3	340.0	264.0
c_2, mg/l	13.0	44.2	18.6
TESC, mgelm/g	2.32	2.96	2.45
ε, %	94.70	87.00	92.95
κ	178.7	66.9	131.9

3. Comparison between cation exchange capacity (CEC) of untreated and treated zeolite with low-frequency sound, regarding Cu, Fe and Zn ions from model sulphate solutions.

3.1. Methods of experiments. A zeolite with 5g weight is placed in glass with distilled water with volume 200 ml and is subjected to low frequency acoustic treatment at amplitude 0.4 mm and frequency 30 Hz for time 15 min. The apparatus for creating of low frequency field is described in details (Kovatcheva et al. 1995), main part of the system is the acoustic emitter immersed into cup with distilled water. For comparison untreated zeolite is put in glass with distilled water with the same volume for the same time. After that both zeolites are filtrated and are put in 50 ml model solution with concentration 1 g/l of $CuSO_4$, $ZnSO_4$ or $FeSO_4$. The adsorption is realized with help of shaking machine CITRON at 150 min^{-1} time from 5 to 45 minutes.

The concentration of investigated elements in the model solutions is determined as was mentioned above by ICP, in mg/l.

3.2. The obtained results

a) CEC of untreated and treated zeolite regarding Cu ions

The concentrations, recovery and distribution coefficient of Cu^{2+} are shown in table 4 and CEC in figure 1.

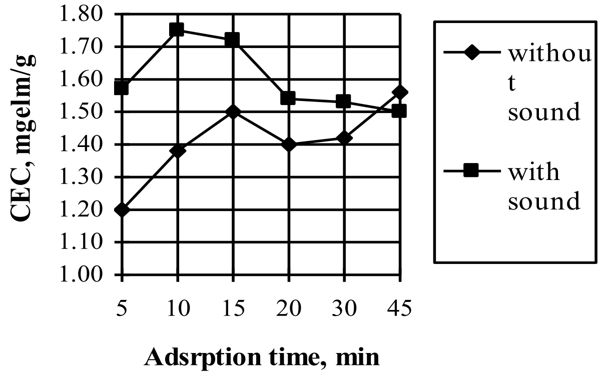

Figure 1. Cation exchange capacity of untreated and treated zeolite with sound regarding Cu ions from $CuSO_4$ solution.

As we seen from table 4 and fig.1 the sorbtional indexes of treated with sound zeolite up to 30-th minute are higher in comparison to untreated zeolite regarding Cu ions. Highest sorption is achieved up to 10-th minute, as the acoustic treatment of zeolite increases CEC with 1.3 times and reaches 75.43% from TESC of Cu ions towards 59.48% for untreated zeolite.

Table 4. Sorbtional indexes of untreated and treated zeolite regarding Cu^{2+} from model solution.

Sorbtion time, min	c_2, mg/l		ε, %		κ	
	without sound	with sound	without sound	with sound	without sound	With sound
Initial concentration c_1=245.3 mg/l						
5	125	88.0	49.04	64.13	9.62	17.88
10	107	70.0	56.38	71.46	12.92	25.04
15	95	73.5	61.27	70.04	15.82	23.37
20	105	91.3	57.19	62.78	13.36	16.87
30	103	92.0	58.01	62.5	13.81	16.66
45	89	91.3	63.72	62.78	17.56	16.87

b) CEC of untreated and treated zeolite regarding Fe ions

The concentrations, recovery and coefficient of distribution of Fe^{2+} are shown in table 5 and CEC in figure 2.

Again the sorbtional indexes of treated with sound zeolite are higher up to 30-th minute in comparison to untreated zeolite regarding Fe ions. Highest sorbtion is achieved up to 15-th minute as the acoustic treatment of zeolite increases CEC with 1.2 times and reaches up to 77.40% from TESC of Fe ions towards 63.30% for untreated zeolite.

Table 5. Sorbtional indexes of untreated and treated zeolite regarding Fe^{2+} from model solution.

Sorbtion time, min	c_2, mg/l		ε, %		κ	
	without sound	with sound	without sound	with sound	Without sound	with sound
Initial concentration c_1=264.0 mg/l						
5	128.0	82.6	51.52	68.71	10.63	21.96
15	109.0	74.8	58.71	71.67	14.22	25.29
30	94.6	87.0	64.17	67.05	17.91	20.34
45	75.1	79.4	71.55	69.92	25.15	23.25
60	74.5	86.0	71.78	67.42	25.44	20.7
90	66.8	91.3	74.7	65.42	29.52	18.92

c) CEC of untreated and treated zeolite regarding Zn ions

The concentrations, recovery and coefficient of distribution of Zn^{2+} are shown in table 6 and CEC in figure 3.

The obtained results again show that the sorption of Zn ions by acoustically treated zeolite is higher up to 30-th minute in comparison to untreated. Highest sorption is obtained up to 15th minute with treated zeolite while the same values are reached at 60-th minute for untreated. CEC of the treated zeolite is 1.2 times higher in 15-th minute in comparison to untreated and 64.2% of TSEC is obtained in comparison to 55.4% for untreated.

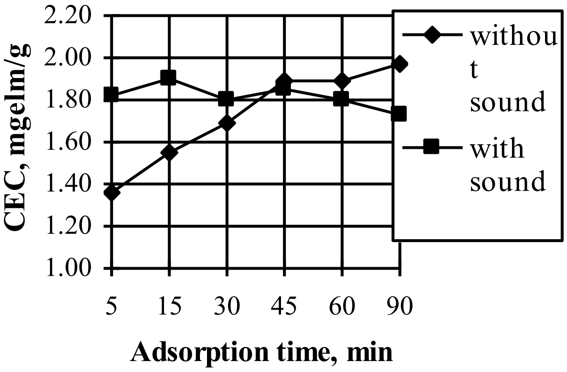

Figure 2.. Cation exchange capacity of untreated and treated zeolite with sound regarding Fe ions from FeSO4 solution.

Table 6. Sorbtional indexes of untreated and treated zeolite regarding Zn^{2+} from model solution.

Sorbtion time, min	c_2, mg/l		ε, %		κ	
	without sound	with sound	Without sound	with sound	Without sound	with sound
Initial concentration c_1=340.0 mg/l						
5	204.0	190.0	40.00	44.12	6.67	7.89
15	176.0	150.0	48.24	55.88	9.32	12.67
30	168.0	160.0	50.59	52.94	10.24	11.25
45	163.0	164.0	52.10	51.76	10.86	10.73
60	150.0	154.0	55.88	54.71	12.67	12.08
90	155.0	151.0	54.41	55.59	11.94	12.52

4. Comparison between sorption indexes of untreated and treated zeolite regarding Cu, Fe and Zn ions when their concentration decreases in the model sulphate solutions.

4.1. Methods of experiments. The methods of the experiments are the same as in point *3.1.* at adsorption time 30 minutes.

4.2. The obtained results. The sorptional indexes are shown in table 7 at decreasing of the Cu^{2+}, Fe^{2+} and Zn^{2+} concentration.

The results from table 7 show identical tendencies for the three elements. With decreasing of the element concentration in initial model solutions, their recovery increases as well as the distribution coefficient, but the value of CEC decreases. This tendency is similar for treated zeolite. This fact confirms that the natural zeolite as sorbent is suitable for purification of low and medium contaminated waste water.

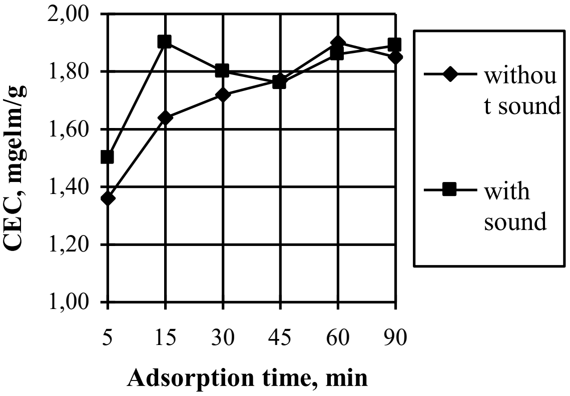

Figure 3. Cation exchange capacity of untreated and treated zeolite with sound regarding Zn ions from ZnSO4 solution.

CONCLUSIONS

On the basis of the investigation work the following conclusions are made:

1. It is confirmed that the clinoptilolite zeolites could be successfully utilized for purification of Cu, Fe and Zn ions from low and medium contaminated waste waters.

2. The possibility for intensification of the sorptional ability of zeolite is established by their treatment with low frequency sound.

3. The positive influence of acoustic field upon the sorption indexes is within the framework of 30-45 minute after treatment and filtration.

4. The reached CEC for 15 minute sorption with treated zeolite towards the three investigated elements Cu, Fe and Zn is around 1.2 times higher in comparison to untreated as well as for distribution coefficient 1.55 times. It is reaching for treated zeolite 75.43%, 77.40% and 64.2% from TESC against 59.48%, 63.30% and 55.40% for untreated respectively for Cu, Fe and Zn ions.

5. Less time is required for reaching same CEC values for treated zeolite in comparison to untreated. The CEC value is reached for 10-15 minutes sorption from treated zeolite towards 30 and more minutes for untreated i.e. the time of sorption is reduced two and more times.

6. The CEC values decrease with decreasing of the studied concentrations of Cu, Fe and Zn ions in model solutions. This remains the same when treated zeolite is used, but the sorptional indexes are higher.

Table 7. The zeolite sorbtion indexes depending on the concentration of Cu^{2+}, Fe^{2+} and Zn^{2+} in model sulphate solutions.

c_1, mg/l	c_2, mg/l		ε, %		CEC, mgelm/g		κ	
	without sound	with sound	without sound	with sound	without sound	with sound	Without sound	with sound
towards Cu ions								
245.3	103.0	92.0	58.01	62.5	1.42	1.53	13.81	16.66
122.65	38.0	31.0	69.02	74.72	0.85	0.92	22.28	29.56
61.33	15.0	12.0	75.54	80.43	0.46	0.49	32.89	41.11
30.67	2.2	0.9	92.83	97.07	0.28	0.30	129.41	330.78
towards Fe ions								
264.0	109.0	74.8	58.71	71.67	1.55	1.90	14.22	25.29
132.0	25.7	20.7	80.53	84.32	1.06	1.11	41.36	53.77
66.0	12.4	11.3	81.21	82.88	0.53	0.55	43.23	48.41
33.0	2.56	1.47	92.24	95.55	0.30	0.32	118.91	214.50
towards Zn ions								
340.0	168.0	160.0	50.59	52.94	1.72	1.80	10.24	11.25
170.0	49.9	33.22	70.65	80.47	1.20	1.40	24.10	41.20
85.0	15.5	13.30	81.76	84.35	0.69	0.72	44.84	53.91
42.5	5.97	3.07	85.95	92.78	0.37	0.40	61.19	128.44

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THE WORKING MEDIA INFLUENCE ON THE KAOLIN VIBRODELAMINATION

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ABSTRACT
In spite of the one-hundred-years history of the vibration milling process, there are still possibilities for solving new technological tasks. An investigation on the influence of the working media elements shape to the process of fine and fine selective milling was carried out. Vibration attrition method for the delamination of the kaolin was used. The possibilities for selective milling with light working elements having density bellow 1 g/cm^3 having lens, short cylindrical and tablet shapes were examined. The frequency of the vibration was between 30 and 75 Hz, the amplitude between 0.25 and 1.8 mm. Dependence between working media elements and the degree of delamination of kaolin was established. The highest efficiency of the process of selective milling by vibration attrition was achieved by usage of lenses as working media.

KEYWORDS: Delamination, kaolin, attrition, fine particles.

INTRODUCTION

The variety of the materials being milled and consumer requirements in respect of granulometric characteristics, maximum size and shape of the particles motivate creating of different in constructions machines, as well as technical flowsheets with high complexity. Vibratory mills with horizontal placed working chamber find wide application for fine milling of ores, industrial minerals, metals, alloys, recycling of technogenic wastes and by-products.

The advantages of the vibratory mills for fine milling of traditional materials are well known and described in wide number of publications (Мадер, 1966, Вибрации в технике, 1981, Роуз, 1964, Стоев, 1979). Vibratory mills with well-defined vibration parameters and working media offers possibilities for new technological solutions for milling of materials considered as hard-milled. There are still obscurity in the process of vibration milling therefore there are unsuspected possibilities for finding of new theoretical and technological solutions.

THEORETICAL PRECONDITIONS

The requirements of the process of fine vibration milling could be generally grouped in:

- Appling of relatively small forces;
- Usage of as high frequency as possible of the vibration impact;
- Ensuring of thin-layered distribution of the material being milled between the milling media.

Appling of high-energy hit impacts for fine milling is not exculpated from economical point of view. Moreover, strong hit impacts cause destroying of the facing and corps as well as working elements surface. The milled materials are contaminated with big quantity of unacceptable impurities, when a high-intensity fine milling is applied. Therefore, in the fine milling, the amplitude is limited in the low values. Variations in the frequency of the vibrations are allowed in the interval up to 50 Hz ensuring the solidity of the mill construction. The easiest way to ensure the thin-layered distribution of the material being milled between the milling media is to be feed in as much packed as possible stricture of the working media with large contact area between working bodies.

The typical value of the vibration parameters in the vibratory mills with horizontal working chamber for producing of fine in size products are:

- Amplitude up to 6 mm.
- Frequency between 15 and 50 Hz;
- The form of the vibration – elliptic or near to the circular.

The technological possibilities of the vibratory mills with horizontal working chamber are frequently realized with fixed vibration parameters. The optimization of these parameters is limited in short interval according to the above shown limits.

The known construction Podmore Boulton Vibro-Energy Mill (Podmore,1969) has specific ring-type form which ensures compact packing of the working media represented by short cylindrical bodies. Compact package ensures the condition of thin-layered distribution of the material being milled between the milling media. The working media ensures large line and area contacts between the elements as well as working elements and vibrating surface of the ring-type chamber. Conditions for ultra fine milling, as a result mostly of the attrition action of the working media elements and hits wit low intensity between them are created in the working chamber.

The attrition is one of the base impacts applied for fine milling of mineral raw materials. Two types of efforts take action together in the attrition process – pressure and tension according to the Joazel theory. The process is schematically illustrated at Figure 1 (Мадер, 1966).

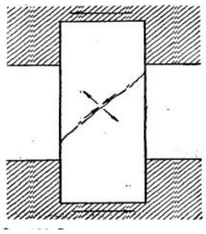

Figure 1. Attrition destroying.

Realizing of the attrition process in the vibratory mill with horizontal chamber could be achieved by 100% filling of the working chamber with working media whereupon the conditions for fine and ultra fine milling are realized. These conditions take place in the process of selective milling of layered minerals (Кузев и др. 1995).

TEST REZULTS

The process of fine and ultra fine milling was examined for delamination of kaolin, for selective milling of fine-flaked hematite, for milling of malleable metals, metal alloys etc.

Delamination of kaolin

The investigations are carried out with bleached kaolin from the current production of the kaolin treatment plant Senovo, having chemical content Al_2O_3 - 32,21%, Fe_2O_3 – 1,02%, TiO_2 – 0,31%, SiO_2 – 51,62%. Two-chamber laboratory vibration mill ensuring amplitude up to 5 mm, and frequency up to 75 Hz was used. Vibration attrition was applied as delaminating process. Light delaminating media with main characteristics given at Table 1 were used. Table 2 shows the granulometric characteristics of the media. (Kuzev, 1997, Кузев, 1998).

Table 1. Characteristics of the delaminating media.

Delaminating media	Density, g/cm^3	Bulk density, g/cm^3		Form
		Free	Shaked	
Polyetilen HH – III group.	0.88	0.539	0.58	Tablet
Polyetilen HH – V group.	0.87	0.557	0.58	Lenses
Pollistyrol	1.16	0.707	0.737	Cylinder

Table 2. Granulometric characteristics of the delaminating medias.

Delaminating media	Yields, %		
	+ 5 mm	-5 +2.5 mm	-2.5 mm
Polyetilen HH – III group.	2.82	96.81	0.37
Polyetilen HH – V group.	1.25	98.39	0.36
Pollistyrol	-	54.93	45.07

The influence of the working elements form on the process of delamination was examined. The differences in the density of the delaminating media pollistyrol and polyetilen are small, thus it be considered that the obtained results, shown at Table 3, are resulted from the different forms of the working media. Short cylinders represent pollistyrol group whereas polyetilen group by tablet and lens forms. The results are obtained with vibration frequency of 50 and 75 Hz and constant amplitude of 0.6 mm. The density of the kaolin suspension is 15% and duration of the delaminating process 10 min.

Table 3. The obtained delamination registered by changes in the suspension viscosity

Material and media form	Vibration frequency, Hz	Viscosity			
		Parts before	Parts after	Difference	cP
Pollistyrol (cylinder)	50	9.5	10.5	1.0	5
Polyetilen III group (tablet)	50	9.5	11.0	1.5	8
Polyetilen V group (lenses)	50	9.5	13.0	2.5	13
Pollistyrol (cylinder)	75	9.5	10.9	1.4	7
Polyetilen III group (tablet)	75	9.5	11.5	2.0	10
Polyetilen V group (lenses)	75	9.5	13.0	3.5	18

The obtained delamination was proved by the variation in the suspension rheology registered with rotation viscosimeter TV (Switzerland) with measuring scale divided to 100 equal parts.

Table 4. The yields of the classes in dependence of the amplitude of the vibrations.

Class, μm	Yields of classes, % at amplitude of the vibrations, mm					
	0	0.25	0.52	0.7	1.10	1.45
+ 60	2.0	1.8	0.5	0.2	0.5	1.5
+ 50	2.2	1.9	0.8	0.2	0.7	1.6
+ 40	2.5	2.0	0.8	0.5	1.1	1.8
+ 30	2.5	2.0	-	0.7	1.3	1.8
+ 20	2.5	2.5	1.2	1.2	1.5	1.9
+ 10	5.5	6.7	4.4	2.4	4.3	6.4
+ 5	20.2	19.2	18.3	18.0	18.0	19.1
+ 4	33.0	24.6	24.0	22.2	21.7	26.0
+ 3	37.7	31.2	30.3	29.3	29.8	37.7
+ 2	42.1	40.4	38.5	37.4	38.3	40.9
- 2	57.9	59.6	61.7	62.6	61.5	59.1

Investigations for determination of the changes in the granulometric characteristics of the part of obtained in laboratory scale delaminated products were carried out. Constant conditions, only variations in the amplitude and frequency, were used for obtaining of delaminated kaolin in the laboratory. The working media was pollistyrol. The treatment duration was 10 min, the frequency of vibration - 50 Hz and the pulp density - 15 %. The amplitude was: 0.25 mm, 0.52 mm, 0.70 mm, 1.10 mm, 1.45 mm. The initial sample is marked with label Zero (0) of the amplitude at Table 4. The size of the particles is determinated as equal spherical particle whereupon the effect of the delaminating process could not be registered. The analyses were performed at "Седиментационен анализ" laboratory in СКАХП at ЦИХП, Gara Iskar with a liquid picnometer and sedimentation balance Sortarius 4610 according to БДС 10550-78.

Table 5. Medial diameter and particle shape defined by microscopic observation.

Sample №	Counted particles, μm						Form of the particles
	- 2 μm	2 - 5μm	5 – 10 μm	+ 10 μm	Sum, numb.	Medial diam,μm	
Bleached k	336	64	39	22	451	2.62	Bulk
Sample 13	2464	338	54	10	2866	1.27	Lenses
Sample 1	3312	336	21	8	3677	1.29	Lenses
Sample 18	1104	584	223	73	2984	1.29	Lenses
Sample 22	3152	228	103	49	3532	1.50	Lenses
Sample 50	1136	496	55	9	1696	2.01	Lenses
Sample 48	848	208	16	14	1086	1.75	Lenses
Sample 52	928	320	102	18	1368	2.25	Lenses
Sample 38	3860	768	99	-	4727	1.54	Lenses

The medial size of the particles in the kaolin suspension before delamination as well as after the delamination in different statistically defined conditions was measured by microscopic observations. In result of the counting of the particles, at Table 5 are shown classes with size -2 μm, 2 – 5 μm, 5 – 10 μm, and +10 μm. The medial diameter is estimated according to the dates of observed sample.

Table 6 shows the conditions for delamination of the samples represented at Table 5.

Table 6. Experimental conditions for delamination.

Sample №	Delamination conditions				
	Frequen, Hz	Amplitud mm	Time, min	Pulp, % density	Medial diam, μm
Bleached kaolin	0	0	0	-	2.62
Constant amplitude					
Sample 13	40	0.25	15	15	1.46
Sample 1	50	0.25	15	15	1.29
Sample 18	60	0.25	15	15	1.29
Sample 22	75	0.25	15	15	1.50
Constant frequency					
Sample 50	50	0.31	10	10	2.01
Sample 48	50	0.70	10	10	1.54
Sample 52	50	1.10	10	10	1.75
Sample 38	50	1.445	10	10	2.25

DISCUSSION

As a result of vibration attrition process, fine dispersed particles with different forms, according to the physical-mechanical properties of the material been milled, could be obtained. The correct definition of the vibration parameters and working media, leads to obtaining of particles with predominantly plate forms from layered minerals such as kaolin, graphite, specular hematite etc. From the same raw material, at different conditions - parameters of the vibrations and working media could be predominantly obtained particles with isometric forms.

For obtaining of kaolin particles with flake forms it is necessary the force in direction of “c” axes ($E = 644x10^{-6}$ cal/cm^2), which keep different crystals in one kaolin stack, to have smaller value, then the attrition force between the slithered surfaces of the working bodies. (Conly,1987, Davis and Dawson, 1989).

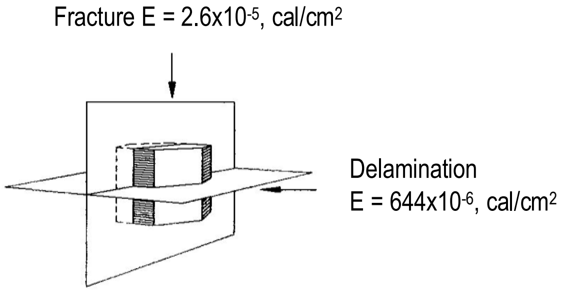

Figure 2. Bonds energy of the kaolin crystals.

The obtained in the investigation results, shown at Table 3, for the viscosity of kaolin suspensions after delamination with different delaminating medias shows:

- The highest value of viscosity increasing is obtained by usage of polyetilen lenses as working media.

- Downstream climax of the efficiency of working elements with different forms is lenses, tablets and cylinders. Arrangement of these forms corresponds to the contact area decreases between the elements. In the case with lenses as working media, contact area is the largest. Contact area is smaller with usage of tablets (or combination between tablets and cylinders) because there are line and area contacts. The smallest contact area is with usage of cylinders as working media, because the contacts between the elements are predominantly lines.

A real effect of grinding could be observed browsing over the numeric data at Table 4, in the columns showing the yields of the different classes. After the delamination with different amplitudes, the number of particles with size over 20 μm decreases. Taking into account the size of classes from 20 to 2 μm a character minimum could be observed with the amplitude of 0.7 mm. The yields of these classes increase with the variations of the amplitude up and down from 0.7 mm. There is an anomaly at first view, but it could be easily explained with the changed attrition conditions. Namely, the glide plane remains constant at different amplitudes and remains independent of the different speed of the working media caused by the vibrations, while the speed of the suspension movement in the contact area of the working elements depends on the amplitude. That is way, at higher suspension speed than the glide speed increases yields of the fine classes. At the equation of the speeds, there is an optimum of the milling, whereupon the finest products are obtained. After the passage of the speed equation, the increases of the amplitude could not increase the fine classes yield. The absolute values for the different classes at Table 4 are small but the quality of the delaminated kaolin could be visualized by Scanning Electron Microscope (SEM) pictures. A general view of the bleached kaolin is shown at Figure 3. Figure 4 shows delaminated kaolin.

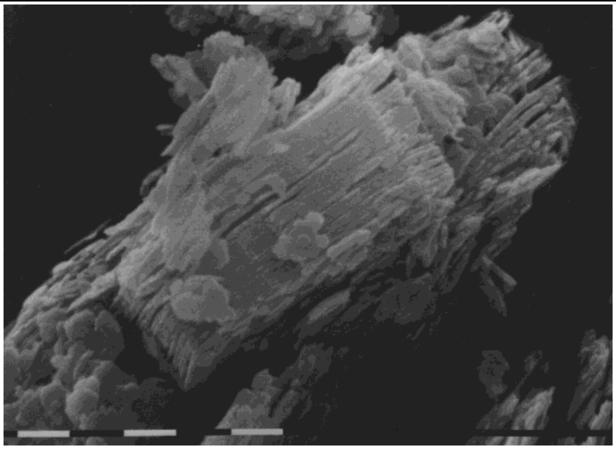

Figure 3. SEM picture of kaolin stack.
Magnification 10 000 times and Marker 1 µm.

Interesting results for changes of the medial size of the particles are perceived by microscope observation of the initial and delaminated in the following conditions samples:

- Constant amplitude 0.25 mm and frequency of 30, 40, 50, 60, 75 Hz.
- Constant frequency 50 Hz and amplitude of 0.31 mm, 0.7 mm, 1.10 mm, 1.45 mm.

Results are shown at Table 6.

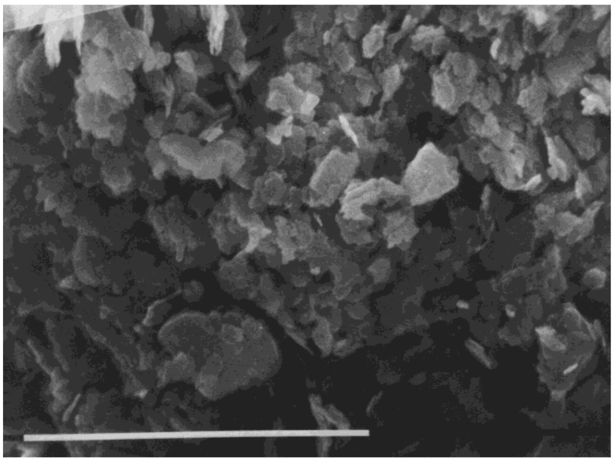

Figure 4. SEM picture of kaolin particles (flakes)
Magnification 6 200 times and Marker 1 µm.

The medial diameter of the bleached kaolin 2.62 µm was decreased to 1.29 µm after the delaminating process by applying of different vibration parameters, duration of the treatment and density of the slurry. The data for the received medial diameter of the kaolin particles at constant frequency and amplitude from 0.31 to 1.45 mm, completely correspond and confirm the data shown at Table 5.

CONCLUSION

An investigation on the influence of the working elements form to the fine selective milling – delamination of kaolin under conditions of vibration milling in the mill with horizontal working chambers was performed. The investigated light working bodies are with inconsiderable differences of the density. The size is between 2.5 to 5.0 mm. Usage of light working bodies as milling media excludes the hit impacts between the bodies and crushing of the material being milled. Under these extremely conductive conditions, the influence of the working elements form on the process of selective milling was investigated. The increasing of contact area between the working elements of the milling media, which is a direct result from the working bodies form, accelerates the process of delamination. The most appropriate form of the working bodies is lenses, followed by tablets and cylinders.

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INDUSTRIAL TRIALS FOR THE “STRUPETZ” STUFFING QUARTZ MASS IN STEEL CASTING

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ABSTRACT

Experiments under industrial scale for using of acid stuffing mass in a 2.5 tone induction furnace located in ZTM Russe have been carried out. The mass originates from the white variety of quartz from the Strupetz deposit. The stuffing mass has been sintered according to the method of pot forming based on the SS221 and SS230 Swedish stuffing masses and has been used for production of steel under the brand of 25 GL. 35 L and 40 XL under discrete operation mode. The maximum temperatures reached under the different melting was 1650 – 1690 °C. The life expectation of the lining under furnace normal working conditions without technical and organisational problems was estimated between 16 and 22 melting cycles. The industrial trials are confirming the superior performance of the raw quartz material and are rendering it suitable for development of a wide range of acid-type stuffing masses for variety of furnaces and molten material

Key words: quartzite, stuffing mass, induction furnace, steel casting.

INTRODUCTION

Following a detailed and time consuming investigations under lab-scale conditions upon different SiO_2 rich materials the acid-type stuff mass has been developed based on the white variety of quartzite deriving from the Strupetz deposit (Kuzev, et al. 1984). The stuffing mass has been tested under industrial conditions in CHLK Ihtiman in direction of formation of a crucible for the 10 tone induction furnace. More than 100 different molten forms were developed from the Strupetz mass under extreme parameters such as:

– fusion of Ni and Cr doped cast iron;
– metal overheating up to 1600 - 1650 °C;
– keeping the molten metal under temperature above 1600 °C in the furnace from 3 to 5 hours before its forming etc.

Following crucible destruction it has been established its linings were partially weared (Kuzev, et al. 1987). This favourable results suggest that there are suitable materials of local origin with whose characteristics differ negligibly from those of the most frequently used masses manufactured by the Forshammer Group. This company offers acid-type stuffing masses developed on a single-source material and used for melting of variety of metals in temperature ranges from 1200 to 1700 °C. The development of a similar masses on the bases of local virgin material presents a challenging and serious task. Regardless of the good lab scale results for the Strupez material, their confirmation under industrial scale provides and added incentive. Stainless steel casting processes are aiming the most difficult ones regarding the stuffing masses, therefore it was decide to test the Strupez material under these conditions.

INDUSTRIAL TESTING

Industrial trials for the Srupez mass have been carried out in the blend melting section of the ZTM Russe on furnaces which originally are working with imported stuffing masses. Table 1 summarises the main characteristics of the principal imported stuffing masses used by that company.

Furnaces characteristics

The induction furnaces used during the experiments were N 3 and N 4, type MPG - 2500 manufactured by AEG ELOTERM. Maximum furnace power - 2000 kW. Their capacity based on molten metals for a single melting was 2500 kg. Furnace dimensions are:

– crucible light diameter 650 mm;
– crucible wall thickness 136 mm;
– crucible height 1400 mm.

The quantity of stuffing mass required for a single lining was 1.4 m^3. The average duration of a melting cycle was According to the technical project guidelines N 3012, 16 melting cycles for a single quartzite lining for cycle duration of 90 minutes are presented in p. 3.2.4. 90 min.

“Strupez” stuffing mass characteristics

The stuffing mass was produced on the basis of the white quartzite variety of Strupez deposit, which deposit is a principal source for production of dynase refractors. Quartzite is characterised by fine grained structure and non-oriented solid structure. Limonite is met upon its micro cracks. Quartzite is presented by rounded grains having mean size of 0,44 mm (from 0,102 to 0,159 mm). The method for material preparation is described in Kuzev and Stoev, 1985. The material taken from the ZTM Russe is characterised by the following parameters: moisture – 0.3%, refractoriness 1730 ^{0}C, density – up to 2,65 g/cm^3, SiO$_2$ - 97,76 %, Al$_2$O$_3$ - 1,1 %, Fe$_2$O$_3$ - 0,8 % and ignition losses - 0,2 %.

Table 1. Characteristics of the imported stuffing masses

Parameter	Stuffing mass type		
	HFP	Rodacorit	Silica mix
Stuffing mass N	SS 221	SS 625	SS 230
SiO$_2$ content, %	98,00 %	13,00 %	98,00 – 99,00 %
Al$_2$O$_3$+ TiO $_2$ content, %	0,3 - 0,6 %	85,00 %	–
Grain size , mm	0 - 4	0 - 6	0 - 4
Maximal operating temperature, ^{0}C	1700	1550	1650
Application	Carbon stainless-steel, Ni-hard, Cr alloys	Bronze	Cast iron, Carbon stainless-steel

Pot stuffing and sintering

The stuffing mass was processed manually by hand magnet for metallic iron rejection by layering into thin film and zigzag moving of the magnet above the layer. About 10 % are removed from the thus cleaned mass, which are homogenised several times with boric acid for 500 kg portions. After the proper homogenisation mixing with the whole mass follows, while for every 10 paddles form the stuff one is from that part which has undergone boric acid homogenisation. The procedure is performed triple to ensure good mixing. Pot stuffing starts from the bottom of the furnace while every care is taken in order to prevent the mass to be at maximum height of 500 mm in order to avoid size segregation. Layer processed without boric acid is placed at about one third of pot filling. The height of the following layers vary from 60 to 80 mm having boric acid content form 0,8 to 1,2 %. The total height is about 20% above those prescribed by the producer. Final densification is accomplished by vibrational studding device. It is placed by means of a crane. After removing of the vibrator the upper surface is levelled and the upper layer is skimmed out. The bottom is also levelled and flattened. A metallic standard cylindrical shape device is used for wall formation. It is placed axially at equal distances to the inductor. It is fixed from outside in 3 points at 120^0. The bottom is filled in with ferrous scrap. Layers having 50 to 70 mm height are thus formed. Each single layer is pressed for ca 2 – 3 minutes after introducing in a new layer. Final pressing is done by e special vibration device for 8 – 10 minutes. Stuffing mass presenting a mixture of 1.5 % boric acid and 6-8 % liquid Na silicate “liquid glass” is used. The final height of the pot walls is 30 to 55 mm above the upper part of the platform. Levelling id accomplished after final sintering. The aim of the stuffing id to reach good air decompression and density of 2,0 - 2,5 kg/dm^3, at which a ceramic body is formed which is able to resist the liquid metal.

Linings sintering is done owing to the working diagrams used of the Swedish quartzite. Temperature was kept constant for certain time under the Fener critical values for quartz phase transformations. Heating rate does note exceed 120^{0}C/h. After melting of the blend which is about 2500 kg a temperature of 1600 ^{0}C is reached, keeping it for ca 50 minutes. Immediately before pouring temperature is increasing up to 1685 ^{0}C.

EXPERIMENTAL RESULTS

The investigation was performed at furnaces N 3 and 4 in due course of several months in an alternative mode of using Strupez and imported masses. Table 2 presents the technological results from several successively sintered pots with Strupez mass as well as the reasons for rejection and destruction of the furnace N 3 pot.

Table 2. Technological results from pots sintering for furnace 3 with Strupez mass and imported stuffing masses

№	No of melts	Type of stuffing mass	Molten metal type number	Max. temperature of overheating, °C	Reason for pot rejection
1	12	SS 221	35L –1, 25GL –11	1670	Interrupted regime
2	13	SS 221	25GL- 13	1675	Interrupted regime
3	14	SS 221	35L - 14	1670	Interrupted regime
4	13	SS 221	25GL - 13	1660	Interrupted regime
5	2	Silica mix	40HL –1, 25GL- 1	1700	Interrupted regime
6	22	Strupez 1	25GL - 22	1690	Interrupted regime
7	16	Strupez 1	40XL – 1, 25GL - 15	1670	Interrupted regime
8	17	Strupez 1	35L - 3; 40XL - 2; 25GL - 12	1680	Interrupted regime

Similar results from furnace N 4 are presented at Table 3.

Table 3. Technological results from pots sintering for furnace No 4 with Strupez mass and imported stuffing masses

N	No of melts	Type of stuffing mass	Molten metal type number	Max. temp. of over-heating, °C	Reason for pot rejection
1	22	SS 221	35Л - 15; 25ГЛ - 5; 45Л - 2	1650	Interrupted regime
2	10	Strupez 1	35Л - 3; 45Л - 3; 25ГЛ - 4	1680	Metal cooling inside pot
3	11	SS 221	25ГЛ - 10; 45Л - 1	1650	Interrupted regime
4	4	SS 625	35Л - 4	1690	Non-suitable stuffing mass
5	7	SS 625	25ГЛ - 4; 35Л - 3	1980	Non-suitable stuffing mass
6	4	Strupez 1	25ГЛ - 2; 40ХЛ - 2	1670	Molten metal boiling for more than 1 hour
7	13	Strupez 1	40ХЛ - 5; 25ГЛ -8;	1670	Interrupted regime
8	7	Strupez 1	25ГЛ – 7	1665	Polluted with carbonate stuffing mass
9	16	Strupez 1	25ГЛ - 16	1670	Interrupted regime

At Table 4 data from the melting map for the performed melting of lining 2 from Table 3 sintered with Strupez material are presented. For melt No 9 after melting of the bled the furnace has been switched off in emergency. The metal remained inside the furnace for 6 hours. Openings were drilled in the cooled metal and are poured about 800 kg metal. At the following day the metal was melted and formed. Upon pot inspections cracks in length up to 200 mm and width 1 mm were detected. A melt No 10 was done. Following its accomplishment further increase in crack size was noticed. Further two melts were done which were not noted at the map. During the second melting the furnace is switched of in emergency again. The following pot inspection has led to its rejection.

Table 4. Data for the melting performed with pot N 2 sintered from Strupez mass shown at Table 3

N	Time мin.	Max. temp. of overheating , ^{0}C	Type of molten metal	Lining status		Mass of molten metal
				Walls	Bottom	
1	120	1680	45Л	New	New	2500
2	120	1685	35Л	Good	Good	2500
3	120	1673	35Л	Good	Good	2500
4	150	1676	35Л	Good	Good	2000
5	240	1678	45Л	Good	Good	2500
6	180	1680	25ГЛ	Good	Good	2500
7	210	1683	25ГЛ	Good	Good	2500
8	120	1680	25ГЛ	Good	Good	2500
9	120	1683	25ГЛ	Good	Good	2000
10	120	1690	45Л	Cracks	Cracks	2500

The following deviations from the technological requirements which have led to faster rejection of pot 2 were established during the experiments

a) discontinuous working mode, i.e. the furnace has been cooled down to ambient temperatures 8 times before the emergency shut down in melting No 9.
b) keeping of overheated material at temperature above 1670 ^{0}C, above which material mobility is intensive and pot wearing is increased
c) increasing melting time in 30-50 % average, and for one of them 2,5 times;
d) pot filling in with scrap non-suitable for furnace dimensions. When coarse scrap is fed in the pot mechanical damages to pot lining occur.

DISCUSSION

The Strupez quartzite stuffing mass tested under industrial condition on ZTM Russe is comparable in exploitation parameters to the imported similar materials type SS 221, SS 230 and others. The Strupez stuffing material is based on quartzite by-product. It derives from a range of acidic quartzite masses finding various applications for the induction furnaces. The hard industrial trial are confirming the feasibility of using Strupez mass in direction of production of acid-type stuffing. The most commonly met defects could be attributed to:

a/ furnaces feeding with scrap having dimensions larger than the required ones;
b/ exceeding the melting time duration – melting for 90 min., followed by pouring of 1/3 to ½ of the molten metal, scrap adding and further pouring of part of the metal or the whole pot. Thus the molten metal is in practice 4 – 5 tones for 270 – 360 min, while at the temperature map only one melting with duration more than 180 min is indicated.

The lack of proper organisation and planning is leading to necessity of interruptions leading to non-steady temperature regime. This is leading to high energy consumption and to pot destruction. Stresses and micro cracks are thus formed resulting in further deformations. The data presented at Table 2 and 3 suggest the following:

a) the Strupez quartzite mass seems robust an resistive for the studied conditions – it could sustain up to 16 melting while for one of the cases 22 were achieved. Organisational problems however are leading to shortening of the cycles
b) the imported masses have a similar technological behaviour
c) Strupez mass sintering is accomplished according to the diagrams used for the Swedish SS 221 mass. It is known form the practice that each mass is sintered according to its individual diagram. This fact suggests that the Strupez mass has not been sintered according to the best possible scheme which takes into consideration the mineralogical compositions and the sizes of SiO$_2$ crystals.

CONCLUSION

The detailed industrial scale investigations of the Strupez quartzite stuffing mass developed on the basis of the white variety of quartzite has suggested that this material possesses the quality which makes it suitable for the different types of pot induction furnaces .

The comparative test method for the Strupez quartzite stuffing mass and the similar Swedish materials SS 221 and SS 230 used in cast-iron and stainless-steel production have confirmed the results obtained under lab-scale concerning their physical and physicochemical characteristics indicating similarities between both quartzite sources. The following investigation stage should aim optimisation in sintering flowhsheet and development of range different materials for each specific case.

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SYNTHESIS OF HYDROBROMIDE OF 2-(GLYCYLCYSTINYLAMINO) – 2-(4-METHOXYPHENYL)-1,3-INDANDIONE AND INVESTIGATION OF ITS EFFECT ON SOME FUNCTIONS OF ISOLATED LIVER MITOCHONDRIA

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ABSTRACT

2-(N-benzyloxycarbonylcystinylamino)-2 -(4-methoxyphenyl)-1,3-indandione (Z-🕡ys-NH-AID)$_2$ (compound **1**) has been obtained as a result of the aminolysis of the activated ester 3-0-(N-benzyloxycarbonylcystinyl)-hydroxy-2-phenylindenone (Z-🕡ys-OA)$_2$ with 2-amino-2-(4-methoxyphenyl)-1,3-indandione H$_2$N-AID. By analogy, the interaction of the activated ester 3-0-(N-benzyloxycarbonylglycyl)-hydroxy-2-phenylindenone (Z-Gly-OA) with (H-🕡ys-NH-AID)$_2$ leads to the synthesis of amide of the dipeptide 2-(N-benzyloxycarbonylglycylcystinyl-amino)-2-(4-methoxyphenyl)-1,3-indandione (Z-Gly-🕡ys-NH-AID)$_2$ (compound **3**). The hydrobromide of 2-(glycylcystinylamino)-2-(4-methoxyphenyl)-1,3-indandione (HBr.H-Gly-🕡ys-NH-AID)$_2$ (compound **4**) has been found to show a stimulatory effect on functions of respiratory chain in isolated rat liver mitochondria.

Key words: 2-phenyl-1,3-indandione and its isomeric form 3-hydroxy-2-phenylindenone, activated ester, aminolysis, 2-amino-2-(4-methoxyphenyl)-1,3-indandione, adenosine tri-phosphatase activity.

INTRODUCTION

Indane compounds exhibit different physiological action. Derivatives of 1,3-indandiones have been investigated in detail (Wanag, 1960). Many of these compounds are used as blood anticoagulants (Ozol, Germane, et al., 1969) or as compounds with pronounced influence on the central nervous system (Belenkii, Germane, et al., 1960; Germane, Kamenov, et al., 1978; Kabat, Stohlman, et al., 1944). According to their relation to the blood, 2-aryl-1,3-indadiones are classified as antagonists of K group vitamins (Quick, Gollentine, 1951; Miloshev, Aleksiev, et al., 1972). Other indandione derivatives decrease adenosine tri-phosphatase (ATF-ase) activity of the myosin (Bogdanov, 1970) and infringe upon the bioenergetical functions of mitochondria (Martins, 1966; Perlick, 1964). The large spectrum of physiological activities of 1,3-indandiones, as well as the ability of the internal membrane of mitochondria to prevent passing of many metabolites including most of the aminoacids, determined the aim of the present work – to investigate the influence of amides of natural aminoacids and peptides with 2-amino-2-(4-methoxyphenyl)-1,3-indandione on mitochondria functions.

Among the investigated hydrobromides of natural aminoacids and dipeptides with 2-amino-2-aryl-1,3-indandiones having generalized formulas I and II, the hydrobromide of 2-(glycylcystinylamino)-2-(4-methoxy-phenyl)-1,3-indandione **4** showed pronounced influence on the mitochondria functions.

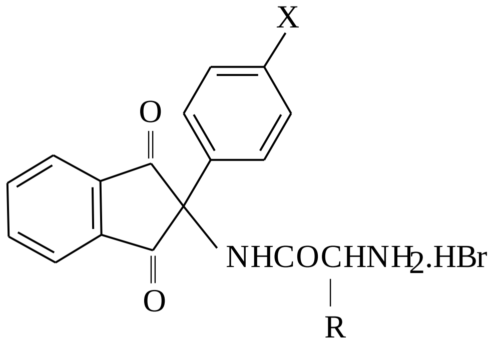
The compound enumerated as **4** can be synthesized in good yield and high purity according to the scheme presented below.

All abbreviations non-described in the paper follow the IUPAC-IUB system (IUPAC-IUB Commission of Biochemical Nomenclature, 1967).

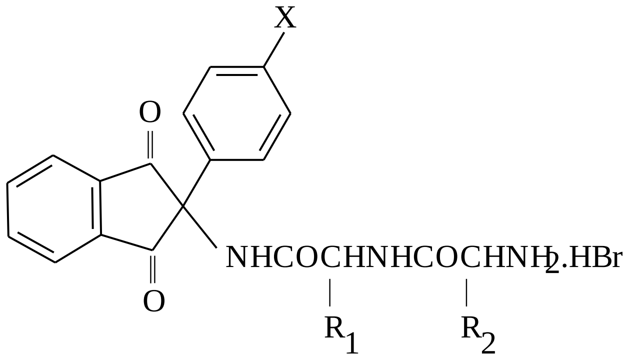
Compounds enumerated as **1**, **3**, and **4** are crystalline, and the hydrobromide **2** is amorphous substance. All data on newly synthesized compounds are presented in “Results and discussion” section.

MATERIALS AND METHODS

The melting points were determined in an opened capillary without correction. The infrared spectra were taken in a nuoil suspension on an IKS-22 spectrophotometer. The optical rotation $[\alpha]_D$ was determined with a CarlZeiss Polarimeter. The homogeneity of the synthesized compounds was checked by TLC on Silufol plates using the following developing systems: B, ethyl acetate – petroleum ether (1:1); C, pyridine – n-butanol – acetic acid – water (10:15:3:12); D, benzene – methanol – acetic acid (15:2:3); E, n-butanol – methanol – water (4:1:1).

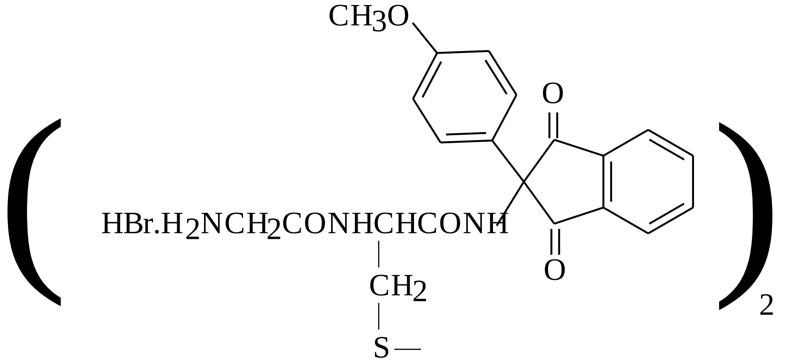


I



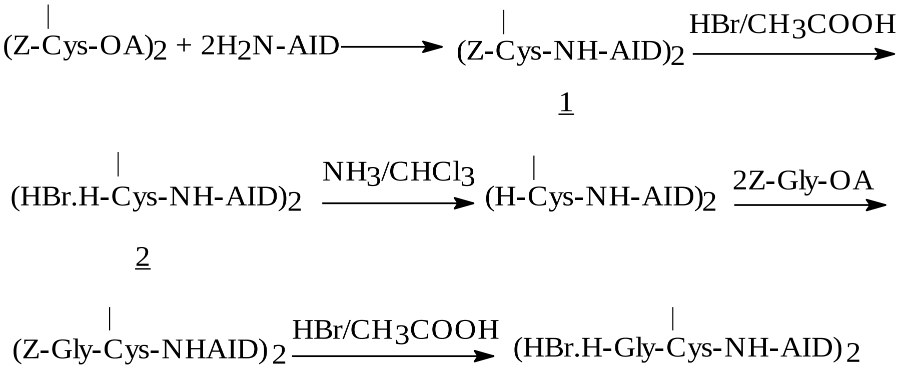
II

X = H, OCH_3



<u>4</u>

The following scheme has been used for synthesis of compound **4**:



$$(\text{Z-}\overset{|}{\text{C}}\text{ys-OA})_2 + 2\text{H}_2\text{N-AID} \longrightarrow (\text{Z-}\overset{|}{\text{C}}\text{ys-NH-AID})_2 \xrightarrow{\text{HBr/CH}_3\text{COOH}}$$

<u>1</u>

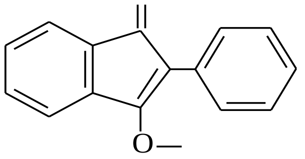
$$(\text{HBr.H-}\overset{|}{\text{C}}\text{ys-NH-AID})_2 \xrightarrow{\text{NH}_3\text{/CHCl}_3} (\text{H-}\overset{|}{\text{C}}\text{ys-NH-AID})_2 \xrightarrow{\text{2Z-Gly-OA}}$$

<u>2</u>

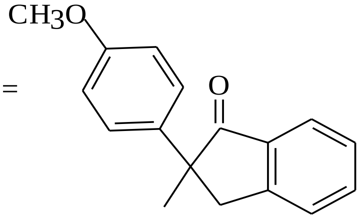
$$(\text{Z-Gly-}\overset{|}{\text{C}}\text{ys-NHAID})_2 \xrightarrow{\text{HBr/CH}_3\text{COOH}} (\text{HBr.H-Gly-}\overset{|}{\text{C}}\text{ys-NH-AID})_2$$

<u>3</u> <u>4</u>

A =



; AID =



The initial compounds were synthesized by known methods: 2-amino-2(4-methoxyphenyl)-1,3-indandione (H_2N-AID) (Aren, Wanag, 1959), 3-0-(N-benzyloxycarbonylglycyl)-hydroxy-2-phenylindenone (Z-Gly-OA) and 3-0-(N-benzyloxycarbonylcystinyl)-hydroxy-2-phenylindenone (Z-Ⓒys-OA)$_2$ (Minchev, Derdowska, et al., 1980).

Intact rat liver mitochondria were isolated with insignificant modifications using Johnson and Lardi method (Johnson, Lardi, 1967). Following Sholts, Ostrovskii (1975) mitochondria respiration was registered with a Universal polarograph OH-105 supplemented with covered Pt electrode combined with chloride-silver electrode as reference electrode. Following Lowry, Lopes (1946) conclusions on the ATF-ase activity were drawn based on the increase of inorganic phosphate.

RESULTS AND DISCUSSION

1. Preparation of 2 - (N-benzyloxycarbonylcystinyl-amino) - 2 - (4-methoxyphenyl) - 1, 3 - indandione (Z-Ⓒys-NH-AID)$_2$ 1.

0.003 M (2.75 g) of activated ester (Z-Ⓒys-OA)$_2$ dissolved in 30 ml of dry ethyl acetate were added to 0.006 M (1.6) g of H_2N-AID dissolved in 25 ml of dry ethyl acetate. The obtained solution was left for 24 hours at room temperature. 2-Phenyl-1,3-indandione released in the aminolysis course was separated by washing the ethyl acetate layer several times with 10 % sodium bicarbonate solution, 2 N HCl, and water. Then the organic phase was dried over anhydrous Na_2SO_4. The ethyl acetate was evaporated in vacuo to dryness. The oily residue was re-crystallized from chloroform/petroleum ether and a light-green crystalline compound was obtained. Yield 2.31 g (76.5 %); m. p. 141-142 °C; $[\alpha]_D^{21}$ = +88.9° (c=1, ethyl acetate); $C_{54}H_{46}N_4O_{12}S_2$ (1007.1); calculated N 5.56; found N5.56; calculated S 6.37; found S 6.11; R_{fB} = 0,43; R_{fE} = 0.90; IR:$\nu_{(C=0)}$ of indandione 1750, 1720; $\nu_{(C=0)}$ amide I 1650; $\delta_{(N-H)}$ + $\nu_{(C-N)}$ 1510; $\nu_{(N-H)}$ 3300-3100; $\nu_{(C-O-C)}$ 1250, 1060 / cm.

2. Preparation of hydrobromide of 2-cystinylamino-2-(4-methoxyphenyl) - 1, 3 - indandione (HBr.H-Ⓒys-NH-AID)$_2$ 2.

2g of hydrogen bromide saturated in glacial acetic acid were added to 0.002 M (2.01 g) of (Z-Ⓒys-NH-AID)$_2$. The reaction flask was preserved from the atmospheric humidity by use of tubule filled with calcium chloride. After the mixture had stayed about 30-40 min the excess hydrogen bromide and glacial acetic acid were removed in vacuo at temperature of 40 °C. 50 ml of dry ethyl ether were added to the oily residue, and the obtained mixture was left for several hours at 0°C. Then the separated amorphous hydrobromide was filtered. The obtained hydrobromide was purified by reprecipitation from absolute methanol/ethyl ether. Yield 1.1 g (61.1 %); R_{fC} = 0.67; R_{fE} = 0.51.

Dehydrobromation of the compound **2** was made by addition of chloroform saturated with gaseous ammonia for an hour at temperature of 5 °C to 0.001 M (0.9 g) of (HBr.H-Ⓒys-NH-AID)$_2$. Having the ammonium bromide separated, the filtrate was evaporated in vacuo. The obtained oily product (H-Ⓒys-NH-AID)$_2$ was used immediately for synthesis of dipeptide **3**.

3. Preparation of 2-(N-benzyloxycarbonylglycylcystinyl-amino)-2-(4-methoxyphenyl)-1,3-indandione (Z-Gly-Ⓒys-NH-AID)$_2$ 3.

0.002 M (0.83 g) of activated ester Z-Gly-OA dissolved in 15 ml of dry ethyl acetate were added to 0.001 M solution of (H-Ⓒys-NH-AID)$_2$ in 15 ml dry ethyl acetate. (The (H-Ⓒys-NH-AID)$_2$ was obtained by dehydro-bromation of 0.001 M (0.9 g) (HBrH-Ⓒys-NH-AID)$_2$ with chloroform saturated with ammonia.) The solution was left for 24 hours at room temperature. The ethyl acetate layer was washed several times with 10 % solution of sodium bicarbonate, 2 N HCl, and water. Then it was treated with activated carbon, dried over anhydrous Na_2SO_4, and evaporated in vacuo to dryness. The oily residue was recrystallized from ethylacetate/petroleum ether and a light-green substance was obtained under the form of fine needles. Yield 0.7 g (62.4 %); m. p. 150-151 °C; $[\alpha]_D^{18}$ = -57.9° (c=1, dimethylformamide); $C_{58}H_{52}N_6O_{14}S_2$ (1121.2); calculated N 7.49; found N 7.44; calculated S 5.72; found S 5.83, R_{fC} = 0.80; R_{fD} = 0.30; IR:$\nu_{(C=0)}$ of indandione 1720, 1710; $\nu_{(C=0)}$ amide I 1650; $\delta_{(N-H)}$ + $\nu_{(C-H)}$ 1510; $\nu_{(N-H)}$ 3300-3000; $\nu_{(C-O-C)}$ 1250, 1040 / cm.

4. Preparation of hydrobromide of 2-(glycylcystinyl-amino) – 2-(4-methoxyphenyl)-1,3-indandione (HBr.H-Gly-Ⓒys-NH- AID)$_2$ 4.

0.0005 M (0.56 g) of (Z-Gly-Ⓒys-NH-AID)$_2$ **3** were treated with 0.5 g of hydrogen bromide dissolved in glacial acetic acid. Having the mixture stayed for 30-40 min, the glacial acetic acid was distilled in vacuo at 40 °C. 30 ml of dry ethyl ether were added to the oily residue obtained. The mixture was kept for several hours at 0 °C and the separated amorphous hydrobromide was crystallized from methanol/diethyl ether. Yield 89.4 % (0.45 g); m. p. 207-209 °C; $[\alpha]_D^{20}$ = -13.4° (c=1, methanol); $C_{42}H_{42}N_6O_{10}S_2Br_2$ (1014.8); calculated N 8.28; found N 8.34; calculated S 6.32; found S 6.36; calculated Br 15.75; found Br 15.93; R_{fC} = 0.70; R_{fE} = 0.40.

5. Determination of ATF-ase activity of rat liver mitochondria

The hypothesis that investigated compound possesses activity similar to the activity of dinitrophenol (DNF) was studied by determination of latent mitochondria ATF-ase. When applied in concentrations doubling the 2,4-dinitrophenol (DNF) concentration, compound **4** stimulates the hydrolysis of ATF-ase – Fig. 1.

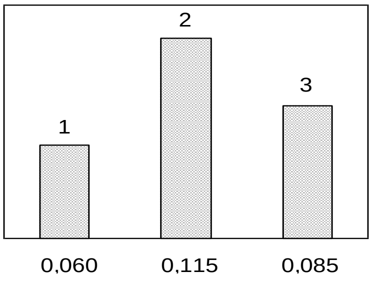


Figure 1. ATF-ase activity of rat liver mitochondria:
*1 – standard; 2 – in the presence of DNF (80 µg); 3 – in the presence of compound **4** (160 µg); reaction medium: 0.2 M saccharose, 0.02 M tris –HCl (pH 7.5), 50 mM KCl, 2mM ATF, mitochondria - 3.72 mg protein; final volume of 4 ml; room temperature.*
Numbers denote the rates of ATF-ase activity in µM of inorganic phosphate for 10 min.

Bearing in mind the results from similar experiments with other indandione modifiers, where physiological effect has not been registered, it could be supposed that the activity of compound **4** is due to its molecule as a whole. That is why the investigation of mitochondria processes in presence of the compound **4** and similar compounds represents an interesting scientific task.

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TREATMENT OF GOLD-BEARING SOLUTIONS BY CEMENTATIONS WITH METALLIC ZINC

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Pregnant solutions containing dissolved gold and silver after leaching of an oxide ore by means of amino acids of microbial origin and thiosulphate ions were treated by cementations with metallic zinc to precipitate the precious metals. The treatment was carried out in cementator with mechanical stirring under batch conditions. The optimum conditions with respect to the pulp density , particle size distribution of the zinc powder , pH ,Eh , temperature and residence time were established . The prior deaeration of the gold-bearing solutions to dissolved oxygen concentrations lower than 1 mg/l facilitated the cementation process by decreasing the zinc consumption. Under the optimum conditions , more than 98% of the gold was precipitated by the cementator from pregnant solutions containing from 0.5 to 5.0 mg/l gold .

INTRODUCTION

Zinc-dust cementation for gold and silver recovery, also well-known as the Merill-Crove process is the one of the most common contact – reducing processes in hydrometallurgy (*Nicol et al., 1979*). Cementation is the electrochemical precipitation of one metal by using another metal as a reducing agent. Zinc is element that has been studied for use as cementing agent for gold/silver pregnant solutions (*Tran et al., 1991*).

$$2Au(CN)^{2-} + Zn^{0} \rightarrow 2Au^{0} + Zn(CN)^{2}_{4}$$

$$2Au(CS(NH_2)_2)^{+}{}_{2} + Zn^{0} \rightarrow 2Au^{0} + 4CS(NH_2)_2 + Zn^{2+}$$

$$Au_2S_2O_3 \quad + \ Zn^{0} \rightarrow ZnS_2O_3 + 2Au^{0}$$

The treatment technologies of mineral row materials contains refractory gold ores , are an aggregate of chemical, biological, and physical processes. Gold –bearing solutions have been treated by means of different type methods. Thiosulphate leaching of gold is a proposed alternative to cyanide leaching (*Potter, 1980; Hsu et al., 1996 and McDougall et al., 1981*), in this technology are well-known that common used adsorption onto active carbon doesn't give a good results. Zinc–dust cementation are only one alternative method for the process.

Technological realizations of cementation process have to obtain and include following stages –clarification of production solution, deaeration, addition of zinc-dust, and extraction of gold-zinc dust. This succession has been determinate by factors effecting into cementation –concentration of Au/Ag in solution, preliminary deaeration, temperature, pH, stirring speed, addition of surface active agents (*Miller et al., 1990; Nguyen et al., 1997*).

Chemical reactors applying for cementation by using zinc powder possess different construction according to kind of zinc and way of reactor operation. In wide spread practice are applying following type reactors- fixed bed reactors, fluid bed reactors, drum type reactors with granular zinc , airlift reactors and stirring type reactors (*Ornelas et al., 1998*). On different examination are investigating to cement noble metals into Fe, Cu, and Al (*Zarraa, 1996; Guerra et al., 1999*).

This study focused on task to testing batch-scale reactors working with zinc powder on real pregnant solutions. Here are investigate how the factors of different suspension conditions, influence of paramilitary deaeration , resistant time affecting gold cementation performance using zinc dust. This data will be give information for scale up the cementation process.

EXPERIMENTAL

Investigation the process for treatment of gold –bearing solutions by cementation with metallic zinc was project and constructed batch –scale installation –fig.1.In this scheme in cementator are combined structures include reaction column where by mechanical stirring are suspended zinc powder and vertical settlings tank for accumulation a cementation product.

A mutual agreement on Fig.1 the way of operation in selected technological scheme is –production solution pumped into peristaltic pump 8 in deaeration column made of acrylic plastic with high 960mm and diameter 100 mm (volume 7,5 dm^3) During the operation are provide for level of liquid phase reach to 2/3 by volume of the column (volume 5 dm^3).

Table 1. Granulometric analyses of zinc dust

µm	**250**	**250 - 160**	**160 - 100**	**100 - 80**	**80 - 63**	**63 - 48.4**	**48.4 - 34.4**	**34.4 - 29.5**
%	5.45	10.42	1.76	25.78	5.09	16.12	0	8.09
µm	**29.5 - 25.5**	**25.5 - 19.3**	**19.3 -16.9**	**16.9 –12.9**	**12.9 -8.6**	**8.6 - 5.0**	**5.0 - 1.3**	**< 1.3**
%	7.06	3.65	4.22	4.17	2.68	3.19	1.65	0.67

Deaeration process was supply with oil vacuum pump “Edwards-4”. Peristaltic pump “Ismatech” delivery a smoothness control for output flow in range 0÷1,150 dm^3 /min. Automatic titration system “Metrom”-7 delivery optimal pH in cementation column reactor. Production solution inflow under bottom the reactor 5 around the thrust bearing and get in touch the zinc dust suspension. The agitator shaft is overall length about 720 mm. The type of agitation system is three –section frame mixer. After precipitation of zinc product in settlings tank, pure solution outflow into collector tank 11.Here is possible to heating reaction column by water shirt with supplying on water bath 8.

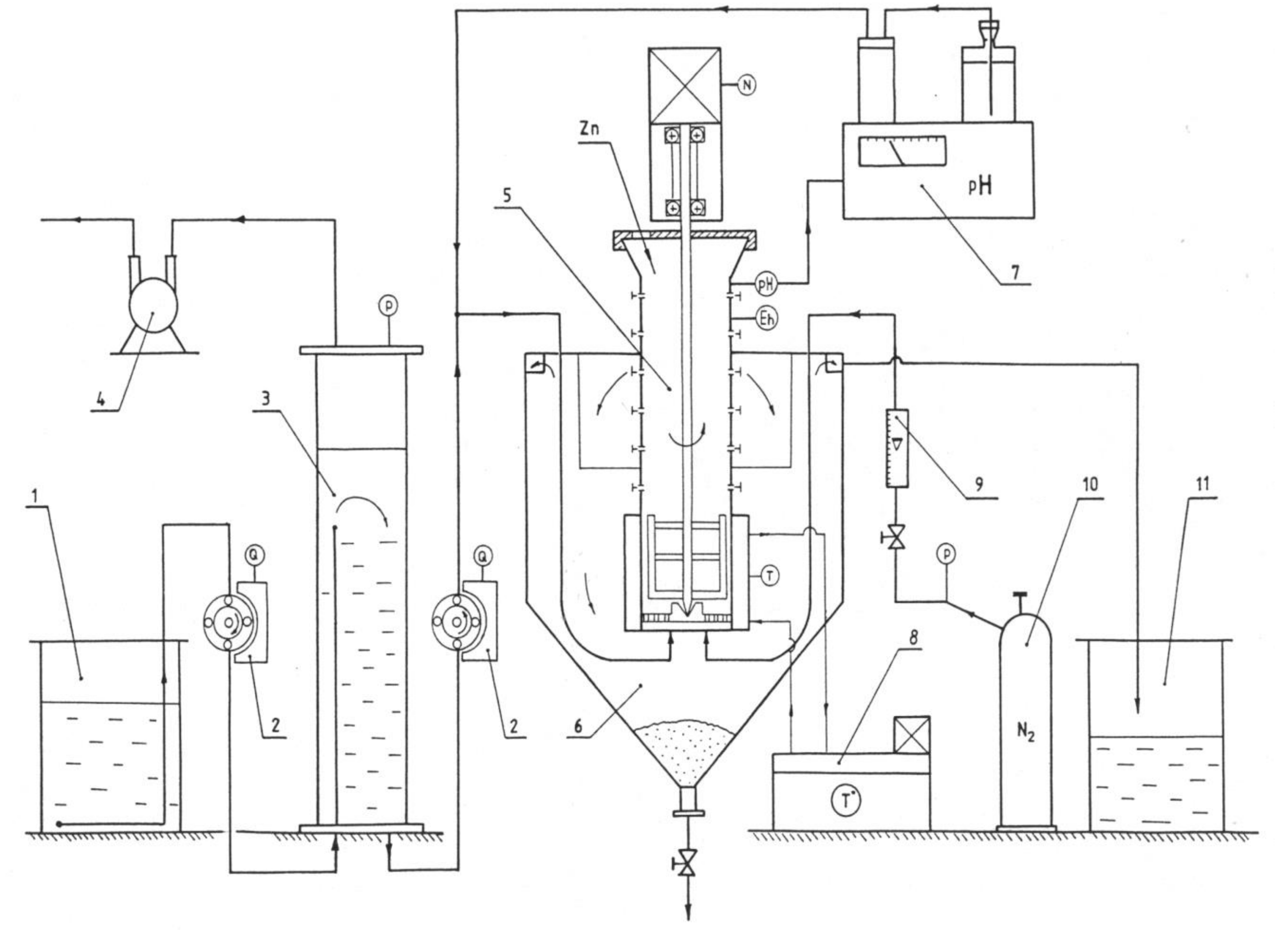

Figure 1. Batch-scale cementation installation

1 – Production solution tank, 2 – Peristaltic pump, 3 – Deaeration column , 4 – Vacuum pump, 5 – Reaction cementation column, 6 – Settlings tank, 7 – Automatic titration system, 8 – water bath, 9 - Rotameter, 10 – Nitrogen cylinder, 11 – Collector tank.

There is a possibility to feed the cementator with nitrogen from bottom into plastic distributor, each hole with range 50÷100 µm in diameter. Zinc dust with is use for the cementation process was made on “KCM”Ltd. Plovdiv with no regular granulometry, Table 1 was showed results on granulometric analyses. For establishment cementation conditions in batch scale installation was made a several group experiments.

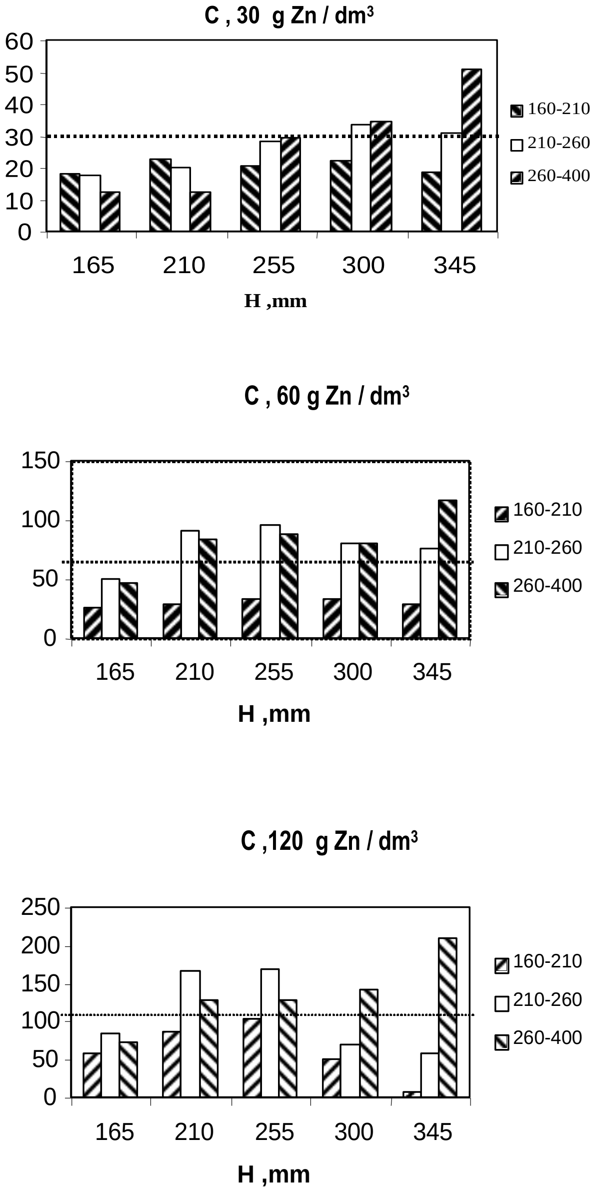

Figure 2. Dispersion of zinc dust suspension on different concentrations

The first series of experiments aim to establish suspension conditions in reactor column. This aim was needed to set conditions of suspending in reactor column volume onto three different concentration of zinc dust -3%,6%,12% . Besides the cementation conditions will be observe onto three different range of stirring (160-210 min^{-1}, 210-260 min^{-1} and 260-400 min^{-1}). Distribution of suspension was established by sampling into five column levels. The samples were filtering through “blue-line” filter paper, drying onto constant dry weight, and measured on analytical balance.

The second series of experiments aim to establish distribution on granulometry of zinc dust in reaction column. These experiments were demand for making to establish suitable conditions on suspending in reactor and sampling of three different points onto column. The granulometry of these samples were compared with starting granulometry of zinc dust.

Other main aim is setting of deaeration condition on production solution inflow to the cementation reactor. This aim have exact for measuring of dissolved oxygen onto different vacuum conditions, temperature influence, and stirring speed influence. For measuring dissolved oxygen was used polarographic sensor “Ingold”.

The last experiments are connected with establishment of precipitation speed by the three different concentration s of zinc powder (3, 6, 12g/dm³) in suspension. The test was made in measure cylinder with 1dm³ volumes and visual reading of clear layer. The part of this experiment is testing a work of settlings tank in steady-state conditions. The mass –input flow onto settlings tank have to be less than resistant time for gold bearing solution.

RESULTS AND DISCUSSION

The distribution of zinc particles were studied of three different concentration of zinc dust on varied rotating speed. This shown on Fig.2 where distribution of zinc powder are steadiness on rotation speed between 210-260 min^{-1} and have a large deviation from average concentration in ranges 260-400 min^{-1} and 160-210 min^{-1}.

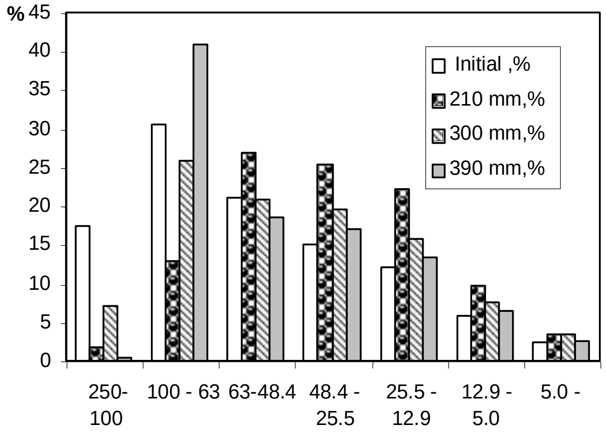

Figure 3. Distribution of classes zinc powder on column high

Distribution of different zinc dust size particles was showed on Fig.3. The reduced results on zinc particles distribution in three different high (210,300,390mm) was obtained into stirring speed 260 min^{-1}. The concentration of zinc dust in this experiment was between 6 -12% and supplying the constant level of liquid in reactor column H = 382 mm (volume 1dm³).

The comparison between zinc dust granulometry of three different high of reaction column and initial zinc dust shown on Table1 ,be able to made a conclusion so , relative particle size classes between + 63 and -100 μm (over 30% in beginning piratical size) was increase on the high column. The coarse-grained zinc dust between +100 and -250μm, was decrease onto high to column. The fine-grained zinc dust particles between -63 and +1,3μm was distributed relatively steadiness in the middle and top of the reaction column. This results show that the zinc particles with most specific surface are present in range 210-345 mm on the column high.

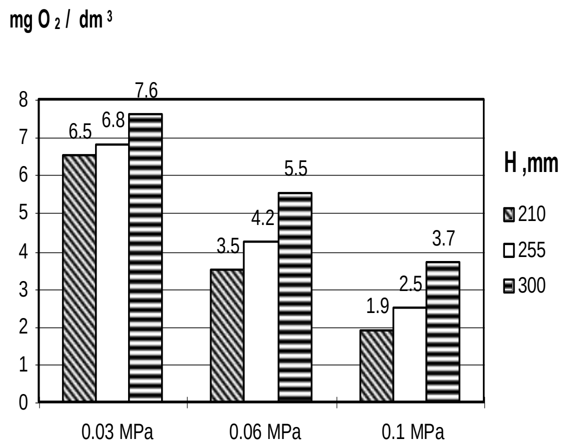

Figure 4. Dynamic of dissolved oxygen on different column high

On other group tests were measured dissolved oxygen content in reaction column with different conditions of deaeration. The input of production solution in all variants is consisting about 0,5dm^3/min. On fig.4 are showed dissolved oxygen concentrations on the column high with three different values of vacuum (0,03 MPa, 0,06 MPa, and 0,1 MPa). The temperature was 18°C and speed of mechanical stirring 210min^{-1}. The resistant time on production solution in deaeration column was 10min (working volume 5 dm^3).

The content of dissolved oxygen on five different variants of deaeration is showed in table 2. The best results were obtained in variants with nitrogen bottom blowing and vacuum deaeration on 0,1MPa with temperature 35°C.

Table 2 Dissolved oxygen content on different deaeration condition

№	Deaeration condition	C, O_2 mg/dm^3
1	0,1 MPa with mixing on 210 min^{-1}, 18 ^{0}C, input flow -0,5 dm^3/min	4,17
2	0,1 MPa without mixing, 18 ^{0}C, input flow - 0,5 dm^3/min	3,96
3	0,1 MPa with mixing on 210 min^{-1}, 35 ^{0}C, , input flow - 0,5 dm^3/min	1,72
4	Deaeration with N_2, 18 ^{0}C, input flow - 2 dm^3/min with mixing on 210 min^{-1}	0,93
5	Deaeration with N_2, 18 ^{0}C, input flow- 2 dm^3/min	0,72

The established dynamics of zinc dust precipitation of three different concentration of suspension are showed on Fig.5. According to obtained results was established over 95% precipitation of zinc dust for time of 300 s – 1,2 mm/s speed of settlings. In real time working the column reaction and settlings tank was established for maximally concentration of zinc dust of 22 s (input-flow 1,15 dm^3/min) in settlings tank was holed back all of zinc particles without size lower than 5 µm.

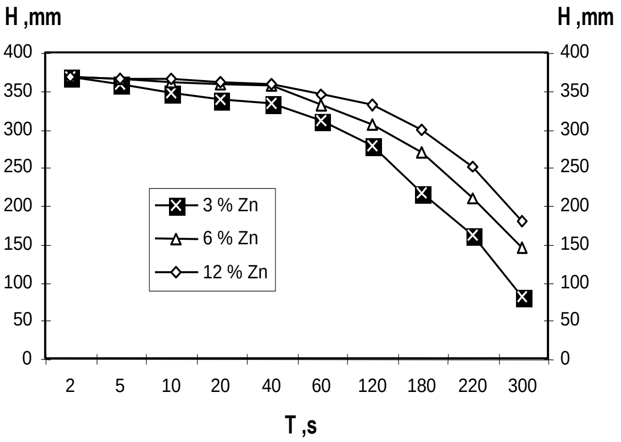

Figure 5. Precipitation diagram of different content on zinc powder

CONCLUSIONS

1. The batch scale cementator was projected and constructed for pregnant solutions containing gold and silver with 1 dm^3 working volume and 450mm high. The basic principle of work in this chemical reactor is a suspending the zinc dust with continuous precipitation in settlings tank.
2. The preparing technological scheme allows controlling cementation process with change of resistant time and, condition of preliminary deaeration.
3. The condition of suspending in cementator column was established in range 160-210 min^{-1}, 210-260min^{-1} and 260-400min^{-1}. The optimal stirring speed in cementator was obtained between 210-260min^{-1},in this conditions concentration of zinc dust change around average on the initial zinc dust material. On stirring speed between 160-210min^{-1} and 260-400min^{-1} was established no regular distribution of zinc particles.
4. Distribution of different classes zinc particles has a large variety. The coarse-grained zinc particles (between –250+160µm) was located in bottom part of column (under 165mm), the basic classes (range +63-100µm)was relatively steadiness distribute in middle part of column (165-300mm) and the fine –grained classes in range –63+1.3µm distributed steadiness in all volume of reactor column.
5. The optimal conditions of deaeration were obtained with value of vacuum over 0,1MPa in deaeration column and under the nitrogen bottom blowing in rector column. The obtained contain of dissolved oxygen in reactor column was under 1 mg/dm^3.
6. Real speed of settlings was measured on 1,2mm/s. Efficiently precipitation of zinc dust was obtain on steady-state type of workof settlings tank in maximum input-flow 1,15dm^3/min
7. Effective way of working of cementator necessary the classes of zinc dust over 160 µm and classes fewer than 5µm have to be removed.

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THE EFFECT OF SOME ESSENTIAL ENVIRONMENTAL FACTORS ON THE MICROBIAL DISSIMILATORY SULPHATE REDUCTION

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ABSTRACT

The effect of some heavy metals (manganese, iron, uranium) and arsenic on microbial dissimilatory sulphate reduction was studied under laboratory conditions. It was found that the sulphate-reducing bacteria were able to grow at concentrations of Mn^{2+}, As^{5+} and U^{6+} as high as 50 mg/l but the rate of sulphate reduction was decreased by about 15 – 55 % in the different experiments. The rate of sulphate reduction, however, was increased in the presence of high concentration of Fe^{2+} (in the range of 0,5 – 2,0 g/l). The sulphate-reducing bacteria efficiently precipitated the above-mentioned agents, as well as the ferrous iron. The microbial sulphate reduction was carried out at pH values higher that 4,9. The bacteria were able to increase the pH of the solutions to neutral or slightly alkaline level by the hydrocarbonate ions generated during the dissimilatory sulphate reduction. In the presence of both nitrate and sulphate ions, the microbial dissimilatory nitrate reduction was always the prevalent process. The concentrations of nitrate as high as 500 mg/l inhibited strongly the rate of sulphate reduction.

INTRODUCTION

Bacterial sulphate reduction has been indentified as a significant mechanism for removing contaminant heavy metals, toxic and radioactive elements from coal and metal-mine drainage (*Gazea et al., 1995; James et al., 1995*). Sulphate-reducing bacteria oxidaze simple organic compounds (such as lactate, acetate, butirate and another products of fermentations) with sulphate under anaerobic conditions, and thereby generate hydrogen sulphide and bicarbonate ions:

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- , \qquad (1)$$

where CH_2O represent the organic matter.

The produced hydrogen sulphide reacts with dissolved metals to form insoluble metal sulphides that subsequently precipitate according to the reaction:

$$M^{2+} + H_2S \rightarrow MS + 2H^+, \qquad (2)$$

where M includes metals such as Fe, Cu, Zn, Ni, Cd.

The hydrogen sulphide can chemically reduce As^{5+} to As^{3+}, resulting in the formation of minerals such as orpiment (As_2S_3) and/or an arsenic-iron sulphide solid phase (*Ronalds et al., 2000*). Some of sulphate-reducing bacteria formed orpiment in culture by mediating biological reduction of As^{5+} followed by the reduction of sulphate during growth.

Certain sulphate-reducing bacteria can enzymatically reduce also highly soluble hexavalent uranium to the sparingly soluble tetravalent form U^{4+}. Reduced uranium then abiotically precipitates as uraninite (UO_2) (*Ganesh et al., 1997*). The reduction of U^{6+} can carried out by a bacterial produced hydrogen sulphide in the presence of high concentrations of both U and sulphide and/or elevated temperatures (*Barnes et al., 1993*) according to the following reaction:

$$4[UO_2(CO_3)_3]^{4-} + HS^- + 15H^+ \rightarrow 4UO_2 + SO_4^{2-} + 12CO_2 + 8H_2O \qquad (3)$$

Although at low pH the growth and activity of sulphate-reducing bacteria are inhibited, their activity results in pH increments in their immediate environment, allowing their viability in the solid organic substrate, independing of drainage extremely acidic waters. Bicarbonate ions formed during sulphate reduction react with protons to form CO_2 and water and remote acidity from solutions as CO_2 gas:

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \qquad (4)$$

The bicarbonate ions buffer the waters pH to a particular value, typically in the range of 6 – 7 (*Darryl et al., 1992*). Raising the pH of acidic water will couse some metals to hydrolyze and precipitate as insoluble hydroxides or oxides; for example,

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \qquad (5)$$

The process of microbial sulphate reduction has been found a large application in treatment of acid mine waters by SRB-bioreactors, reactive barriers and passive systems. The pollutants are retained in strict anaerobic conditions by used of waste organic mater (a mixture of cow, horse and sheep manure, spent mushroom compost and sawdust) or chip row materials (acetate, ethanol, est.) as sources of carbon and energy by sulphate-reducing bacteria.

The purpose of this study was to evaluate the effect of heavy metals Mn, U, Fe and arsenic on the growth and activity of sulphate-reducing bacteria; the efficiency of precipitation of above-mentioned toxic elements; to find the lowest pH value, in which the bacterial sulphate-reduction is possible; to evaluate the effect of high concentrations nitrate on the rate of the process.

MATERIALS AND METHODS

Batch experiments were carried out in 500 ml glasses bottles containing organic substrates and nutrient solution. Simple organic compounds (Na-lactate, Na-acetate, Na-propionate, glycerol) or solid organic matter (cow manure, spent mushroom compost and sawdust) were used as organic substrates. The bottles were inoculated with mixed enrichment culture of sulphate-reducing bacteria belong to p.Desulfotomaculum, p.Desulfovibrio and p.Desulfobacter.

The effect of U, As, Mn and Fe on dissimilatory sulphate reduction

The nutrient solution used in these tests contained (in g/l): Na_2SO_4, 3.0; KH_2PO_4, 0.2; $(NH_4)_2SO_4$, 0.5; KCl, 0.5; $CaCl_2.2H_2O$, 0.15; $MgSO_4.7H_2O$, 0.2; yeast extract, 0,1; trace element solution – 1 ml. Na-lactate, Na-acetate, Na-propionate, and glycerol (3:1:1:1) – 6 g/l were used as source of carbon and energy for sulphate-reducing bacteria. Uranium (in the form of uranyl acetate), arsenic ($Na_3AsO_4.7H_2O$) and manganese ($MnSO_4.H_2O$) were added separately to the bottles reach to final concentration in the range of 5 to 50 mg/l for the different experiments. Iron ($FeSO_4.7H_2O$) was added in final concentration 50 – 3000 mg/l. pH of inoculated solutions was adjusted to 6,5. The oxygen diffusion was eliminated by 1 cm layer sterile liquid paraffin. The bottles were incubated at 35 ^{o}C.

The effect of pH on dissimilatory sulphate reduction

Sulphate-reducing bacteria were grown in a medium with Na-lactate – 6 g/l as a source of carbon and energy. The nutrient solution had the previously mentioned composition. The initial pH of the inoculated solutions was adjusted to levels varying from 2.0 to 7.0 by adding HCl. The bottles were incubated at 30 ^{o}C.

The effect of high concentration nitrate on dissimilatory sulphate reduction

Three different kind of medium were used for growth of sulphate-reducing bacteria, depending of source of organic carbon: I - Na-lactate – 10.0 g/l: II – Na – acetate - 10 g/l; III – solid organic matter (mix of cow manure, spent mushroom compost and sawdust) – 100 g/l. The nutrient solution used in these tests contained (in g/l) Na_2SO_4 – 3.0; KH_2PO_4 – 0.2; KNO_3 – 4.9; $(NH_4)_2SO_4$ – 0.5; KCl – 0.5; $MgSO_4.7H_2O$ – 0.1; $FeSO_4.7H_2O$ – 0.1. The concentration of sulphate and nitrate were accordingly 2,5 and 3,0 g/l. pH of solutions was adjusted to 7,0. The bottles were inoculated with mixed enrichment culture of sulphate-reducing bacteria and other metabolically interdependent microorganisms. The bacteria were incubated at 30 ^{o}C.

Analytical techniques

The dissolved metal concentrations were determined by ICP spectrophotometry. Uranium concentration was measured photometrically using the arsenazo III reagent. Sulphate and nitrate concentrations were determined photometrically. The content of soluble organic compounds was determined by measuring its oxidativity (by $KMnO_4$).

The identification and enumeration of the microorganisms inhabiting the bottles were carried out by standart microbiological methods.

RESULTS AND DISCUTION

The data about maximum and average rate of the bacterial sulphate-reduction and inhibition of the process (in %) by used concentration U, As and Mn are represented at table 1. Change of sulphate concentration in presence of As, U and Mn, accordingly 5,15, 25 and 50 mg/l and control (without toxic elements) are represented at figure 1. The maximum rate of sulphate reduction was calculated during logarithmic phase (up to 10 day) of bacterial growth for all tests, whereas the average rate – for overall cultivation (30 days).

The concentrations of U, As and Mn, which were typically for real drainage waters have been no essential reducing influence on the rate of the dissimilatory sulphate reduction.

The concentrations of uranium, below 10 mg/l and manganese – below 15 mg/l have brought to decrease of the rate of sulphate reduction in range 7 to 25% for different experiments. The abovementioned toxic elements have been proved much more negative effect (44 – 52%) in higher concentration – 50 mg/l.

Table 1. The effect of U, As and Mn in different concentration on dissimilatory sulphate reduction

Element	Contents, mg/l	Maximum rate, mg SO_4^{2-}/l.d	Average rate, mg SO_4^{2-}/l.d	Iinhibition, %
Control	0	98,0	74.4	
U	5	85,0	69.5	7– 14
	10	75.3	62.2	17 – 24
	15	66.4	57.9	22 – 32
	25	57,6	46,5	38 – 42
	50	47,3	40,6	46 – 52
As	5	81.2	64.2	14 – 17
	10	73.7	57.8	25 – 32
	15	69.8	48.4	29 – 35
	25	60,5	41,6	41 – 45
	50	51,0	31,7	48 – 57
Mn	5	89.2	69.2	7 – 9
	10	82.0	66.8	10 – 16
	15	74.0	60.3	19 – 25
	25	63,7	54,6	26 – 35
	50	52,3	41,7	44 - 47

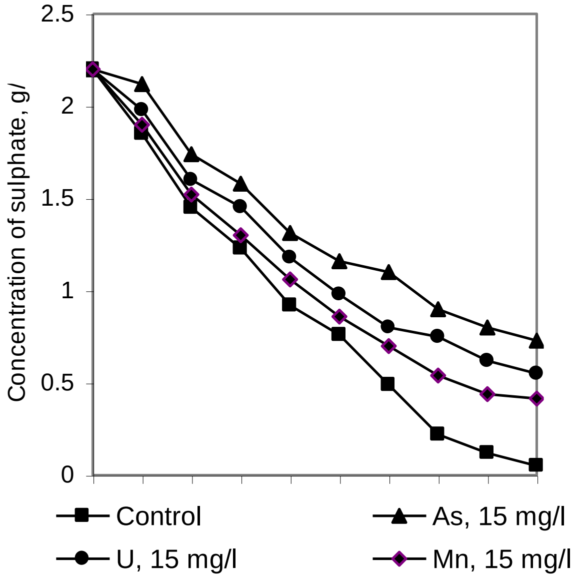

Figure 1. The effect on U, As and Mn, 15 mg/l on dissimilative sulphate reduction

It was found that arsenate ions have most toxic effect on sulphate reducing bacteria. Even low concentration of As^{5+} - 5 – 10 mg/l has bought to abatement of the process rate with 14 – 32%, while in presence of 50 mg As/l the rate of sulphate reduction has fallen more than twice.

The cat ions of arsenic and manganese also had negative effect on growth of sulphate reducing bacteria. It was counted maximum number of microorganisms – 10^4 – 10^6 cells/ml at stationary phase, while their number in control was 10^7 cell/ml. It wasn't found influence of studied concentrations uranium on number of sulphate reducing bacteria independent of measured lower rate of sulphate reduction.

The concentrations of dissolved toxic elements were decrease by carry out of dissimilatory sulphate reduction. Sulphate reducing bacteria enzimatically reduced highly soluble hexavalent uranium, wherefore it was found efficiently precipitation (98 – 99%) of radioactive element as far back as 20 day. The cat ionic analyses showed gradual decrease of concentrations of arsenic and manganese during the experiments. Lower concentration of Mn^{2+} measured at the end of test probably to be due to processes such as biosorption and bioaccumulation by present micro flora, as well as by formation of $MnCO_3$. Reducing conditions in medium didn't allow oxidation of Mn^{2+} and formation of insoluble MnO_2. Major part of arsenic was removed by means of both precipitation of As_2S_3 and As_2S_5, and sorption by microbial biomass. It was found 60 – 80% removal of manganese at the end of different experiments.

The concentrations of ferrous ions in range 0,5 to 2 g/l were raised the rate of sulphate reduction in difference of U, Mn and As, because Fe^{2+} consumed microbial generated H_2S, which is toxic for sulphate reducing bacteria in high concentration. It was measured highest rate of the process - 118 mg SO_4^{2-}/l.d in the presence of 1,5 g Fe/l at first to 21 day of cultivation. Subsequently it was found the lack of change of sulphate concentration by reason of exhausted source of carbon and energy for sulphate reducing bacteria (figure 2). Concentration of ferrous ions about 3 g/l lead to materially reduce of the microbial sulphate reduction (42%) because of partial oxidized of Fe^{2+}, succeeded of hydrolyze and precipitation of $Fe(OH)_3$, as well as increased of Eh of medium to unfavourable value for carry out of the process.

It was found efficiently precipitation of iron in form of FeS (96,5 – 99%), when initial concentration of ferrous ions was 0,5 – 1,5 g/l.

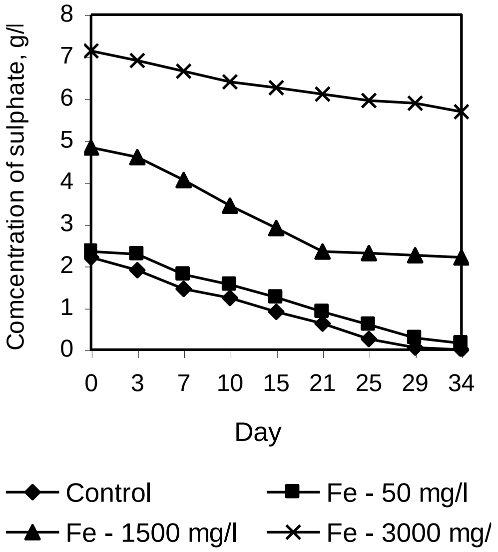

Figure 2. The effect of Fe^{2+} on dissimilative microbial sulphate reduction.

Contents of 3 g Fe/l decreased both the rate of microbial sulphate reduction and growth of sulphate reducing bacteria – their number in stationary phase was only 10^4 cells/ml. Amount of microbial generated H_2S was not enough to react with all quantity ferrous ions – only 39% of iron was precipitated at the end of experiment.

The effect of pH on dissimilative microbial sulphate-reduction

It was observed neutralization of medium independently of initial values of pH in all experiments.

The change of acidity at time was due to both of microbial sulphate-reduction, related with producing of bicarbonate ions (when pH is neutral or slight acid) and amonification of rich of proteins yeast extract, involved in medium of anaerobic microflora.

The highest rate of dissimilative sulphate-reduction - 94 mg SO_4^{2-}/l.d was measured to 17 day from beginning of experiment in case of initial pH 7(Figure 4). The rate of sulphate-reduction on slightly acid level was in range 50 to 80 mg SO_4^{2-}/l.d.

Sulphate reducing bacteria had activity after increasing pH of medium above 4,9 – 5,1 for different experiments. It was found very low rate of sulfate-reduction when initial pH of solutions were strongly acid. The process was began after 24 day, when the conditions for growth of sulphate reducing bacteria was unfavorable because a part of soluble organic matter was used of remaining anaerobic heterotrophic microflora.

It was enumerated highest number of sulphate reducing bacteria at stationary phase – 10^7 – 10^8 cells/ml in cases of initial pH values from 5.0 to 7.0.Their number was in range 10^2 – 10^3 cells/ml for the rest of experiments.

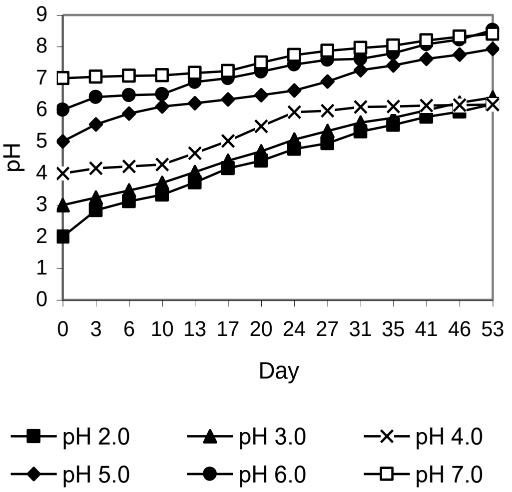

Figure 3. Dynamic of pH of medium during microbial sulphate reduction

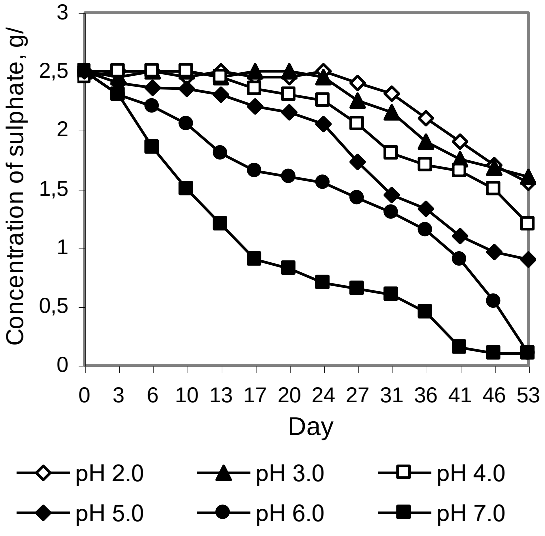

Figure 4. The effect of pH on dissimilative microbial sulphate reduction

The effect of high concentration of nitrate on dissimilatory sulphate reduction

It was found dominance of reduction of nitrate at concomitant carried out of sulphate-reduction and denitrification. Microbial sulphate-reduction was began after decreased nitrate concentration below 0,5 g/l for all tests (Figure 5).The type of used sources of carbon and energy influenced on the rate of both processes. It was measured highest rate of nitrate reduction - 400 mg NO_3^-/l.d at the beginning of experiment with used of acetate

Maximum rate of sulphate-reduction - 80 mg SO_4^{2-}/l.d was estimated with used of waste organic matter (mix of cow manure, spent mushroom compost and sawdust) as source of carbon and energy. The sulphate concentration was increased to 4,2 g/l at beginning of experiment because dissolution of gypsum, which have been added in mushroom compost preparation.

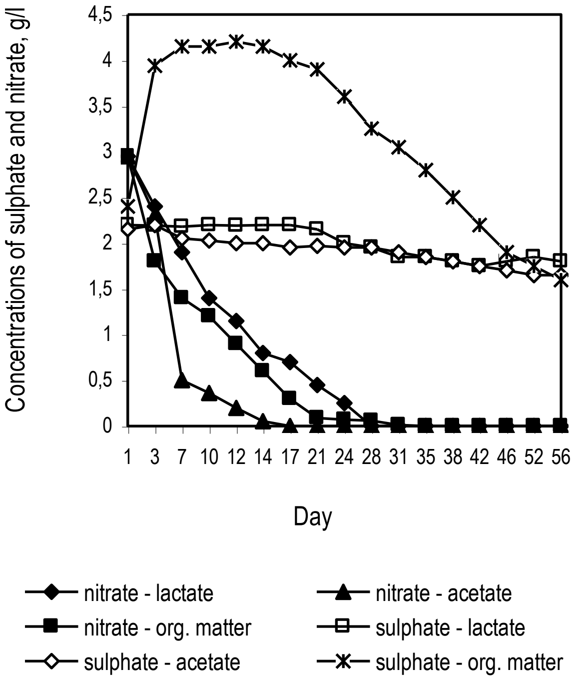

Figure 5. Dynamic of the concentrations of sulphate and nitrate at concomitant carried out of sulphate and nitrate reduction.

Insoluble biopolymers (cellulose, hemicellulose and etc.) in anaerobic conditions were slowly digested by complex of metaboliticaly related microorganisms. As a result of this the concentrations of soluble organic acids and alcohols (donors of electrons for sulphate reducing bacteria) were high. The microbial sulphate reduction was limited for remaining experiments as result of exhausted of assimilated organic during the process of genitrification, as well as increased of pH above 8,5 – 9,0.The microflora date revealed dynamics in population density involved in complex microbial cenoses. At the beginning the denitrified bacteria were dominant (their number reached 10^6 – 10^7 cells/ml at 20 day). The sulphate reducing bacteria number started to increase after 30 day and reach 10^5 – 10^7 cells/ml. It was found a large number of cellulolytic, fermenting bacteria and other anaerobic microorganisms in the liquid phase of waste organic matter.

CONCLUSIONS

The sulphate reducing bacteria showed high resistance to ionic forms of U, Mn and As. The process carried out with rate, which enable generation of high concentrations H_2S even at concentration of toxic elements 50 mg/l, which are much then real of drainage waters of mining areas. The strong reducing agent has precipitated most of heavy metals as insoluble sulfides. The concentration of hexavalent uranium in range 5 to 50 mg/l has efficiently removed (98 – 99%) as insoluble uraninite by microbial sulphate reduction. The presence of ferrous ions in range 40 – 2 000 mg/l stimulated both the process and its efficiency.

The bicarbonate ions generated by activity of sulphate-reducing bacteria lead to increase of pH in surround environment. After forming of these microzones with neutral pH is possible to outgoing of the process even in strong acid drainage waters and precipitation of some pollutants in the form as hydroxides.

The process of microbial sulphate reduction has been inhibited completely in presence of nitrates in concentration above 0.5 g/ l. This limitation has been important at the biological treatment of mixed acid drainage waters with sewage/ industrial waters, which contain high concentration of nitrates.

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OBSERVATION AND STUDY OF POLLUTION IN THE REGION OF THE "LEAD-ZINC FACTORY" - KARDZALI

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SUMMARY

A detailed geological and hydrogeological characterization of the area of the examined stage in the region of the " Lead-zinc factory " - Kardzali is done.

The study which is performed shows that in accordance with the utmost allowable concentration the ground layers with thickness up to 1 m are high polluted with Pb, Cu,Zn,Cd,Fe,Mn and As ions.

In depth approximately up to 2,5 m the concentration of these substances decreases several times. Below this depth, where is the level of ground waters, pollution above the values of the utmost allowable concentration with water soluble ions of Pb, Cu, Zn, Cd is established.

The underground waters are from the quaternary horizon of the tertiary depositions and they are semi-pressure, fissure and with shallow circulation. They are distinguished for predominating of sulphate and chloride ions, with high content of Na, K ions and ions of metals which are a result of the main activity of the " Lead-zinc factory", with several times exceeding of the average concentrations compared to the regional background.

The reasons for the established pollutants are shown and a programme for their limitation and elimination is proposed.

INTRODUCTION

The high industrialization of the economy inevitably leads to global pollution of the environment all around the world as well as in the Republic of Bulgaria.The action of toxic and poisonous substances appears especially clear in the regions with developed chemical or metallurgic productions.

The purpose of the task is to be gathered additional information about damages on the environment as a result of the influence of the lead-zinc production of the " Lead-zinc factory"-Joint-stock company, Kardzali, to be given an assessment for the soil and hydrogeological conditions in order to be determined the presence and quantity of the toxic components and their spreading in vertical and horizontal direction, to be planned measures for limitation and non-admission of additional pollution. In order to realize this purpose, on the area of the project additional works for gathering information about the ecological situation of the ground foundation, hydrogeological studies and content of elements which can be controlled in the soil and waters are performed.

GEOLOGICAL AND HYDROGEOLOGICAL CONDITIONS IN THE REGION OF THE "LEAD-ZINC FACTORY" - KARDZALI

The geological and hydrogeological research works of the examined stage are performed with autodrill URB 2A-2 by the rotary method, in dry conditions, in short raids (0,5 m), core drilling, with diameter ϕ=146 mm. Nineteen motor test holes with total footage of 169,7 m are made.

In order to fix the migration of the main pollutants in depth, nineteen piezometers (fig. 1) with total footage of 169,7 m are constructed. After the designed depth is reached, the trunk of the drillhole is widened to 190,5 mm and this is followed by assembling of PVC pipes and filters with ϕ=110 mm.

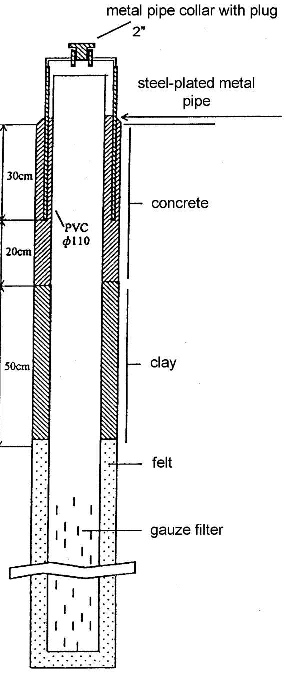

Figure 1. Construction of piezometer

The region is plain terrain with slight slant from south to northeast and in geological respect it is characterized with development of tertiary and quaternary depositions. The tertiary depositions are presented by paleogenic limestones - white to beige-pink in colour, very dense. They are, in fact, the pad on which sandy-marly depositions occur. They are presented mainly by greenish-blue zeolites with thickness of 0,2-0,3 m which are covered with bentonite clay on the south side of the factory. The yellow bentonite clay with solid-plastic to solid consistence is with thickness of the layer up to 1,5 m. In some spots, the total thickness of the depositions, which cover the limestones, reaches 20 m. The quaternary depositions occur over the paleogenic marly depositions and are presented by gravel wash and deluvial wash. The alluvial layer, which is defined by medium to pebble stones with sandy-clayey to clayey-sandy filler, is with thickness of 1,5-5,0 m.

The deluvial depositions are presented mainly by alternation of silty and sandy clays with limy inclusions and medium to coarse sands, in some spots with rubbles. The thickness of this layer reaches 2,8-6,0 m. The total thickness of alluvial and deluvial depositions reaches up to 10 m.

According to the hydrogeological dividing of Bulgaria into districts, the examined stage is situated in subdistrict East Rhodope Mountains, region Perperek-Efrem and from geological point of view it is situated in inner structural trough with sedimental and tuffed materials with limited occurrence of volcanites and with limited plenty of water. Here the underground waters are mainly fissure, with shallow circulation and in some sections they are pressure. They are fresh, with qualities in accordance with the Bulgarian State Standard - Drinkable water. In the region of Kardzali as well as in the examined district they are protected against penetrating of surface pollutants by a thick layer of bentonite clays as well as by natural filters of zeolite tuffs situated under them.

The fluvial terrace in the lower course of the Arda river is formed by alluvial and deluvial depositions, presented by clays, rubbles with different size with clayey filler and sands, which reach thickness up to 10 m. Here a non-pressured water bearing horizon is formed which receives surface waters which are in direct contact with the area of the factory.

DYNAMICS OF THE UNDERGROUND WATERS IN THE EXAMINED REGION

Since the pollution of the underground waters in the tertiary depositions is limited by the bentonite clays and zeolites in them, only the quaternary water bearing horizon is examined. The underground waters in this horizon are semi-pressure because of the geological structure of the ground foundation. In a diagram it may be shown as diploblasic - first layer in the bottom, strongly permeable (gravels and sands) and second one, above it, with low water permeability (sandy clays). It is clear from the drillholes that the water level is in the second layer. The quaternary water bearing horizon, isolated from the occured zones with plenty of water under it, with the help of water tight bentonite clays, reaches thickness up to 10 m.

By the constructed hydrogeological profiles of the examined stage, the conductivity of the layer is determined in the interval 14,8-31,5 m^2 /d. Its average value for the region is approximately 22 m^2 /d which characterizes it as a region without plenty of water in accordance with the gradation in drawing up the hydrogeological maps M 1: 25 000.

The single filtration cost of the underground waters is q=0,126 - 0,214 m^3 /d and the total filtration cost of the underflow, which crossed the area of the factory (with average length of 1150 m) is approximately 190 m^3 /d.

ESTABLISHED POLLUTION IN THE REGION OF THE EXAMINED STAGE

On the basis of the performed investigations is given an assessment of the pollution of the ground foundation (with the different lithological varieties) of the examined region from the area of the “ Lead-zinc factory” - Kardzali and the areas which border on it. It is found that the soils in the region of Kardzali are polluted and are called “ very high polluted” (in accordance with the content of the toxic elements, the assessment is with 5 degrees - unsoiled, light polluted, medium polluted, high polluted and very high polluted soils) in accordance with the content of Pb, Cu, Zn, Cd, Fe, Mn, As.

Our investigations aim to be found to which depth these toxic substances are in the ground layers. That’s why 42 ground samples of the different lithological varieties of the quaternary are taken and investigated. The results of the laboratory analyses are presented in table 1 and table 2.

The obtained results permit to be said that the surface layers to depth of 1 m from the area of the factory are polluted with Pb, Cu, Zn, Cd. Their content is many times above the allowable content. In depth between 1m and 2,5 m the concentration of the ions of heavy metals decreases several times because of the sorption properties of the soil. Below 2,5 m, in the zone where is the fixed level of the ground waters, there is active movement of the water soluble ions of heavy metals and in this zone is found pollution with Pb, Cu, Zn, Cd above the allowable rate. The reason is the depots for waste and warehouses for raw materials on this area.

In the additional performed investigations of the underground waters and migration of the pollutants are presented other 50 components and indicators too. The established anions and cations as well as organic substances are presented in table 3 and table 4.

In the region of feeding the underground waters there isn’t ore and non-metalliferous mineralization which could change the geochemical background. That’s why the natural factors for the formation of these waters in the examined region are the reason for predominating of hydrocarbonaceous and calcium ions, neutral and light alkaline environment, low content of biogenic components and ions of heavy metals as well as nitric-oxygenous composition. All examined waters from the main stage (including those from the region of the purifying station) are distinguished for predominating of sulphate and chloride ions, high concentrations of Na and K, ions of heavy metals as a result of the main activity of the “ Lead-zinc factory” or from the harmfull admixtures in the raw materials and waste as well as phenols, petroleum products and nitric compounds. The degree of exceeding of the average concentrations in relation to the regional background is several times higher - table 5. Only about few situations it may be said that the reason of this predominating is due to technogenic pollution and pollution of life.

Table 3. Content of ions, petroleum products and volatile phenol in waters, mg/dm^3.

No of test sample	pH	NO_2^-	NO_3^-	NH_4^+	HPO_4^{2+}	volatile phenol	Con-tent
C1	7,2	0,99	7	0,120	0,6		
C2	7,0						
C2-A	6,7						
C3	6,7						
C4	5,7					0,955	1,3
C5	6,8					0,299	0,9
C6	7,4						
C7	7,3					0,287	1,1
C8	7,2						
C9	7,1	0,12	0	0,140	4,4		
C10	7,5	0,07	2	0,004	0,8		
C11	7,3						
C12	7,4						
C13	7,2	5,50	52	0,540	1,4	0,259	1,2
C14	7,1						
C1A	7,4						
C1B	7,1	0,07	2	0,270	1,2	1,142	2,6
C2B	7,2						
C3B	7,3	0,29	16	0,180	2,2		

Table 5. Degree of exceeding of the average contents of ions in underground waters in the region of the “ Lead-zinc factory” - Kardzali towards the regional background

component	degree of exceeding (times)
SO_4^{2-}	6,6
Cl^-	8,1
Mg^{2+}	2,3
Ca^{2+}	6,6
Na^+	6,4
K^+	7,5
Cu^{2+}	283,0
Mn^{2+}	146,0
Pb^{2+}	81,0
As^{3+}	4,3
Ni^{2+}	105,0
Al^{3+}	51,0
Fe^{2+}	144,0
Zn^{2+}	370,0

On the basis of this assessment for the damages on the environment from the activity of the “ Lead-zinc factory” - Kardzali in the past and nowadays, measures are planned for their liquidation and limitation for the future which are presented in a special programme in another project.

CONCLUSION

On the basis of performed investigations in the region of the “ Lead-zinc factory” - Kardzali is found that the ground foundation and underground waters are polluted above the utmost allowable concentrations in relation to heavy metals and other components.

The main reason for the pollution in the past is the outdated production process and the unprotected depots with waste and warehouses with raw materials.

In order to eliminate the damages from the pollution on the environment in the region of the “ Lead-zinc factory” - Kardzali is recommended to be realized the measures and taken decisions which are pointed out in the “ Programme for elimination the dangerous influence over the underground waters and ground foundation from the production activity of the “ Lead-zinc factory” - Kardzali”.

It is proposed the results of performed measurements to be bounded with the data for the technological processes and actualized ruler’s decisions. That’s how the monitoring of the underground waters will achieve its purpose.

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Table 1. Content of heavy metals and metalloids in soil test samples from the “Lead-zinc factory” - Kardzali, mg/kg

Drillhole test sample No	depth (m)	PH	As	Cd	Cu	Pb	Zn
1	2	3	4	5	6	7	8
1-1	0,2-0,4	7,27	13	25,600	142	298	1596
1-2	1,8-2,0	7,25	2	0,200	11	51	216
2-5	0,5-0,7	7,16	102	117,400	1996	11858	28196
2-6	3,1-3,2	6,80	1	3,373	108	1408	1162
3-9	0,8-1,0	6,40	352	1275,250	7604	15144	470
3-10	2,2-2,4	6,98	10	10,119	50	90	10076
4-13	0,4-0,6	6,13	427	1468,056	24800	45828	125194
4-14	2,0-2,2	6,75	3	51,992	66	112	9896
5-17	0,5-0,7	5,76	8	14,712	187	908	2024
5-18	2,4-2,6	7,22	5	< 0,200	26	260	107
7-23	0,6-0,8	6,08	5	3,168	104	2055	2036
7-24	1,4-1,6	7,48	27	3,792	206	900	433
7-26	7,0-7,2	7,46	2	0,000	11	258	18
2-27	0,6-0,8	6,61	3	< 0,200	31	1363	218
8-28	4,8-4,9	7,56	5	0,598	22	220	104
1A-30	0,8-1,0	7,07	88	222,244	1316	4977	17141
1A-31	3,3-3,4	7,74	3	9,543	24	153	421
2A-34	0,6-0,8	3,56	114	54,800	290	386	7136
2A-35	1,4-1,6	8,10	0,8	3,386	40	264	337
2A-36	3,8-4,1	5,95	107	80,312	814	4441	6544
9-37	0,6-0,8	7,67	13	0,998	59	265	339
9-38	2,0-2,1	7,55	12	1,786	49	210	264
9-40	6,5-6,6	6,89	58	13,944	421	1400	1849
10-41	0,6-0,8	7,63	0,2	< 0,200	8	63	76
10-42	3,8-4,0	7,15	4	< 0,200	28	85	186
1B-44	0,3-0,5	6,89	154	18,327	1025	5833	1627
1B-45	2,0-2,2	8,22	8	2,376	92	408	245
13-47	0,4-0,6	5,50	38	49,008	502	2141	5234
13-48	2,5-2,6	6,26	5	< 0,200	21	82	212
6-50	0,6-0,8	6,91	1	< 0,200	23	119	84
6-51	1,3-1,5	6,46	0,4	< 0,200	13	47	64
12-53	0,6-0,8	7,77	29	0,599	23	230	138
12-54	2,2-2,4	7,42	8	4,854	118	592	611
3B-56	0,4-0,6	6,95	5	0,200	14	66	168
3B-57	2,3-2,5	7,82	0,4	< 0,200	8	35	102
2B-60	2,4-2,6	5,98	0,6	< 0,200	6	44	20
11-62	0,4-0,6	7,44	0,2	1,590	121	1968	335
11-63	2,4-2,6	7,63	1	< 0,200	9	95	54
14-65	0,3-1	6,53	11	31,412	176	1477	3590
14-66	1-2,5	7,39	3	3,769	32	105	266

Table 2. Content of metals in soil test samples from the area of the “Lead-zinc factory” - Kardzali, mg/kg

Drillhole test sample No	depth (m)	Fe	Mn	Cr	Ni	Co	Ba	Mo	Bi	Sn
1	2	3	4	5	6	7	8	9	10	11
1-1	0,2-0,4	11160	458	20,8	13,0	32,2	34,2	1,0	<0,2	<10
1-2	1,8-2,0	16620	624	39,2	28,2	18,4	52,4	1,0	<0,2	<10
2-5	0,5-0,7	68800	1825	36,4	32,2	78,0	116	18,6	21,8	<10
2-6	3,1-3,2	12120	592	19,6	12,6	27,2	28,0	0,2	1,6	<10
3-9	0,8-1,0	59800	7480	79,6	71,2	1200	31,0	8,0	<0,2	10,4
3-10	2,2-2,4	16400	1426	59,4	59,0	1004	136	0,4	0,8	10,1
4-13	0,4-0,6	186200	14680	152	75,0	148,4	31,4	15,0	<0,2	<10
4-14	2,0-2,2	19380	1738	35,0	22,2	12,8	23,4	0,8	0,4	<10
5-17	0,5-0,7	20540	1318	57,2	42,6	37,2	45,2	2,8	0,8	<10
5-18	2,4-2,6	3360	564	5,00	12,0	7,40	31,8	0,4	<0,2	<10
7-23	0,6-0,8	23800	1158	77,8	69,6	32,4	131	1,6	<0,2	10,6
7-24	1,4-1,6	3640	642	42,0	11,6	8,40	33,2	1,4	<0,2	<10
7-26	7,0-7,2	1770	93,8	3,60	2,60	5,00	20,4	0,4	<0,2	<10
8-27	0,6-0,8	23200	958	80,6	67,8	15,8	92,0	2,4	<0,2	<10
8-28	4,8-4,9	3000	326	3,20	7,60	15,2	26,4	1,4	<0,2	<10
1A-30	0,8-1,0	26200	2080	31,6	30,2	57,2	35,8	<0,2	40,6	<10
1A-31	3,3-3,4	17740	634	28,4	28,0	9,00	50,6	0,4	1,8	<10
2A-34	0,6-0,8	32600	524	30,8	21,0	7,6	68,8	2,6	<0,2	<10
2A-35	1,4-1,6	14240	630	19,2	20,4	9,0	36,4	<0,2	<0,2	<10
2A-36	3,8-4,0	26720	972	39,0	23,6	18,0	34,0	1,0	<0,2	<10
9-37	0,6-0,8	22000	890	45,0	37,4	14,2	92,0	1,4	<0,2	<10
9-38	2,0-2,1	2660	384	7,60	9,00	4,60	18,4	0,8	<0,2	<10
9-40	6,5-6,6	18900	778	35,8	29,6	17,8	37,0	2,6	1,2	
10-41	0,6-0,8	13700	706	21,4	26,2	10,4	45,6	<0,2	5,0	<10
10-42	3,8-4,0	20380	648	25,8	19,8	10,2	46,2	0,2	<0,2	<10
1B-44	0,3-0,5	18540	756	38,4	37,0	14,2	61,2	0,2	20,6	<10
1B-45	2,0-2,2	14900	958	21,4	16,8	12,4	67,0	1,0	1,2	<10
13-47	0,4-0,6	18320	934	25,8	17,8	42,2	44,2	0,6	0,2	<10
13-48	2,5-2,6	18220	598	23,6	18,8	7,40	37,4	1,6	5,6	<10
6-50	0,6-0,8	17580	728	35,4	28,6	9,00	57,0	0,6	0,8	<10
6-51	1,3-1,5	19520	722	26,8	29,0	11,2	61,0	<0,2	0,4	<10
12-53	0,6-0,8	16700	698	29,8	28,8	11,0	40,6	0,6	<0,2	<10
12-54	2,2-2,4	20360	582	49,2	50,2	11,0	78,8	0,6	6,4	<10
3B-56	0,4-0,6	14340	654	23,0	24,0	8,20	43,0	0,4	1,4	<10
3B-57	2,3-2,5	13900	546	20,6	22,6	6,80	28,2	1,2	<0,2	10,8
2B-59	0,4-0,6	16200	728	35,0	35,8	12,4	70,6	0,2	<0,2	<10
2B-60	2,4-2,6	16520	642	27,6	25,6	9,60	70,8	13,2	2,6	<10
11-62	0,4-0,6	20020	756	47,0	39,6	12,4	71,2	0,4	0,4	<10
11-63	2,4-2,6	15200	610	24,0	21,8	9,60	35,0	<0,2	0,6	<10
14-65		16700	726	26,6	24,8	14,8	49,2	<0,2	1,8	<10
14-66		18610	680	31,5	29,3	10,2	45,1	0,4	0,3	<10

Table 4. Element analysis of waters

Indicators	Dimension	C 7	C 8	C 9	C 10	C 11	C 12	C 13	C 14	LZF I	LZF II	LZF III	Studen Kladenets Dam
Chlorides (Cl^{-})	mg/dm^3	38,99	38,90	88,62	14,18	60,26	28,36	177,25	14,18	46,08	38,99	12,40	14,18
Magnesium (Mg^{2+})	mg/dm^3	38,99	29,54	62,8	11,64	4,85	21,45	27,32	10,21	40,4	54,9	38,92	6,94
Calcium (Ca^{2+})	mg/dm^3	231,2	178,4	282,5	76,1	242,6	130,7	246,0	108,8	351,4	523,2	294,7	64,3
Sodium (Na^{+})	mg/dm^3	100,9	81,0	283,3	53,7	113,4	79,0	119,7	36,56	193,5	105,6	55,1	28,92
Potassium (K^{+})	mg/dm^3	8,75	10,03	9,72	3,75	9,44	9,60	16,86	14,03	22,76	20,1	11,84	3,69
Copper (Cu^{2+})	mg/dm^3	0,009	0,01	0,083	0,011	0,229	0,119	0,035	0,71	2,98	3,93	0,16	0,01
Manganese (Mn^{2+})	mg/dm^3	0,52	0,14	0,249	0,166	1,97	0,91	1,66	5,65	10,79	8,73	0,83	0,47
Lead (Pb^{2+})	mg/dm^3	0,257	0,669	<0,02	0,577	3,64	1,05	0,093	3,34	0,28	9,40	2,61	0,226
Arsenic (As^{3+} и As^{5+})	mg/dm^3	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	0,023	0,011	0,082	<0,01	<0,01
Selenium (Se^{2+})	mg/dm^3	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02
Cadmium (Cd^{2+})	mg/dm^3	<0,004	<0,004	0,062	0,006	0,013	0,009	0,025	0,67	0,008	0,185	0,011	0,033
Nickel (Ni^{2+})	mg/dm^3	<0,004	<0,004	<0,004	<0,004	0,015	0,007	<0,004	0,029	0,063	0,107	<0,004	<0,004
Aluminium ($A1^{3+}$)	mg/dm^3	1,82	2,26	1,35	1,01	9,50	6,05	3,21	9,70	0,11	19,5	4,58	0,134
Iron (Fe^{2+} и Fe^{3+})	mg/dm^3	2,67	2,13	1,21	1,19	10,67	4,12	2,28	5,34	1,28	4,18	5,12	0,186
Zinc (Zn^{2+})	mg/dm^3	0,21	0,146	0,53	0,407	0,73	0,77	0,43	40,80	8,84	63,3	1,69	0,91
Phosphorus (P^{5+})	mg/dm^3	0,167	0,212	0,218	0,215	1,80	1,81	0,329	1,87	0,119	1,41	0,588	0,31
Sulphur (S^{6+})	mg/dm^3	230,8	160,0	379,9	38,07	147,1	66,0	141,1	34,94	403,7	366,1	257,1	40,86
Antimony (Sb^{3+} и Sb^{5+})	mg/dm^3	0,020	<0,02	<0,02	<0,02	<0,02	0,039	<0,02	<0,02	0,037	<0,02	<0,02	0,022
Cobalt (Co^{3+})	mg/dm^3	<0,004	<0,004	<0,004	<0,004	0,023	0,014	0,006	0,054	0,093	0,099	<0,004	40,86
Bismuth (Bi^{3+})	mg/dm^3	<0,02	0,123	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	0,044	<0,02	<0,02	<0,02
Tin (Sn^{2+} и Sn^{4+})	mg/dm^3	<0,02	<0,02	<0,02	<0,02	0,021	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02
Tungsten (W^{5+} и W^{6+})	mg/dm^3	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02

Indicators	Dimension	C1 A	C2 A	C1 B	C2 B	C3 B	C 1	C 2	C 3	C 4	C 5	C 6
Chlorides (Cl^{-})	mg/dm^3	60,26	957,15	38,9	42,5	46,08	177,25	1098,9	602,6	77,99	15,95	46,08
Magnesium (Mg^{2+})	mg/dm^3	36,33	53,2	30,07	16,46	18,88	59,3	104,19	65,6	85,3	25,89	17,33
Calcium (Ca^{2+})	mg/dm^3	225,4	439,5	268,9	121,6	238,2	566	685	606	593,2	203,3	198,5
Sodium (Na^{+})	mg/dm^3	151,8	346,5	83,5	21,28	20,35	191,9	338,5	350,1	123,8	27,4	31,58
Potassium (K^{+})	mg/dm^3	16,1	22,65	22,05	12,57	14,73	21,82	21,96	22,96	30,3	11,39	8,61
Copper (Cu^{2+})	mg/dm^3	0,885	0,052	0,71	0,113	0,039	0,013	0,333	0,44	185,0	0,025	0,11
Manganese (Mn^{2+})	mg/dm^3	2,42	3,82	3,91	4,53	0,337	1,54	4,699	5,16	39,56	1,44	1,24
Lead (Pb^{2+})	mg/dm^3	1,55	0,038	4,20	0,37	0,054	<0,02	2,05	0,346	0,74	0,21	5,54
Arsenic (As^{3+} и As^{5+})	mg/dm^3	0,115	<0,01	0,04	<0,01	<0,01	0,012	0,01	<0,01	<0,01	<0,01	<0,01
Selenium (Se^{2+})	mg/dm^3	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	0,056	<0,02
Cadmium (Cd^{2+})	mg/dm^3	0,073	0,009	0,068	0,013	<0,004	0,004	0,019	0,647	144,6	0,043	0,033
Nickel (Ni^{2+})	mg/dm^3	<0,004	<0,004	0,036	21,28	0,065	<0,004	0,015	0,009	2,49	<0,004	<0,004
Aluminium ($A1^{3+}$)	mg/dm^3	5,88	2,41	14,63	6,98	3,60	8,90	1,23	4,42	1,83	4,34	4,57
Iron (Fe^{2+} и Fe^{3+})	mg/dm^3	5,54	3,78	12,74	5,03	3,92	6,29	2,40	4,66	13,68	4,94	3,88
Zinc (Zn^{2+})	mg/dm^3	8,07	1,46	4,17	1,48	0,71	0,32	3,16	40,6	1096	2,77	0,92
Phosphorus (P^{5+})	mg/dm^3	0,682	0,377	1,83	1,24	0,33	0,287	0,206	0,406	0,145	0,22	1,12
Sulphur (S^{6+})	mg/dm^3	220,0	274	70,2	41,61	134,5	587	400	497,5	1400	165,2	96,4
Antimony (Sb^{2+} и Sb^{5+})	mg/dm^3	0,053	<0,02	0,044	<0,02	0,026	<0,02	0,148	<0,02	0,032	0,056	0,048
Cobalt (Co^{3+})	mg/dm^3	0,045	<0,004	0,02	0,013	0,006	<0,004	<0,004	0,476	0,67	0,008	0,009
Bismuth (Bi^{3+})	mg/dm^3	<0,02	<0,02	<0,02	<0,02	0,075	<0,02	0,062	<0,02	<0,02	<0,02	<0,02
Tin (Sn^{2+} и Sn^{4+})	mg/dm^3	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02
Tungsten (W^{5+} и W^{6+})	mg/dm^3	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02
Permanganate oxidizability	mg/dm^3			16,48	12,80	24,16						

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ENVIRONMENTAL AND TECHNOLOGICAL PROBLEMS WITH SEPARATION OF "MAXIM" WASTE DUMP MATERIAL

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ABSTRACT
It is well acknowledged fact that solving of certain environmental problems is connected to development of specific technological methods. The liquidation of Maxim dump in the city of Pernik coupled with elimination of the whole spectra of air and water pollution problems linked to that dump is both possible and highly welcome, since dump elimination itself will be self financed via realization of the rejected coal product and its utilization as a fuel in the Thermo power Station. The results from the exploitation testing of Maxim dump material performed in Belgium suggest the technological feasibility for hydrocyclone separation in an autogenous suspension. When tests were performed under 1.44 g/cm^3 suspension density, the dynamic conditions of the media secure real separation density of 1.65 g/cm^3 under which one could obtain coal concentrate with yield 21.43% with 21.5 % ash content. During the course of the industrial trials at the Belgian installation designed for recovery of black coal form local dumps, some negative factors were figured out having influence upon Maxim dump material treatment by which elimination better economic efficiency could be target in the case of hydrocyclone separation of the material in an autogenous suspension. These factors are: the existence of coal particles or intergrowths larger than 40 mm; the high tixotropic features of the clay met in Maxim dump which under increased moisture content of the material tend to form aggregates between coal and shale and their rejecting as 40 mm oversize; coarser dispersion of the clays in comparison to the granulometric characteristic of the autogenous suspension used in the industrial scale testing and others.

Key words: dump, coal, autogenous suspension, hydrocycloning.

INTRODUCTION

During the recent years countries such as UK, Belgium, France and others are allocating appreciable investments for processing of high ash coals and waste materials extracted from past not existing anymore mines. These investments are characterised by high rate of return. Parallel, devastated landscapes are improving and harmful gaseous, dust and liquid emissions are eliminated.

The improvement in the local environment in the city of Pernik is an urgent need, since this region is known as one having heaviest pollutants load on Bulgaria. Great deal of this pollution is due to chemical erosion from the coal dumps as a result of which sulphurous compounds, dust and heavy metals are emitted. During rainfalls these pollutants report into water courses and subsequently enter into soil system.

ENVIRONMENTAL INCENTIVES FOR MAXIM DUMP ELIMINATION

Maxim dump – characteristics

The Maxim waste dump or tip is located in the northern part of Pernik city vicinity, west to Divotinska river and in close proximity with the "St. Ana" coal mine. The outside view of the tip is a non-uniform cut cone having axis dimension 390 x 240 m with 28 m mean height. There are slopes reaching 30-40 % tilt. The upper surface is flattened at 0.5 - 2^o elevation. The dump is characterised by the following physical properties: moisture content – above 30 %, density 2,2 - 2,7 t/m^3, porosity 50 - 65 %. During 1972 the dump with a total area of 76 decars was transferred to Pernik municipal Council for further management. A plantation/biological rehabilitation has been performed in 1974. At the present time young not very well developed plantations remained only at about 30% of the tip surface mainly on its northern part. On the remaining part of the tip the wood plantations are dried as a result of the processes occurring inside the tip.

Up to 1992 six exploration wells were established for convenient for drilling spots however without an exploration grid after which further testing was not carried out. Hence, no sufficient data concerning the energy bearing mass distribution inside the tip is present. Data about ash content from each well differ significantly in a range from 70 % to nil. According to expert estimation about 200000 tones of coal are contained inside the tip.

Environmental problems

Maxim tip is a burning dump. Self ignition of the coal particles results as a result of oxygen contact. As a result of hemisorption oxygen molecules diffuse towards pores and adsorbs onto coal active centres. There compound of peroxide type are formed. These are non-stable compounds and according to chain-radical process theory they dissociate into radicals having high reaction affinity. The later attract coal organic structure and form intermediate compounds which are also non-stable and undergo dissociation. This formation of non-stable compounds is going fast and is accompanied by constant increase in temperature. When temperature reaches coal ignition point, burning takes place accompanied by release of fume gases. They contain CO, CO_2, SO_2, CS_2 and others. Since temperature abstraction from the materials surrounding the burning center is not effective, this is leading to temperature increase as a result of which processes known from gassification occurs leading to release of both HS_2 and other CH containing gasses like ethane, ethylene, acetylene and others. It is possible in some zones an anoxic regime of coal organic matter destruction to be formed which is leading to formation of tar containing various chemical compounds some of which like benzopyrrene are cancerogenic. Oxygen containing compounds like phenols are also emitted as well as amines. These product penetrate under gravity through pit volume, which process is facilitated by the increased porosity of the material. Surface waters coming from rainfalls collect these compounds and dispersed them towards the closest water catchments.

The fumes released via cracks and caverns coming in contact with atmospheric moisture are leading to acid generation which pollute both surface and underground water courses.

As a result of the erosion occurring in the South-east part of the tip the running near by river which is tributary to Struma river is polluted with non-dissolved solids. In dry seasons surrounding soils are polluted from the dust carried on by the winds carving the tip surface. It is obvious that Maxim tip with its burning features is highly environmentally harmful object. Burning processes are difficult to be forecast since they suddenly seize and start again depending on natural factors. It is not possible to evaluate the duration of complete burning process for the coal contained. It could last for decades. The above mentioned process provide a sound incentive for a search of mitigating options leading to their elimination.

Technological possibilities

Three principle directions are known from practice concerning coal wastes utilisation (Shpirt M.J., 1986):

a) wastes re-processing;
b) development of complex processing flow sheets enabling to use products with low content of burning mass;
c) utilisation of coal wastes in other industrial sectors.

Belgium is among the leading countries in extraction of coals from tips containing mixed materials (cut-off-grade coals and rock mass). Gravity methods aiming for burning mass recovery are widely practised in Belgium. Among the gravity methods the following are employed frequently: heavy media separation, separation in jigs, spirals, concentrating tables, hydrocyclones etc. The Belgian company WAUTELET offers technological flowsheets of installations designed for coal processing in hydrocyclones working with autogenerated suspension. The suspension is generated from the components coming with the raw material – mainly clay, sands and rock mass. From historical prospective coal washing is closely linked with the use of heavy media. Separation in such a media is characterised by not very strongly pronounced dynamic effects. An alternative option to such a heavy media separation is the separation in an autogenous self-generated media which has lower density and significant dynamic effects. The density practically required is compensated by the vortex and centrifugal currents which are generated inside separation devices aiming the recovery of burning components from the rock gangue.

EXPERIMENTAL

In order to prove the practical possibility for processing and utilisation of Maxim dump material an industrial scale trials were needed. Since in Bulgaria there is no installation for processing raw materials of such kind industrial testing was carried out in Belgium at WAUTELET installation in the Charleroi vicinity. The objective of the testing was twofold – first to prove or to reject that possibility and second to evaluate the technical and economic feasibility for the eventual future tip re-processing.

Sample representativeness

Obtaining of a mean representative sample seems a difficult task since waste tip has been formed non-uniformly and under non-constant time intervals. Nevertheless, the quantity of the sample raw material subjected to experimental testing should comply with the granulometric composition of the material inside the tip and with the maximal particle size. Mean sample has been prepared by sampling of six randomly chosen points at tip surface via bucket elevator. From each point about 20 tones were digger out from a depth limited by bucket elevator arm. The material taken out has been stored as cone-shaped on a special site from where after three times joining and dispersion about 60 tones were collected by quart method. Separate sample for laboratory studies has been collected immediately upon material loading onto the railway carriage.

Laboratory studies

Preliminary laboratory tests have proved that the material from Maxim pit has 16 % moisture content and 70 % ash content. Material fractionation (sink/float analysis) in a bromoform as a heavy media was carried out as well. The results obtained are presented at Table 1.

Table 1. Sink/float results for Maxim dump material

Density g /cm^3	Float fractions, %	
	Yield	Cumulative yield
Below 1,6	28,25	28,25
1,6 - 1,7	23,71	51,96
1,7 - 1,8	22,97	74,93
1,8 - 1,9	15,17	90,10
1,9	9,89	100,00

Table 1 analysis data were used for construction of the theoretical processing curves presented at Figure 1 below.

Industrial testing method

The method used for industrial scale testing is comparatively-simulative. It presumes subjecting the Maxim tip material by interruption of a working installation with parameters optimised in advanced for processing of black coal tips. It was decide to envisage 5 minutes time interval in order to precisely delineate between start-up and finishing for the two materials – the one originally processed at the installation and the Maxim dump material. However, the originally generated suspension is used for the Maxim materials well, since the quantity of the material and its residence time inside installation are both enough for generation of self-suspension. Suspension density has been monitored every 2 minutes. Same time interval was used for sampling, when two equal samples from the suspension were taken, and were joined by the end of the experiments. In a 4 minute intervals samples from concentrate and collective tails were taken by means of pulp sectioning. In order to satisfy data compilation the following items were additionally estimated:

- overall quantity of treated material;
- quantity of coal concentrate yielded;
- ash and moisture content of the coal concentrate.

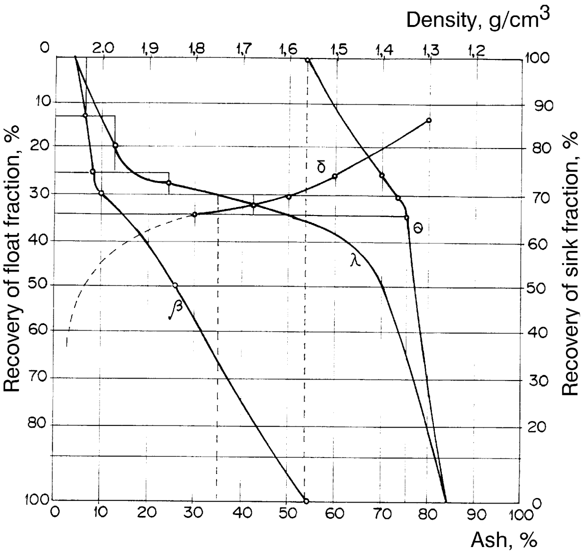

Figure 1. Theoretical processing curves for Maxim dump material

Industrial installation

The principal sequence of the industrial installation is shown at Fig. 2

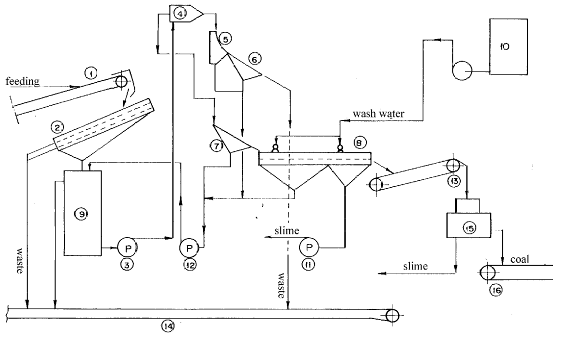

Figure 2.. Black coal waste separation flow-sheet- unit sequence

1- feeding belt; 2- double deck vibration screen; 3- pump; 4- hydrocyclone; 5- arc screen; 6- drainage screen for waste; 7- drainage screen for hydrocyclone overflow; 8- wash screen; 9- washing drum "Barrel"; 10- wash water tank; 11- slime pump; 12- recycled water pump; 13- rubber transportation belt for washed coal; 14- rubber transportation belt for waste material; 15- drainage centrifuge; 16- rubber transportation belt for coal concentrate to storage.

Experimental results

The experimental testing has followed an initially agreed routine for and established technological regime. Experimental start-up has coincide with hour four after initial installation running. The Maxim dump material has been processed on one of both modules. Total test duration has been set to 24 minutes. The total amount of material processed was 56 tonnes with an ash content of 70 % and 18 % moisture. 12 tonnes of concentrate were obtained having ash content of 21,5 % and 15,3 % moisture. Representative samples from the following products were collected – autogenous suspension, coal concentrate, tail. They were subjected to lab studies at the UMG in Sofia. The suspension density measured with aerometer ranging form 1,0 - 1,5 g/ cm^3 at 18 ^{0}C has indicated 1,44 g/ cm^3. Its granulometric composition was obtained by means of a laser particle sizer Analyzzette 22 and is given ate Figure 3 .

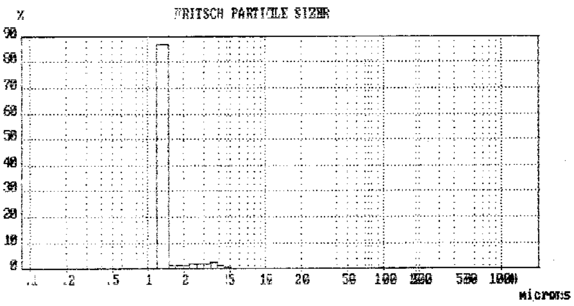

Figure 3. Granulometric characteristic of autogenous suspension used for black coal waste tips hydrocycloning in Belgium

Table 2. Size analysis for washed onto 0,063 mm sieve coal concentrate obtained during an industrial testing in Belgium

Size class mm	Yield %	Ash content %	Cumulative mass "+", %	
			Yield, %	Ash content, %
+ 20,0	2,59	24,5	2,59	24,80
- 20,0 + 9,0	16,05	11,0	18,64	12,87
- 9,0 + 5,0	22,33	10,7	40,97	11,69
- 5,0 + 2,5	24,25	14,1	65,22	12,58
- 2,5 + 1,25	20,50	16,4	85,72	13,50
- 1,25 + 0,5	9,13	25,8	94,85	14,68
- 0,5 + 0,63	5,15	42,2	100,00	16,10
Total	100,0	16,1	-	-

For the coal concentrate sample as taken from the installation moisture content after drying at 105 ^{0}C, has been estimated as 5,3 %. After further concentrate washing with tap water on 0,063 mm sieve a granulometric analysis of the oversized dry product has been done. Data from that analysis are presented ate Table 2. During concentrate washing a clayey-slime products was collected which was settled and dried. Its mass yield was 8,05 % and ash content 67,6 %.

The tailing sample was wet sieved on 40 mm screen. It was found out that size class + 40 mm encompasses two groups of particles:

a) massive lumps;
b) aggregates consisting of coal and loamy marl particles glued by wet clay.

Table 3 presents the granulometric composition of class 40 mm undersize with the respective ash content for each class.

Table 3. Granulometric composition of class 40 mm undersize for the tailing obtained during industrial testing in Belgium

Size class mm	Yield %	Ash content %	Cumulative results "+", %	
			Yield, %	Ash content, %
+ 20,0	7,34	84,60	7,34	84,60
- 20,0 + 9,0	2,60	79,10	9,94	83,10
- 9,0 + 5,0	10,53	83,30	20,47	83,23
- 5,0 + 2,5	13,85	81,60	34,32	82,57
- 2,5 + 1,25	16,21	85,20	50,53	83,42
- 1,25 + 0,5	20,36	88,70	70,89	84,93
- 0,5 + 0,63	15,03	89,10	85,92	85,66
- 0,063	14,08	88,20	100,00	86,02
Total	100,00	86,02	-	-

By means of hand sorting massive lumps were separated from the aggregates of + 40 mm class after which loamy marl particles were separated from the coal particles. The aggregates between loamy marl and coal particles are glued by the clay. After disintegration and washing of this fraction the results shown ate Table 4 were obtained.

Table 4. Granulometric composition of class 40 mm oversize for the tailing obtained during industrial testing in Belgium

Size class, mm	Yield, %	Ash content, %	Cumulative yield, "+"	
			Mass, %	Ash content, %
above 40 mm shales	14,70	90,80	-	-
> 40	6,48	34,10	53,83	73,45
40 - 0,5	12,92	69,30	86,68	71,88
< 0,5	5,24	81,30	100,00	73,13
Total + 40	39,34	81,30	-	-

From the clayey product (- 0,063 mm) shown at Table 3 a sample for sieve analysis has been taken. It was subjected to Analyzzette 22 particle sizer. Figure 4 presents the result form that analysis. This class was generally responsible for autosuspension formation during Maxim dump material processing.

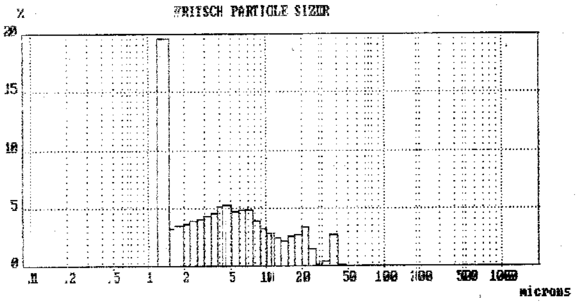

Figure 4. Granulometric characteristic of clayey product - 0,063 mm from Maxim dump

DISCUSSION

Maxim dump material is suitable for separation by means of autogenous suspension which itself presents the finest part of clayey-sandy fraction of the material. Data at Figure 3 support the fact that the Belgian suspension consists predominately of fine particles – about 90 % under 2 micrometers. These are fine loamy particles, since there is no clay in the host rocks. In contrast, the finest part of Maxim tip material is presented predominately by clay and fine rock (mostly marl) particles. Owing to data at Figure 4 the fraction 2 micrometers undersize is around 30 %, and the maximal grain size exceeds 40 microns. Particles in the range 2 - 20 microns are characterised by relatively random distribution. The clay found in Maxim dump is sticky and has high plasticity. These features of the material are additionally supported by the fact that significant aggregates are present in class + 40 mm consisting of fine coal and loamy marl particles coated with clay.

The analysis of the gangue obtained during the industrial testing suggests that definite reserves for improving separation efficiency exist. Coal particles are found in class + 40 mm, which is not subjected to treatment. These particles have low ash content which makes them suitable as power plant fuel. This class consists of two groups:

a) monolithic coal and loamy marl lumps;
b) aggregates.

Coal fractions having 16,48 % mass and A^d - 34,1 % has been separated from the class + 40 mm during hand sorting based on colour and blister. This material could not be treated via hydrocycloning according to the flow sheet tested , but it could be successfully separated by the means of Barrel washing drum and joined the concentrate obtained after hydrocycloning. The other option for utilisation of this product is to subject it to size reduction down to - 40 mm and to processed it according to the flowsheet given at Figure 2, however with lower recovery anticipated.

The aggregates rejected in class + 40 mm present also an interesting reserve. Based on distribution, size and ash content, the aggregates which form this class are similar to the particles met in the coal concentrate and in the tailing - 40 mm. Obviously, if a conditions under which clay does not manifest its plasticity and adhesives are maintained, they will report in the concentrate and in the tails in ratio estimated during the experiments, which will lead to overall increase in concentrate yield. The unwanted effects of clay could be eliminated also either by initial increase in its moisture content or by its preliminary drying.

These reserves are proving the relatively large difference in the quality and amount of the obtained concentrate compared to the data suggested by the theoretical processing curves.

The autogenous suspension density during experimental test was 1,44 g/cm^3 demonstrating strong dynamic effects, which is equal to separation density of 1,6 - 1,65 g/cm^3 for calm media. The shape of the (λ) curve (elementary fractions curve) suggests that the Maxim dump coals are easily beneficiated. The theoretically possible yield is 33,2 % with A^d - 42,8 %.

The experimental results, however are indicating yield of 21,43 % for A^d - 21,50 %, which are fairly below those suggested by the curves. Provided some correction in the flowsheet are taken into consideration, accounting some of the reserves mentioned above, yield could be increased above 30 % for A^d lower than 40 %. These results are approaching those suggested by the theoretical curves. Density of 1,6 - 1,65 g/cm^3 is a suitable one for recovery of energy material from brown coals such as those met in Maxim dump, while such a density does not work effectively for black coals where concentrate with low ash content suitable for the coke industry could be recovered only. Gives this issue, the choice of the industrial testing installation for the material coming from Maxim dump seems the right one.

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CONCLUSION

The industrial testing performed with the Maxim tip material with objective of recovery of burning fraction suitable for Thermo Power Stations fuel, provide a positive answer to the problem of tip liquidation. By means of extraction of the burning-prone fractions from the tip, the potential source of environmental pollution are eliminated. Qualitative and quantitative characteristics of the concentrate obtained are quite convincing, while the economic estimations suggest that the costs associated with material re-processing are entirely covered by realisation of the concentrate with about 15 – 40 % profit depending upon installation capacity.

The separation of Maxim dump material via installation working with hydrocyclone scalping is a suitable method. A special emphasis should be placed on the following technological peculiarities during the course of operation:

a) clay met in Maxim dump material possess high plasticity and adhesives when moisture is above 15 %;
b) coal lumps are present in the fraction rejected ahead of the separation, i.e. + 40 mm;
c) thin (1 - 2 mm) coal layers are met inside loamy marl particles.

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FEASIBLE SOLUTIONS FOR URANIUM PRODUCTION SITES DEMOLUTION

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ABSTRACT
This paper reviews the major solutions for demolition of Uranium production sites in the Republic of Bulgaria, emphasizing on the existing sites in the Buhovo Mining Area. It briefs the characteristics, the current conditions, the proposed project phases, and the feasible solutions for demolition of the sites, and presents an evaluation of the environmental risks associated with each method. In conclusion, it summarizes the findings and highlights the advantages of the blast method of demolition for this type of radioactive sites.

BASIC CHARACTERISTICS OF THE URANIUM MINING AND PRODUCTION IN THE BUHOVO MINING AREA

The Uranium production in Bulgaria began in 1920 in the first Bulgarian Uranium Mine located in the Goten Phacoidal Fault to the north of the town of Buhovo.

The first exploration trenches, small pits, two shafts and one adit were build in 1936-1938, and in 1939 the annual production of the mine was approximately 300 tons of uranium ore.

The Uranium production stopped during the WWII (1941-1944), however the research and production were relaunched after the war, and expanded into the Buhovo Mining Area, which contained 9 separate mines: Goten 1, 2 and 3; Chamilov Kamak, Borche, Chora, etc. The Uranium production of the area was approximately 26 % of the national Uranium production. The Uranium ore mined in the Buhovo Mining Area contained approximately 0,084 % Uranium.

The mining operations were conducted primarily under the surface. Geotechnological block lixiviation by sodium solutions was introduces in the area in 1987. These two mining methods constrain the processing of the Uranium ore.

The first Uranium processing plant in Bulgaria was build in 1947, 1 km north-east of Buhovo. It was a multipurpose plant for processing ore with high or average Uranium content. The plant consisted of 6 integrated technological units which performed the complete processing, dressing, sorbing and extraction of Uranium concentrate in two basic forms: ammonium-uranil-carbonate and 3-uranium-8-oxide, which were sold on the market.

In the early days (1947-1956), the production waste was dumped directly in the Yaneshnitsa River, which floats in close proximity to the plant. Two permanent tailings ponds with a total capacity of 660,000 m^2 were build later.

The environmental effects of the Uranium production in the area are: destruction of the landscape, surface pollution from the ore transport facilities, deposition of waste earth and rock material in waste banks, pollution of the ground waters, especially after implementation of the geotechnological lixiviation, however, the most severe environmental damage results from the operation of the processing plan. The waste dumped directly in the Yaneshnitsa River resulted in large waste deposits in the river bed, known as “Yana Spillover”, with a total estimated area of 120 hectares.

The severe environmental disbalance extends to the whole Buhovo Mining Area, which includes: the villages of Kremikovtsi, Yana, Gorni Bogrov, Seslavtsi and the town of Buhovo; and seriously damages forest and agricultural areas. As noted above, the pollution results primarily from the processing operations.

The total impacted area in the region is approximately 160,000 decares, which is inhabited (primarily in the urban parts) approximately 10,200 people.

CURRENT STATE AND PHASES IN THE PROCESS OF ENVIRONMENTAL REHABILITATION.

In 1992, the Decree of the Council of Ministers terminated all Uranium production in the territory of the Republic of Bulgaria and launched the process of environmental rehabilitation of the Buhovo Mining Area.

Decree No. 56 of the Council of Ministers dd 1994 defines the staged rehabilitation of the environment from the impact of Uranium mining and production operations. The phases take into account the complex pollution, the feasible rehabilitation solutions and the changing balance of the impacted ecosystems. The decree defined the following phases: demolition of the production facilities, mechanical rehabilitation biological rehabilitation, cleaning the water pollution and monitoring the impacted areas.

The different phases of the environmental rehabilitation process take care of different types and levels of radioactive and other physical, chemical or biological pollution, which require different rehabilitation procedures.

The types of pollution can be subdivided into two categories: pollution generated by the mining and the processing operations and pollution generated in the process of demolition of the production facilities and environmental rehabilitation.

The first type of pollution includes waste piles, banks, pits, quarries, damaged areas around the shafts, waste waters. However, the most serious problems are the waste deposits in the river bed of Yaneshnitsa River, which accumulated before the building of the tailings ponds, and the impact of the inappropriate demolition of the tailings ponds. The environmental rehabilitation for this type of pollution involves primarily mechanical and biological procedures.

The second type of pollution includes the mining and processing infrastructure, in this case, the Metallurg Processing Plant. However the demolition of the processing facilities will render new radioactive waste.

We have to take consideration of the environmental risks involved in the different implementation stages of the plant demolition. The environmental risk in general, depends on the following: the method and the concrete solution for the demolition of the plant. There are two feasible solutions, one involves manual and machine demolition, the other – blast demolition; the transportation method of the resulting waste; and the depositing of the waste material.

FEASIBLE SOLUTIONS FOR DEMOLITION OF THE URANIUM PRODUCTION FACILITIES AND EVALUATION OF THE ENVIRONMENTAL RISK.

The purpose of the demolition of the production facilities (buildings and equipment) for mining and processing Uranium is to eliminate the high radiation in the area, and to provide normal work condition on the site.

The first mechanical stage of the demolition process of the Metallurg Processing Plant is already completed. Some of the facilities were demolished manually or by demolition machines, the other – by pinpoint blasts.

The implementation of both methods met all requirements of the relevant control authorities concerning the health and environmental risks. This paper describes the method of prioritizing and selecting the appropriated demolition method during this stage.

Some of the problems during the demolition process are the prolonged exposure of the workers to radioactive radiation, contact with radioactive waste and objects, generating mechanical pollution (dust) and its distribution.

The first two problems dominate the manual and machine demolition of the facilities, and require a brief stay of the workers on the project site. Here, the management of the health and environmental risk boils down to limiting the period of time when the workers are on the site, providing appropriate protective equipment and clothing. Any failure to meet the health and environmental requirements results in unreasonably high health and environmental risk. This method of demolition also fails to eliminate the dust pollution completely. The falling pieces of the buildings and the construction waste create a distinct area impacted by dust pollution, but it is smaller that the impacted area when using blast demolition.

Blast demolition was used for most of the facilities (especially for the demolition of facility No 7 - Sushka). The demolition of facility No.7 required minimum number of workers, who made holes in the building and placed the explosives for a minimum time and in highly radioactive environment.

The scope of the dust pollution, determined during monitoring the blast operation indicated that the changes in the amount of dust within 30 m of the blast are very small. The level of the dust increased from 0.63 mg/m^3 before the blast to 0.72 mg/m^3 after the blast. In addition to that the gamma-radiation remained 75-310 mR/h, the beta-radiation and the specific radioactivity of Radon at 1 m of the surface of the demolished structure did not change. This information indicates that there is only negligible environmental impact from the blast.

All measurement were taken with respect to the measurement of the atmosphere, which enables comparison with results measured by conventional methods.

The lower environmental impact of this demolition method results from the method for management of the blast of the radioactive material, which is governed by the following principle:

- description of the landscape and all air-drafts and currents.
- determining the distance from the demolished objects to potential objects of impact, and defining the safety (guarded) zone around the blast.
- classification of the types of power and utilities supply to the facility, machines, instruments, types of bearing structures, construction of external and internal walls.
- optimizing the direction of falling of the demolished object.
- defining the number, sequences and stages in the blast demolition on non-electric detonation (NONEL with delay of milliseconds) and electric detonation (in the second demolition phase – secondary blast).
- estimating and defining the parameters of the holes, including specific depth of the charge hole of 140-190 mm, diameter of a dice. Space 35-40 mm; type BB pulverous ammonium-nitrate - cartridged, the optimal quantity for one charge – 0.055-0.065 kg, total number of charges for the building/facility – 680-790 units, blast separated in time by 4-stage intervals of up to 2000 ms.

- specific data of the environmental and health safety, and classification as preliminary, technological and supplementary actions immediately after the blast process. One of the characteristics of the process is the dismantling of all machines, equipment and pipes, washing with high-pressure water of the bearing structures, walls, etc, meeting or achieving compliance with all labor safety and health provisions and other regulations applicable to the blast process. Immediately after the blast, the dust is liquidated by water curtains and screens.

These basic rules and principles of the blast process in radioactive environment are the fundamental concept of the project implementation for blast demolition of the plant facilities and infrastructure. The project is customized to specialized blast operations, and is in compliance with all applicable legislation, including those concerning the use of nuclear energy, radiation protection, qualifications, etc. At the same time, the project is coordinated with all respective control authorities and parties, who have any interest in the project implementation (institutions)

Based on the observations and analysis of the conditions and restrictions for the implementation of the demolition phase of the project, we can make the following conclusions:

1. There are no significant differences in the extent of the dust pollution resulting from the two different demolition methods (manual and blast).
2. The blast demolition ensures lower exposure of the workers to radiation.
3. In normal atmospheric condition, the environmental impact is negligible.
4. The blast demolition method should be preferred, since it renders waste material of size, which facilitates the load and transport operations.

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UTILIZATION OF WASTE OIL-DERIVATIVES

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ABSTRACT
The results and the opportunities offered by the method of liquid fuels emulsification with water or effluents containing oil derivatives with the objective of utilization of waste oil products from Burgas refinery are presented. Problems are outlined and experimental results from masout emulsification with waste products inside a burning installation located at the refinery petrol harbor are pointed out. An installation encompassing system for waste escavation from the lagoons and a system for rendering this product up to the conditions (stipulating suspended solids) enabling their use in burners is proposed.

INTRODUCTION

A definite amount of waste products, mostly liquid, are inevitably present during crude oil processing at the Lukoil-Neftochim oil refinery in Burgas. In order to contain these wastes, waste lagoons are erected at the refinery site which store some more than several thousand cubic meters liquid wastes. They contain the whole spectra of liquid oil derivatives, paraffin, plastics and all varieties of solid wastes together with water. Water is due to the constant influx of process effluents containing liquid pollutants and dispersed solids and also because of rainfalls since the lagoons are located under open air. An installation for waste burning exists, however such is its capacity that it could not handle the whole amount and moreover the oil contaminated effluents are a serious environmental problem. Recently a project bid was announced by the refinery with objective of complex solution of this mounting problem.

Some 10 years ago, the “Vibroacoustical intensification of technological processes” laboratory at the University of Mining and Geology in close cooperation with “Thermochim Engineering” Co. from Veliko Tarnovo has placed an attempt for solving the above problem based on our past experience which the lab posses in direction of emulsification water-liquid fuels, i.e. the so called water-burnable emulsions. Masout emulsification by means of water addition up to 10 – 15 % is leading to: superior burning process; reduction in the overall amount of soot generation; reduction of nitrous and sulphurous oxides emissions and under certain circumstances is economizing fuel. This technology adapted to the specific conditions of the refinery, could enable a certain amount of liquid waste, freed form solids, to be added to the masout produced by the refinery. Such a masout mixture could be gladly used for local needs of the refinery, i.e. to be burnt in the local Thermal Station or could be offered to other clients with similar demands.

PREPARATION OF WASTE PRODUCTS FOR BURNING

In order to accomplish waste products burning process, one has to remove the solid phase, i.e. all solid waste components having maximal size up to 0,063 mm, which is a compulsory requirement in order to guarantee normal functioning for the pumps and the burners. For the initial experimental set-up a definite quantity from the waste product needs to be prepared and further on this amount should be experimentally burned in the chamber in order to verify the correct mixing ratio of the product.

The experimental sequence of the proposed technology has involved taking sample in amount of about 300 L which was subjected to purification. The first “rough purification” step has involved screening the material on 10 and 1 mm sieves which enables significant part of the rough sold contaminants to be removed. Following the “rougher” stage the sample was further subjected to filtration with 0.3 mm openings, the resulting filtrate being fed to a tank – auto cistern. The liquid fraction thus obtained carries a definite amount of burnable fractions on the basis of the initial oil wastes – water and solid phase with size range – 0.3 mm. The concentration of burnable fractions depends solely on the spot where the sample is taken, i.e. the lagoon type and the sampling depth. Going through the vertical profile of the lagoon, one could notice that the content of the various products is changing: the oil fractions which are lighter than the water are met bot on the surface and on certain depth; going further down, the concentration of heaviest burnable fractions and paraffin, as well as layers of roughly emulsified in water oil derivatives, water itself and solid dense wastes is increased. In order for the liquid fraction purified from suspended solids to be subjected to burning, a specific regime which eliminates or masks the water presence effect need to be maintained. The emulsification takes place in a special installation which design offers the possibility for the additional liquid phase supplied and mixed with masout to be dispersed in micron sized drops. If pure water is added, this quantity could be 10 to 15 % as noted earlier in the text, which mode offers certain advantages; when contaminated effluents are used this quantity could be several times higher depending on the concentration of burnable fractions and upon the operating mode of the installation – whether it is used for clean-up purposes only or a definite energy effects are pursuit. When such types of fuel wastes coming from refinery lagoons are burnt, an account on their water content should be taken and knowing this figure the additional water quantity should be estimated. The emulsification installation (shown at Figure1) which has possibility for supplying different quantity from the additional liquid to be emulsified, is dispersing the liquid by means of vibroacoustical autopulsating emulgator (Metodiev, Stoev et al. 1987, Metodiev 1994) which hydrodynamical parameters enable the liquid to be vortex cut onto fine drops.

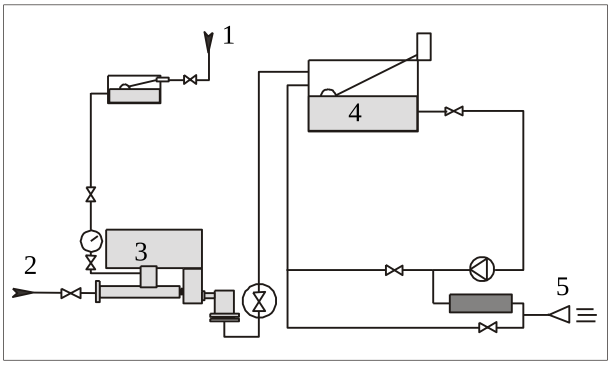

Figure 1. Installation for emulsification.
1-waste products, 2-masout 3- emulsification system, 4-daily tank, 5-burner

The drops produced are then homogenized via the autopulsating vibration impact resulting from the valve which vibrates as a result from the pulsating pressure. The combination of several type of impacts enables effective stream dispersion to occur and the possibility for using of nozzle with relatively large openings generating fine emulsion drops at large throughput of passing media.

In an attempt to study the possibility for burning of the liquid fraction obtained by the above described method, the boiler installation existing at the refinery harbor was used. The waste product leaving the cistern was mixed with pure masout by means of emulsification installation working in two modes – 15 and 20 % waste product composition. The ready-make emulsion was stored in an intermediate tank belonging to the boiler installation. Steady-state burning regime was observed when emulsified fuel was fed meaning that the boiler could be run in a continuous mode for three hours securing the required amount of energy until finishing the whole amount of emulsion prepared for the batch. This experiment has proved the possibility for utilization of oily waste waters by means of their burning in a boiler system, without perturbations in its operation regime.

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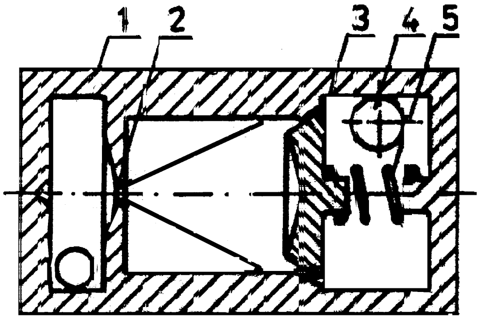

Figure 2. An emulsifier
1-chamber, 2-nozzle, 3-valve, 4-exit, 5-spring

In order to realize the suggested method parallel to burning of a definite amount of emulsion, few principal issues regarding waste products escavation and processing were needed to be addressed. The mode of products transportation from the lagoons to the installation needs to secure relatively constant parameters for the different fraction in time, since these are vital for the additional quantity of waste which the pure masout can accommodate. Moreover, the rejection of the rough solid wastes needs to secure their storage without generation of additional liquid waste.

THE CONDITIONING INTSALLATION

In order to realize the process for waste utilization the flowsheet shown at Figure 3 was suggested. The escavation of the wastes from the lagoons was accomplished by means of pump installed on a floating platform equipped with suction piping with definite length (close to the surface) which enables material suction to be maintained at a constant depth. A preventive screen was mounted around the suction pipe, which prevents larger lumps to enter the piping which could eventually block the pump. A membrane type pump needs to be used due to the need for transportation of both solid and liquid products. The floating platform could be situated close to the shore and there is no need of frequent reallocation of the platform owing to the fact that the wastes are sufficiently mobile. Rough wastes rejection is done via conveyor press having perforated body with 5 mm openings.

The press is used to compress solid wastes down to liquid free products. This action is controlled by means of spring fixation at the bottom cover. The rejected liquid phase passes either through the arch screen having 1 mm openings or via the vibration screen having similar openings. The arch screen is more easy to maintain, however the coarse product has higher moisture content in comparison with the same product from the vibration screen. The solid products rejected depending on their liquid phase composition could be either burnt or additionally pressed further. The liquid phase is directed towards filtering system, arranged in several successive steps securing its decontamination up to 0,063 mm. Each cleaning stage involves several filters which are automatically switched when pressure increases up to a predetermined value due to their over filling with solids.

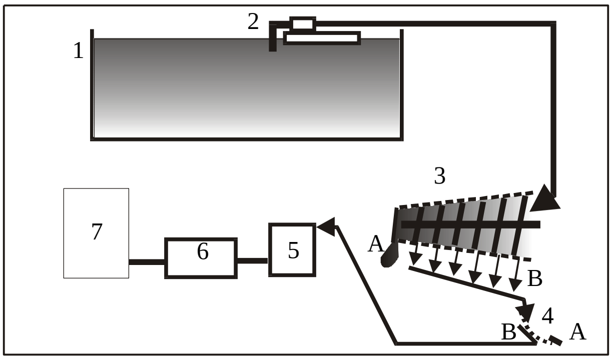

Figure 3. Conditioning installation flowsheet
1-lagoon, 2-floating platform with pump, 3- conveyor press, 4-arch screen, 5- filters, 6-emulsification system, 7-reservoir

This occurs at point which is experimentally estimated during installation adjustment. The percentage of contaminated effluent is determined upon the burnable fractions content. This percentage is higher at the beginning of pumping process, when pumping is done at levels closer to the surface and it starts to drop gradually when pumping area is moved towards the deeper levels of the lagoon when water predominates.

The realization of the suggested method for oil derived wastes utilization will eliminate significant part of them and the costs associated with their treatment will be entirely counterbalanced by the profits anticipated with their burning. Due to the large amount of the stated wastes, the masout thus produced apart for covering local needs, could be offered to outside clients at reduced prices. Besides, masout emulsification is expecting to has a favorable effect upon burning process inside boiler chambers, since at normal temperatures due to the increased viscosity no water lamination is evident. This expectation is supported by the results coming from the long lasting experience which various industrial establishments in the country have in using water-emulsified masout. The fuel emulsions thus treated have been proved stable in a long time period.

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USING OF MODIFIED ZEOLITES FOR PURIFICATION OF HEAVY METALS IONS FROM WASTEWATER

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ABSTRACT
Natural zeolites represent low-cost exchange and sorbent materials. The influence of different parameters, such as zeolite’s mass to treat water volume, water’s pH value, zeolite particles size and zeolite’s modification has been investigated. The goal of the experiments was investigation of the ability of Bulgarian natural zeolite to remove heavy metal ions from wastewater.

Key words:zeolite, modification, industrial waste water

INTRODUCTION

Zeolite exchangeable ions are relatively harmless and makes them attractive native materials for removing undesirable heavy metal ions from industrial and processing effluent water. In addition, zeolite loaded with heavy metal ions can be easily regenerated.

Mine-supplied zeolite (2-0.8 mm) (run-off-mine) sample from Beli Plast deposit, Kardzhali, Bulgaria, was using for experiments. The goal of the experiments was investigation of the processes kinetics and influence of the obstructive ions upon the purification of waste water in different initial concentrations of heavy metals ions.

INVESTIGATION OF THE ABILITY OF BULGARIAN NATURAL ZEOLITE TO REMOVE Cu^{2+}FROM WASTE WATER

A complex X-Ray Thermal analysis was made of initial and modified zeolites. The mineralogical composition is shown on Table 1.

Table 1. Mineralogical composition of initial and modified zeolites.

	Initial Z	NaZ	SMNaZ 250	SMHZ 250
Clinoptilolite	81%	83%	89%	93%
Albite	6%	3%	5%	-
Potassium feldspar	4%	6%	3%	-
Calcite	4%	-	1%	2%
Cristobalite	3%	3%	1%	3%
Tridymite	-	3%	-	-
Organic matter	-	-	Available	Available

The following abbreviations and ways of zeolite modifying are used:

Initial Z- Mine-supplied zeolite (2-0.8 mm) (run-off-mine) sample from Beli Plast deposit, Kardzhali, Bulgaria

NaZ **-** Na-zeolite single contact (i.e. NaZ) – Contacting the zeolite with 0.1M HCL for 5 hours. After 4 washes with tap water (about 40-45 % of mass of zeolite is lost) (since carbonates, clays etc. are leached). Further on in order to render the zeolite into Na form it was contacted in same manner with 1 M NaCl for 24h. All the conditioning was done before grinding.

SMNaZ 250 -25 grams from the dried zeolite representing the three initial forms described above (Na) were contacted with 100 ml of HDTMA solution with different concentration
250 % of the external CEC in 250 ml flasks for 24 hours under a shaking machine action.

SMHZ 250- 25 grams from the dried zeolite representing the three initial forms described above (H) were contacted with
100 ml of HDTMA solution with different concentration 250 % of the external CEC in 250 ml flasks for 24 hours under a shaking machine action.

Clinoptilolite was found to be the predominant material
(Table 1).

Pretreatment with HCl increases to some extent Si/Al.

Treatment with NaCl causes an increase in Na^+ and a decrease in Ca^{2+} concentrations in zeolite, leading to an increase of the ratios Na^+/K^+ and Mg^{2+}/Ca^{2+} (Teppen, et. al., 1995; Sullivan, et. al., 1997).

Determination of Na^+, Mg^{2+}, Cu^{2+} and Pb^{2+} concentrations in treated solution was made with an ICP-AES analysis. Values of pH were measured with a Metrohm E 588 pH-mV-meter.

Each experimental result was obtained by averaging the data from two parallel experiments.

Adsorption procedure is carried out in following conditions:

Cations:	Cu^{2+}, Pb^{2+} as nitrate salts.; No mixture, just one heavy metal.
Temperature:	20 °C
Ion strength:	Cations 500ppm of Na^+ and 500ppm of Mg^{2+} as nitrate salts.
Concentration of BA:	5 g (dry weight)/l.
Particle size:	71-100 µm.
pH:	Not too far from neutrality
Treatment time:	10 min

The influence of a specific process parameter was determined by calculating Cu^{2+} extraction by zeolite and changing that parameter. Uptake efficiency was calculated using the equation (1):

$$\text{Extraction, \%} = [(C_o - C_{eq}) / C_0] \times 100, \qquad (1)$$

where C_o and C_{eq} are the initial and the equilibrium concentration of pollutant, mg/l.

Series of parallel experiments were made with initial contents of Cu^{2+} ions from 50 to 400 mg/l without obstructive ions and in the presence of ions with concentrations from 500 mg/l respectively of Na^+, Mg^{2+} - Table 2.

The kinetic curve of sorption process is investigated in concentration of Cu^{2+} - 50 mg/l without and in the presence of obstructive ions Figure 3.

Table 2**.** Data for extent of the extraction of Cu^{2+} of NaZ with and without obstructive ions: Na^+ - 500 mg/l and Mg^{2+} - 500 mg/l in different concentrations of Cu^{2+} in the initial solutions, mg/l

	Without obstructive ions				With obstructive ions			
Initial solution, mg/l Cu	51,3	104,2	201,7	410,3	51,3	104,2	201,7	410,3
Residual concentration mg/l Cu	6,7	8,4	26,0	172,0	29,2	76,6	158,0	255,0
Extraction, %	86,94	91,94	87,11	58,08	43,08	26,49	21,67	37,85
Capacity, mMol/l	0,140	0,302	0,553	0,751	0,07	0,087	0,138	0,489

From the results obtained (Table 2) is obvious that in the absence of obstructive ions, a high extent of extraction of copper ions with NaZ is achieved.

At the same time a maximum of extraction (92 %) is observed in initial content of copper ions with concentration 100 mg/l, after which with increasing of the initial concentration up to 400 mg/l the extraction extent decreases to 48%. With increasing of the copper concentration in initial solutions without obstructive ions, capacity of the copper is increased too, reaching at 400 mg/l initial solution –0,751 mMol/g, which value is the maximum possible for this type of zeolites.

In the presence of obstructive ions – Na^+ and Mg^{2+}, the extraction extent decreases significantly (from 20 to 75% at different concentrations) (.Figure 1) With increasing of copper concentration in the initial solutions, a reverse dependence of the copper extraction is observed in relation to the same without obstructive ions. Higher values of extraction are obtained in copper initial concentrations 50 и 400 mg\l, respectively 43 and 38%, and the lowest at 200 mg\l – 21,6%.

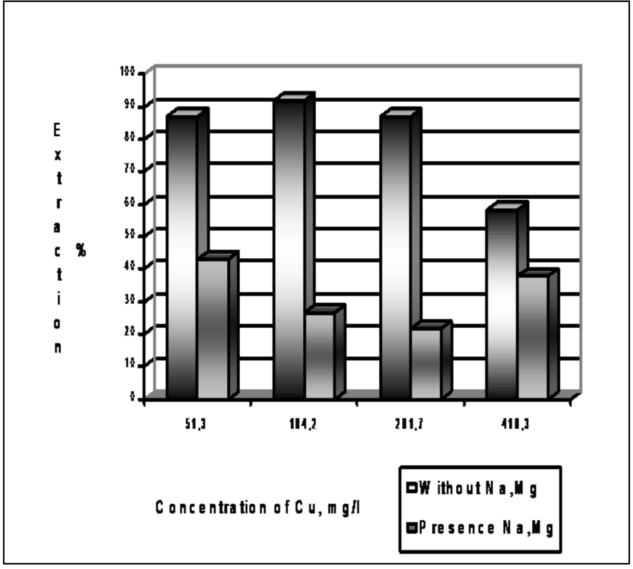

Figure 1. Dependence of the extraction extent from the copper ions concentration in the initial solution

With increasing of copper concentration in the presence of obstructive ions the capacity of copper is increased too(.Figure 2), but is significantly lower from the respective without obstructive ions, reaching at 400 mg/l initial solution –0,49 mMol/g.

Explanation of the dependence obtained, as well as the significant decrease of extraction extent, could be found in the presence of obstructive ions in comparatively high concentrations. On the one hand changing the solution ion power they influence upon the activity of the ions and compete the ion-exchange process of the copper ions with cations from the zeolite structure and causes change in the diffusive double layer of sorbent particles.

Experiments for determination of extraction kinetic curve at copper initial concentration – 50mg\l, with and without presence of sodium and magnesium ions were carried out Figure 3.

As it can be seen on the Figure 3, the maximum extraction extent in both cases is achieved at treating time 10 min.

Low extraction extent - (below 50%) at the presence of obstructive ions – Na^+ and Mg^{2+}(above 500mg/l) at initial solutions with copper concentration above 50 mg/l does not give a reason for their effective using as BA for purification of industrial waste water.

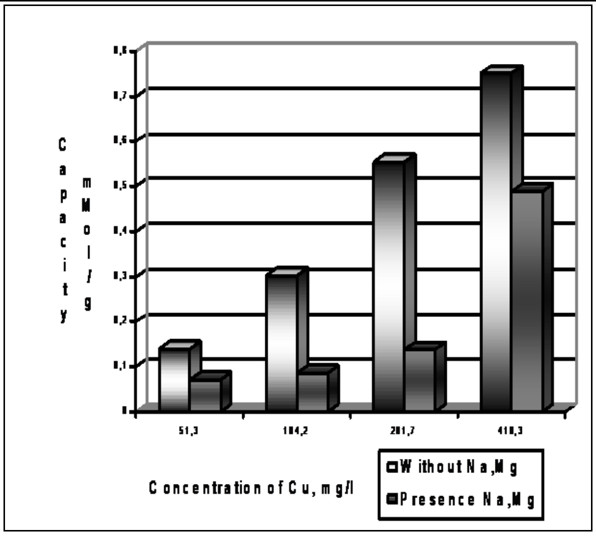

Figure 2. Dependence of the of zeolites capacity from the copper ions concentration in the initial solution

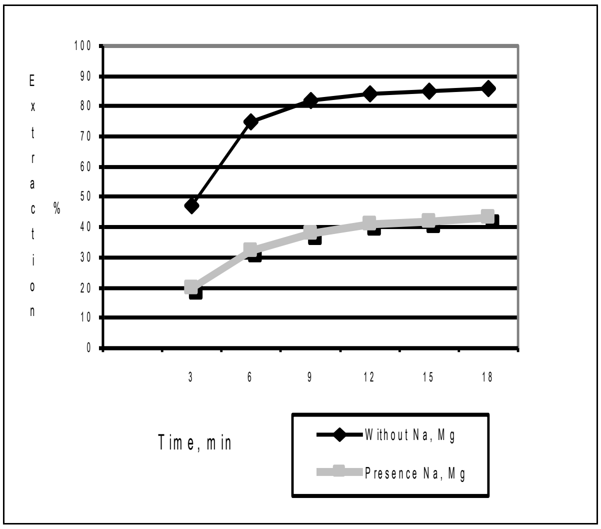

Figure 3. Kinetics of Cu^{2+} extraction. concentration of Cu^{2+}-50mg\l without and in presence of Na^{+} and Mg^{2+} - 500mg\l

INVESTIGATION OF PROCESS KINETICS AND THE INFLUENCE OF OBSTRUCTIVE IONS AT Cu^{2+} AND Pb^{2+} CONCENTRATIONS BELOW 50 mg/l

Zeolites' cation selectivity in ion-exchange reactions is determined by the type of zeolite, distance between anionic sites, cationic radii and cationic hydration energy of ions to be removed. Data on radii and hydration energy for cations investigated are presented in Table 3.

Table 3.Radii and energy of hydration for some cations:

Ion	Ionic radius, A	Energy of hydration, KJ/mol
Ca^{2+}	0,99	-1577
Cd^{2+}	1,03	-1807
Cu^{2+}	0,80	-2100
Mg^{2+}	0,65	-1921
Pb^{2+}	1,21	-1481

Natural water, consequently the main part of industrial wastewater, contains Na and Mg, but the average concentrations of them for example in Bulgarian water are 50-100mg\l and 20-50mg\l, respectively. That is why, the influence of Na and Mg presence on the extraction of Cu and Pb was investigated during the simultaneous addition of Na and Mg to Cu solution, in concentrations giving ratios of C_{Na+}/C_{Me2+}= 1-8 and C_{Mg+}/C_{Me2+} =1.

The influence of Na^{+} presence (in different concentrations) on heavy metals removal is presented in Figure. 4 – 5.

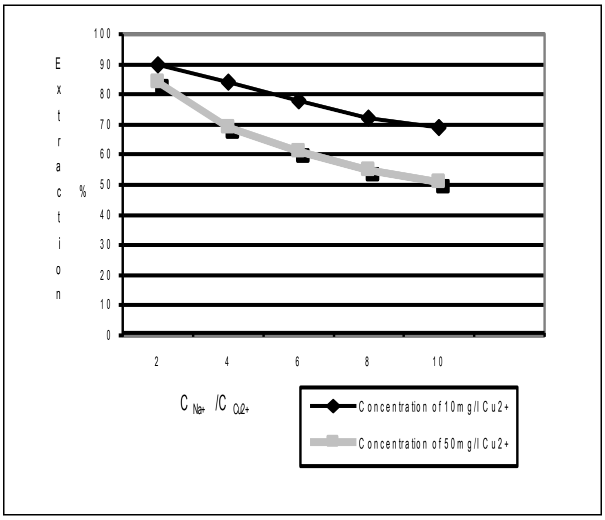

Figure 4. Extraction of Cu^{2+} in the presence of Na^{+}

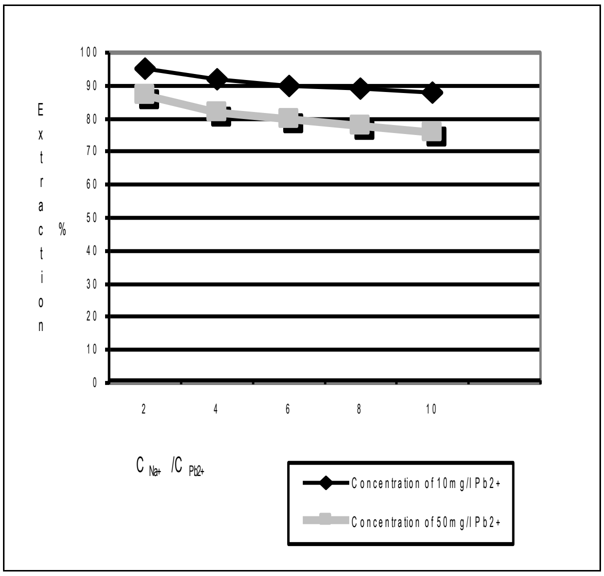

Figure 5. Extraction of Pb^{2+} in the presence of Na^{+}

As it can be seen from the figures, the higher is the ratio C_{Na+}/C_{Me2+} , the more pronounced is the decrease in heavy metals' extraction.

The decrease in heavy metal's extraction in the presence of Na^{+} can be explained by competing ion-exchange of Na^{+}. This results in the decrease of the sites of zeolite available to heavy metal ions.

Although the presence of Na^{+} in different concentrations has a negative influence upon the copper extraction, it is in a small extent in sodium concentrations close to the real (about 100 mg/l) in initial solutions in low copper concentrations - 10 and 50 mg/l. The extraction extent decreases from 90 % to 69 % in solutions with 10 mg/l copper and from 88 % to 69 % at 50 mg/l copper.

Still lower is their obstructive influence with regard to lead, where the extraction extent decreases from 95 % to 88 % in initial solutions with 10 mg/l lead and from
87 % to 82 % at 50 mg/l lead.

Table 4 presents the influence of Mg^{2+} in concentrations, equal to concentrations of corresponding heavy metal ions in solution on the extraction of heavy metal ions. These Mg^{2+} amounts are in range of concentrations most often met in natural water.

Table 4. Extraction of heavy metal ions in presence of Mg^{2+} in concentrations, equal to concentrations of corresponding heavy metal ions in solution.

Metal ion, Concentration mg/l	Extraction, %	Extraction, % from single metal ions solutions
Pb, 10	93,6	95,7
Pb, 50	88,0	94,5
Cu, 10	81,1	87,8
Cu, 50	84,2	88,2

As it can be seen from Table 4, magnesium influence in these concentrations is negligible and it decreases the extent of copper and lead extraction at their different concentrations from 3 up to 6 %.

The decrease observed for Cu^{2+} and Pb^{2+}extraction by zeolite in the presence of Mg^{2+}could be explained by the higher affinity of clinoptiolite to Mg^{2+} ions.

CONCLUSIONS

NaZ producing from natural zeolite from Kardjali deposit can be applied to remove Pb^{2+} and Cu^{2+} from wastewater in the presence of Mg^{2+} in concentrations similar to those found in natural water. Extraction of Cu^{2+} and Pb^{2+} by natural zeolite is decreased, if Na^+ concentrations in wastewater are higher than concentrations of heavy metal ions to be removed. The decrease is less pronounced for solution containing Pb^{2+} in low concentrations. Requirements of Bulgarian standards for industrial wastewater can be met by a one-stage process for an initial Pb^{2+} or Cu^{2+} concentration of 10 mg/l, and by a two- stage process for an initial concentration of 50 mg/l.

Extraction of Cu^{2+} by zeolite from neutral wastewater has proved to be as effective as Cu^{2+} removal by precipitation of copper hydroxide. Contacting with 2 mol/l NaCl solution can easily regenerate loaded zeolites.

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ON SAFE COMBUSTIBILITY OF MIXTURES OF PROPELLANTS AND POLYMERS FOR MINES AND QUARRIES

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ABSTRACT

Mixtures of single-base propellant with chlorine and bromine-containing polymers in different ratios, applied in mines and quarries abroad, were investigated. The exo-effects: maximum temperature of the peak, quantity of released heat and loss of mass were determined by a differential scanning calorimetry, after a standard aging of 120 and 240 hours under conditions imitating the sunshine. Combustibility of mixtures was analyzed according to a standardized factor of combustibility (K), Mixtures were subdivided into four groups depending on their values: easily combustible, combustible, self-extinguishing and non-combustible. Effective action of selected compounds depended on speed of formation of combustion retardants, which depended on temperature of thermal destruction. That was the reason for mixing propellants with polymers, whose initial temperature of destruction had been lower than the temperature individual combustion of propellant. Thus effective combustion retardant was created in the initial stage of mixture heating.

Controllable fuel characteristics of recipes improve the safety of transport, storage and use of offered materials.

INTRODUCTION

Explosion transformation of propellant represents combustion with a maximum liberation of gas and minimum release of solid refuse. Propellant is continuously more often applied into mixtures with other explosives or additive as a new high-power source for mines and quarries. Raw material is easily achieved due to the excess and liberation from its main designation - in military arms and equipment.

Adding of polymers for regulating the combustibility of explosives is applied in different fields as pocket-building Kitano Y. (1997), pyrotechnics - Fire Retardant system(1996), processing of polymers - Wang Xu (1996).

Objective of the report, which is a continuation of the investigation of Ganev R., Glavchev I. (2002), is to characterize the safe combustibility of explosive mixtures of propellant and halogen-containing polymers, co-polymers and oligomers for mines and quarries.

EXPERIMENTAL

Subject of investigation are mixtures of single-base propellant (SBP) of Arsenal, Bulgaria with chlorine and bromine-containing polymers:

- Brominated epoxy oligomer (EOB),
- Vinyl chloride/Vinyl acetate (VC/VA),
- Epoxide oligomer of bisphenol (D600),
- Chlorinated rubber (CR),
- perchlorinevinyl (PCV),
- chlorinated paraffin (CP),
- mixed with the dillutors of acetone and cycloxexanone in the ratio of 1:1.

Mixture is coated over sheets of twice pickled steel of 120 x 90 mm size as films 20μm thick.

The factor of combustibility (K) is specified as a ratio of time for individual combustion of test samples to time for moving front of combustion to certain position of the test body Bulgarian State Standard SS 10457-(1998).

RESULTS AND DISCUSSION

Preliminary experiments revealed that not all the halogen-containing polymers posses the properties of effective additives for quarantining the safe combustibility of mixtures. Availability of enough chlorine and bromine is a required precondition. Bromine-containing epoxide compounds are more effective, and therefore the Br quantity in mixtures may be lower for achieving the required category of combustibility. Chlorine-containing polymers are less effective but cheaper and more widely applied.

The requirement for more effective action of Cl- or Br-containing polymers is determined by the speed of formation of combustion retardants, which depends on the temperature of polymer destruction. That was the reason for mixing single-base propellant SBP with polymers of initial temperature of destruction lower than the destruction temperature of single-base propellant SBP. Thus effective retardants of combustion are created in the beginning of heating.

Content of dry substance in the mixtures effects not only the mechanism and the speed of evaporation of solvents, but oalso on the kinetics of combustion transformation. Percent content of halogen and dry residue of mixtures of single-base propellant (SBP) with bromine and chlorine-containing polymers .is calculated. Mixtures consist of two or three components, and one of the pairs uses polyisocianate as a hardening agent. (table 1).

Table 1. Determination of the factor of combustibility K of coatings of coatings of single-base propellant SBP with polymers, co-polymers and oligomers

Test №	Composition of mixture	Ratio [%]	Dry substance [%]	Content of halogen [%]	Factor of combustibility **K**
1.1	SBP + EOB	80 : 20	13	Br 1,08	combustible
1.2		60 : 40	13	Br 2,16	self-extinguishing
1.3		40 : 60	13	Br 3,24	**high-flammability point**
2.1	SBP + EOB + hardener*	80 : 20	13	Br 1,06	combustible
2.2		60 : 40	13	Br 2,10	self-extinguishing
2.3		40 : 60	13	Br 3,12	self-extinguishing
2.4		20 : 80	13	Br 4,25	**high-flammability point**
3.1	SBP + EOB + D600	20 : 40 : 40	25	Br 4,16	self-extinguishing
4.1	SBP + D600 + CP	20 : 80 : 10	25	Cl 1,71	self-extinguishing
4.2		20 : 80 : 20	25	Cl 3,20	self-extinguishing
4.3		20 : 80 : 30	25	Cl 4,33	**high-flammability point**
5.1	SBP + D600 + PCV	20 : 80 : 12	25	Cl 1,96	self-extinguishing
5.2		20 : 80 : 18	25	Cl 2,78	**high-flammability point**
6.1	SBP + D600 + CR	20:80:20	25	Cl 1,67	self-extinguishing
6.2		20 : 80 : 40	25	Cl 2,87	**high-flammability point**

* The hardener used was toluene 2,4- diisocyanate (

Data in table 1 show that with the increase of halogen the concentration resistance against combustion rises also. Halogen-containing polymers decompose themselves and form halogens, halogen-hydrogen or halogen carbon-hydrogens, which expose their protecting effect in the gaseous phase mainly.

Due to the higher atomic mass of Br, the number of HBr molecules is lower than the number of HCl molecules for equal percent content of halogen. This explains the fact that comparatively low contents of halogen achieve a certain good effect, which is evidently shown for mixtures 1.2, 6.1 and 2.2, 5.1.

The other explanation is based on the structure of halogen-containing polymers or oligomers. Chlorine in the polymer is bound to a carbon atom of aliphatic molecule, while Bromine is bound to a carbon atom of aromatic core. It is known that the length of C-X bound in the first case is longer, therefore an atom Cl will easily separate and form HCl. On the contrary, the C-Br bound in EOB is shorter and atom of Bromine will separate with more difficulty as HBr, under same conditions.

Evaporation of solvent also effects on properties of spontaneous extinguishing – see mixtures 5.1 and 6.1 in the table. Evidently, the liberated quantity of solvents is higher for these mixtures. Data reveal that the combustibility of coating with lower content of halogen has a value analogous to the factor of combustibility K of coating, obtained from mixtures, characterized with lower speed of evaporation of solvents.

It might be suggested that type of combustibility of coating of single-base propellant SBP+polymer depends on the concentration, energy of tearing of X-X, H-X, C-X bonds, density of gases or vapours, temperature of evaporation and other less important factors. With the decrease of energy of binding in halogen-hydrogen, the density of vapours increases. This increases the concentration of non-combustible gases of the film surface, which starts in the initial stage of combustion and brings to reduction of the probability of firing.

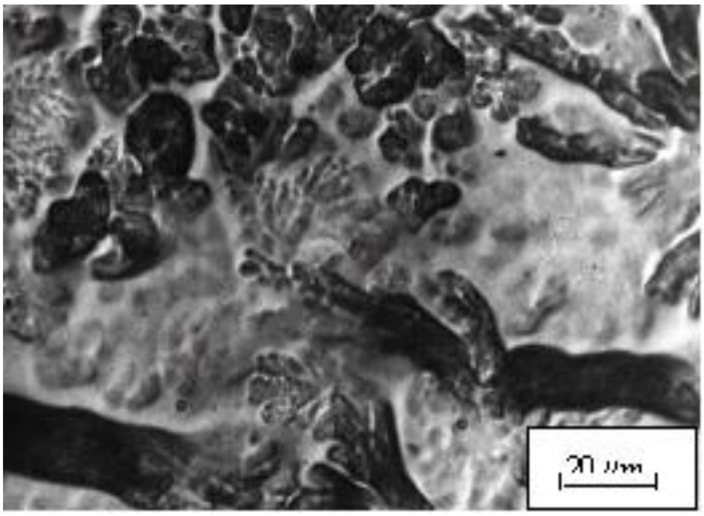
Inhibiting from active centres, able to form meshes in the beginning of destruction is possible. Other centres may impede the interaction between active radicals and macromolecules of pyroxiline or products of destruction, thus reducing the concentration of combustion gases. Meshing of coatings (mixtures 1.3 and 2.3) evidently makes difficult the evaporation of solvents, and this brings to reduction of the efficiency of selected polymers. For those mixtures, content of bromine is analogous, but mixture with hardening agent is spontaneously extinguishing, and without hardening agent is low combustible.

Results correlate to the data of Radhakrishnan G. (1992), but mixture of nitrocellulose with other polymers are used there. The above investigations are one more proof that polymers may be used to regulate the required safe combustibility of explosive compositions.

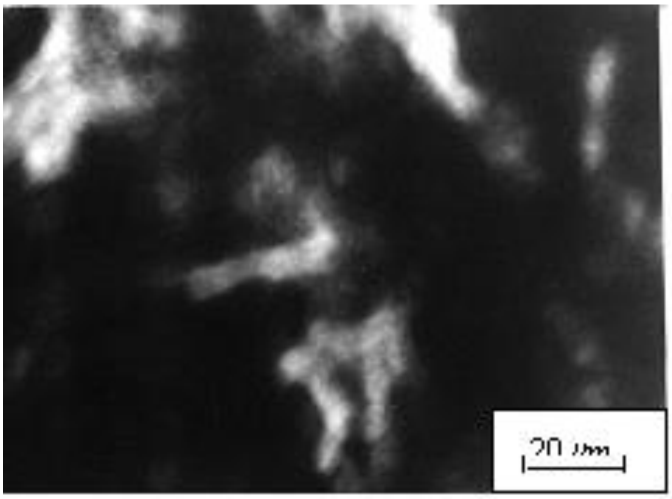
When single-base propellant SBP is mixed with a non-crystallizing polymer in a 1:1 ratio in CX as a solvent, even an amorphizing of films is not observed. (Fig. 1).

The microscopic photoes reveal the difference between over-molecule structures obtained from SBP+PCV (Fig.1a) and SBP+ПВХ (Fig.1б).

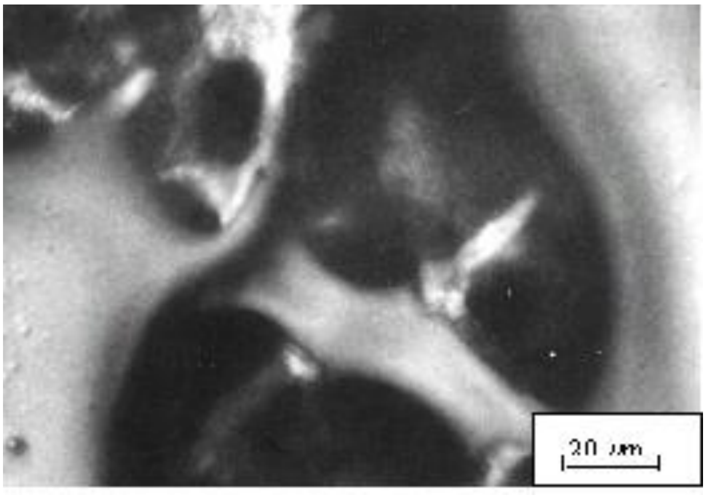
Over-molecule structures of 10 μm size are registered due to the amorphizing of film of single-base propellant under the action of PCV .For the mixture of SBP+PCB over-molecule formations are even heavilty amorphized.



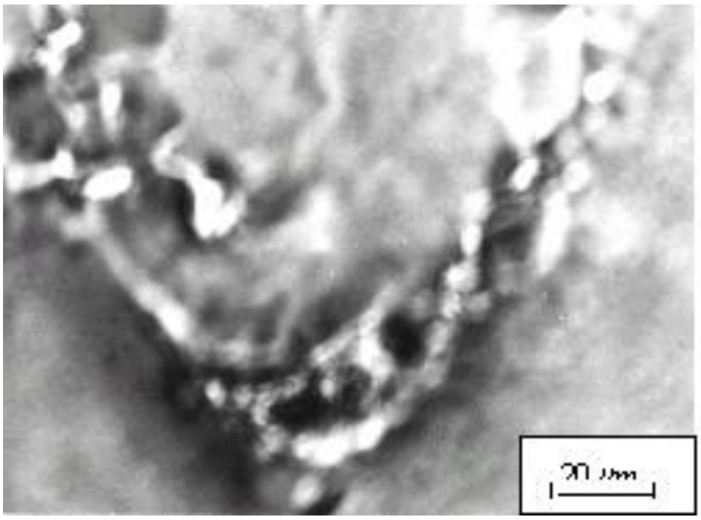
a) SBP+PCV $(\times 560)$



b) (ЕЦ + PCV) $(\times 560)$



c) SBP + D600 $(\times 560)$



d) *SBP + PVB* $(\times 560)$

Figure 1. Microscopic photoes of films of the analyzed mixtures

Films of mixtures SBP+D600 (fig.1в) and SBP+PVB (fig.1г) have images of irregular shapes and show even an amorphizing of initial SBP. Amorphied fields surround the crystal structures. In those fields the macromolecules show increased movability, and crystal formations show lower volume.

There is no layering in the microscopic photoes, which is a proof for the thermodynamic compatibility of SBP with analyzed polymers, co-polymers and oligomers.

CONCLUSION

Analysis of results from determining the factor of combustibility K, from differential-scanning calorimetry and microscopic observations revealed that safe combustibility of explosive mixtures of propellant and polymers may be controlled effectively.

This conclusion proved the possibility for industrial modification of combustibility of produced single-base propellant for successful practical application into other non-military sectors, mine and quarries including. Improved safety of transport, storage and use will be a fact. The manufactured industrial product plastic or solid, depends on the requirements of technology, where it will be applied.

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TOXIC GASES AT INDUSTRIAL BLASTING OPERATIONS. NORMATIVE REQUIREMENTS AND RECENT RESULTS

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SUMMARY

The objective of the present paper is the problem with the emission of toxic gases as a result of blasting operations in the mining, construction and other industries and the affect of their release on the environment. The presented problem has wide implications as extensive blasting operations are performed almost everywhere. Based on the new methodology developed through the contract with the American Agency for International Development for measuring the quantity of the toxic gas emissions, new results have been obtained with the performance of extensive testing as the factor constricted conditions have been eliminated. The obtained results pose very seriously the question for solving the problems associated with toxic gases emissions, which substantially deviate from the approved and circulated in the technical scientific literature. Those problems are to be solved in the future.

The conducted tests and investigation of the industrial blasting agents permitted for use in Bulgaria indicate that their parameters are not compliant with the legal requirements in Bulgaria namely with the Ordinance for labor safety in blasting operations -- 1997:

1. All safety explosives exceed the standard for toxic gases up to 100 litters and are in the range from 93 to 183 l/kg of explosive.
2. All explosives of second degree for underground mines not hazardous for gas and dust as well exceed the norms and are in the range form 165 to 215 l/kg of explosive (excluding Elazit 710)
3. The majority of the explosives used in surface blasting operations as the explosives type ANFO and emulsion explosives emit more toxic gases 222-275 l/kg of the regulatory determined 200 l/kg at usage of the Bulgarian produced ammonium nitrate. Less toxic gases are being emitted when the more expensive porous imported ammonium nitrate is used 165 l/kg.

The current paper deals with the issue of toxic gas emissions resulting form industrial blasting operations in the mining, construction and other industries and their impact on the environment.

As it is widely known, blasting operations are extensively used in all sectors of the economy. The blasting energy is the cheapest which people use in their activity. Historically blasting operations have been extensively used for excavation of inert materials and mineral exploration. Now days we could hardly imagine production process at underground and in particular surface mining operations at ore mines and quarries and in the construction industry, not involving blasting. This extensive use of explosives and blasting operations, however, inevitably poses some environmental issues as the not completely controlled negative effects of blasting, the seismic effects, extensive fuming among many others.

Here is an example that would demonstrate the importance of the problem. Few years ago at quarry Sheremetia, Veliko Turnovo during detonation of about 18 t explosive (medium size blasting) in perimeter with diameter of about 10m above the pile of blasting agents few hours after the explosion at second explosion seven people die. At a distance of 3-3,5 km from the quarry and the adjacent region 36 people staff and bystanders suffer poisoning of different degree.

According to the municipal authorities of the city of Panagurishte the problem with systematic ecological pollution with gas and dust emitted through the blasting operation in the quarry above Panagurishte is up to 50 t explosives detonated at once.

Similar disturbing signals have being received from many communities surrounding open pit mines and quarries. The impact of such events is visible in the tremendous destruction of flora and fauna in their vicinity and on people living in the area regardless of whether employed in the industry or not. The problem reaches global dimensions taking into account that extensive blasting operations are performed almost everywhere.

The phenomenon explosion represents very rapid transformation of energy. In particular, the commonly used chemical components in Bulgaria that undergo rapid burning are C and H, as the process according to the classical literatures could be represented as follows.

$$\begin{tikzcd} C+H+N+O \arrow[r, "\text{Blast}"] & CO_2 \arrow[d] & + H_2O + & N_2 \arrow[d] \\ & CO & & NO_x \end{tikzcd} \qquad (1)$$

This chemical composition releases from 600 to 1000 litters gases from 1kg explosive at temperature in the range of 2500 to 4500^0 C and pressure 200-300 MPa. At those parameters part of C is transformed into the toxic CO, whereas N_2 transforms into nitrogen oxides NO_X. It is a common practice in the blasting technology to convert the nitrogen oxides NO_X into conditional carbon monoxide as the nitrogen oxides NO_X are equated to the poisoning action CO as the liters of NO_X are multiplied with the coefficient 6,5.

$$\text{cond.CO} = 1\text{CO} + 6.5\ NO_X \ \text{l/kg} \tag{2}$$

Of the emitted 600 to 1000 litters gases from 1 kg explosive, 100-120 to 350 litters are toxic gases.

The factors contributing to the emission of toxic gases during blasting operation are varied. However they could be grouped in four major classes:

1. Explosive is said to have an oxygen balance when the burning elements C and H equal the quantity of O_2. It is well known that an explosive with the so called zero oxygen balance release the least toxic gases, whereas explosive containing slack or excess of oxygen emits more of both CO and NO_X.
2. The physic-mechanical characteristic of the explosives as homogeneity (density), granular-metric composure, water resistance, packaging and others. Each inconsistence of the explosive's characteristics with the standardized requirements set forth during its development leads to distortion of the detonation process and to the larger release of toxic gases.
3. The chemical composition, strength, and structure of the rock. When detonating rocks with fissures and cracks, whether filled with clay materials or not, the released toxic gases are substantially larger.
4. The technology of the conducted blasting operation and the manner and tools of initiation of the charges. Our investigation suggests that this factor is even more important in regard to toxic gas emissions than the oxygen balance, considered being most significant up till now.

We are able to knowingly influence the listed group of factors through the selection of the blasting agent for conducting blasting operations as well as through development of legal basis preventing the usage of explosives emitting large quantities of toxic gases. We could also influence the problem through the application of new technology through complex mechanization of the blasting operations.

Let us have a look at the current state of affairs.

I. The ordinance for work safety prohibits the usage of blasting agents with oxygen balance different from the standard zero, as the regulatory allowable quantity toxic gases to be emitted from 1 kg explosive is 100l. While this standard seeks to achieve very desirable level of gas emissions it is highly unattainable and unrealistic. In Bulgaria, in all sectors of the economy, we continue to use outdated technology and hand set cartridges, able to achieve density of 0,6 g/cm^3 at ammonium nitrate explosive materials to 0,8 g/cm^3 at TNT explosives. This small density cannot achieve the necessary velocity of detonation, which results in larger quantities of toxic gases emissions. It is imperative that all facilities, where possible, switch to bulk emulsions and mechanization of the blasting preparation and process.

II. The situation in surface mining is catastrophic due to the lack of normative base until recently. Numerous open-pit mines and quarries still employ explosive materials with highly negative balance e.g. explosive type "Granutolol", which emits 360 CO/kg. Moreover at single mass detonation of 50 tons, in the environment are released at once approximately 18 million litters CO. According to the newest industrial testing, the predominantly used blasting agent in Bulgaria type coarse ammonite emits from 103-to 201-l/kg conditional CO.

Of most significant importance at surface mining is the extensive application of the technology for demolition of over sized rocky pieces with open charges. The relative expense of explosive materials is over twice larger and the blasting ineffective leading to large-scale pollution of the environment.

Through the contract with the American Agency of International Development – EcoLinks we have developed a new technology for environmentally friendly blasting operations designed for demolition of large size rocky pieces. The technology uses classical cartridge explosives types Amonit and Lazarit and new charge construction with cumulative action build up at place of application. Its implementation has achieved double reduction of the toxic gases emissions resulting from the blasting as the effectiveness of demolition of the oversized rock has been considerably improved. The technology is currently available at quarry Skakavtisa, part of the Bulgarian State Railway Company (Kamburova, G. & Lazarov S.,2001).

Currently, in Bulgaria for industrial applications are used over 20,000 tons explosive materials at which detonation are emitted about 3 billions litters toxic gases. By solving some of the existing technological and regulatory problems we would be able to reduce this toxic emission over 2-3 times up 1,5 billion litters.

The minimization of these toxic emissions could be achieved through:

1. New explosive material recommended for wet applications. The basis for this technical solution is the experience of developed countries, namely Switzerland, USA, and Germany in their use of explosives types Emuliti, consisting of water oil emulsion of ammonium nitrate (dense water solution with oil). Those blasting agents are water resistant and do not contain any materials classified as explosives (TNT, nitroglycerin) in clean form. They are very safe and emit 70-275 l/kg toxic gases of one kg explosive, could be loaded with equipment or manually when necessary, and are designed for both surface and underground mining. At present Bulgaria is capable of producing those blasting agents at Elazite and Asarel Medet.
2. In dry environmental conditions transition to explosives type ANFO in surface as well in underground mining with complex or partial mechanization of the blasting operations.
3. Reconsidered should be the data for toxic gases and the applicable regulatory norms. Oт Through the contract with AAID-Ecolinks developed was new methodology for

determination of toxic gases. As a result of extensive testing obtained were new data as the factor narrowed conditions, compared to the normative documents, was eliminated. The charges of the utilized blasting agents weighted 400-1000g, instead of the 10 to 40 grams as prescribed in the normative methods used in Bulgaria. The tested probes of explosives were placed in the mortar in metal tube and for comparison in free hanging condition in plastic folio. This methodology enables us to conduct testing in condition very close to reality.

The preliminary results of the conducted tests emphasize the necessity of finding solution for toxic gases, the emission of which greatly diverge from the currently accepted and circulated in the technical literature. Those problems are yet to be solved. Based on the conducted testing, however, we could state with certainty that the majority of the admitted for use industrial explosives in Bulgaria do not comply with the requirements of the Ordinance for Labor Safety in blasting operations (1997), namely:

1. All Powder Safety Explosives emission of toxic gases exceed the regulatory norms up to 100 l and are from 93 to 183 l/kg explosive.
2. The toxic gases release of all explosives of class II, for use in underground mines not dangerous for gas and dust exceed the regulatory determined ones and are from165 to 215 l/kg. (excluding Elazit 710).
3. The majority of the explosives used in surface mining as explosives type ANFO and emulsion explosives emit more toxic gases– 222-275 l/kg than the regulatory allowed -200 l/kg when mixed with ammonium nitrate production of Neohim, Dimitrovgrad. The quantity of the toxic gases is much less (165 l/kg) when the blasting agents are prepared with the significantly more expensive imported porous ammonium nitrate.

The conducted investigation suggests the need for improvement and modification of the regulatory requirements for monitoring the production of explosives in regard to toxic gases. Specifically we advise that the calculations are based on the assumption that toxic gas emission is over 150 l/kg, and not less than 100 l/kg, as it was considered till now.

As the results obtained by the new methodology for measurement of toxic gas emissions for industrial purposes suggest, new regulatory requirements are necessary for the allowable emission of toxic gases for all industrial explosives whether they are used for surface or underground conditions.

Through the application of alternative technological solutions we would be able to perform extensive blasting operations that are acceptable from environmental standpoint.

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DRAWING UP INTEGRATED MECHANIZATION STRUCTURES FOR HUMUS LAND RECLAMATION IN COAL MINING

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ABSTRACT
Integrated mechanization structures for land reclamation have been drawn up, analyzed and compared with existing ones for particular conditions of humus layer removal and technical reclamation at Maritsa East mines.

Mining and civil construction on agricultural land (categories 1-6) is carried out only after the humus layer has been removed in accordance with the Farm Land Protection Act. It is removed from the ground except in areas envisaged for afforestation, cemeteries, sanitary protection and other zones. When the humus layer thickness is less than 0.20 m, it is not removed. The humus layer stripped from lands and planned for constructing mines, quarries and engineering structures, is used for reclaiming those lands or other disrupted ground.

The conditions under which the lands are disturbed predetermine the application of various integrated mechanization structures for land reclamation.

The concept **integrated mechanization structure** for land reclamation involves the integration of various types of machines required for the humus layer removal and technical reclamation. According to Rzhevski (1968), integrated mechanization structures are formed on the basis of maximum integration of the *output and power* parameters of each machine with observing the technological requirements to the implementation of technical reclamation.

On the basis of observations and analysis of the conditions and factors for implementing the technical and biological reclamation in open-pit coal mines in Bulgaria and abroad, we can draw up the following integrated mechanization structures for land reclamation under Bulgarian conditions of humus layer removal within the open-pit mine (Fig. 1).

Fig. 1 shows that the integrated mechanization structure generally involves a set of serially produced mining, construction and load-haul-dump machines used for removing, loading, transporting and spreading the humus material. The complexity of selecting the integrated mechanization structure results from the possibilities for applying various types of mechanization with continuous and cyclic operation.

The reclamation of disturbed ground is carried out by two schemes: direct and indirect (Fig. 2).

The integrated mechanization structures in the first scheme include combinations of basic machines with continuous operation. They permit the selective overburden and humus layer removal with simultaneous spreading over reclaimed ground. This scheme requires the storage of humus directly on the ground or in temporary humus sheds. When using tractor mechanization (bulldozers, scrapers, graders, etc.), intermediate humus sheds are often established where the soil is loaded and transported to the reclaimed land areas (Fig. 3).

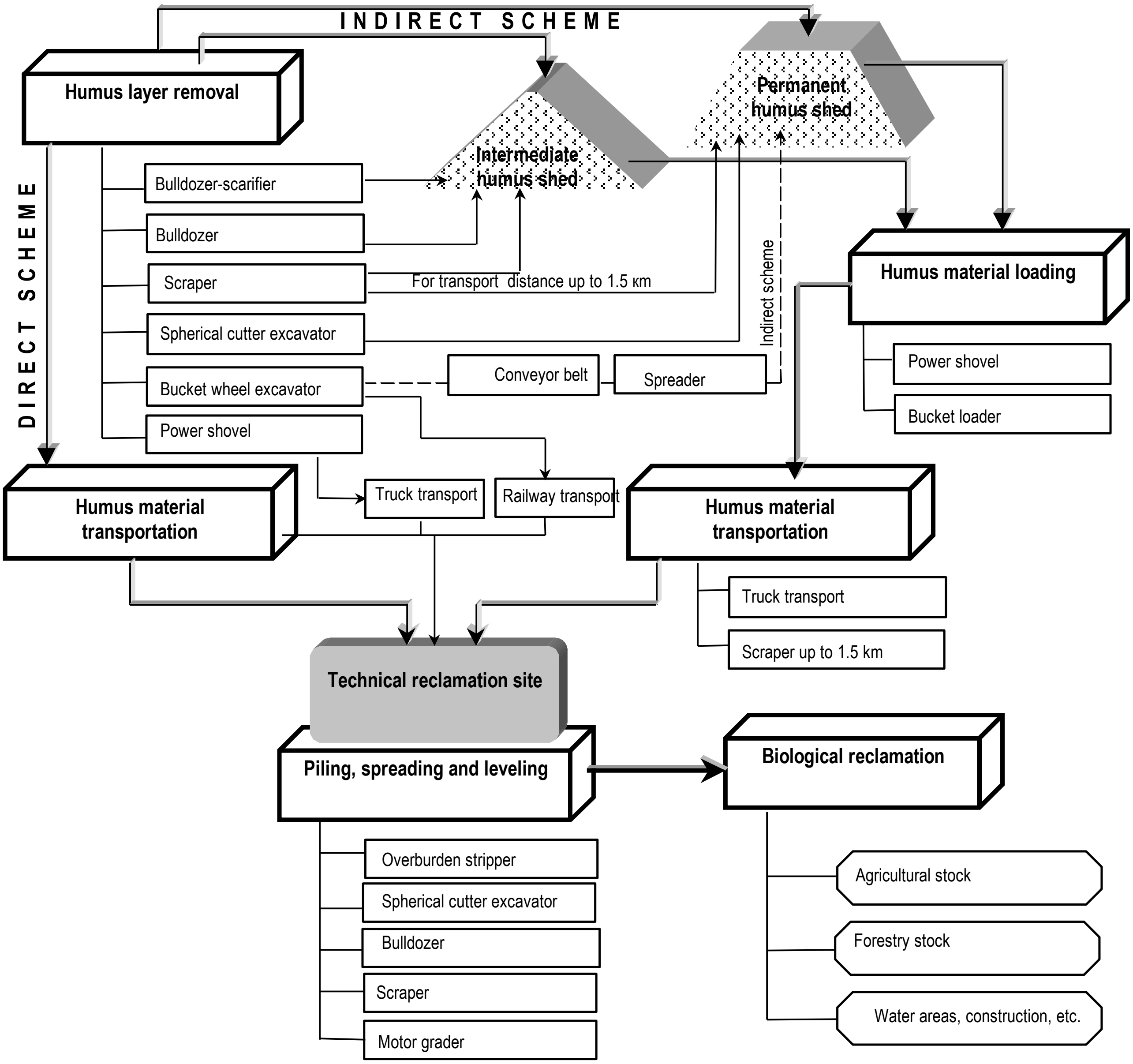

Figure 1. Integrated mechanization structures for humus layer reclamation of coal basins

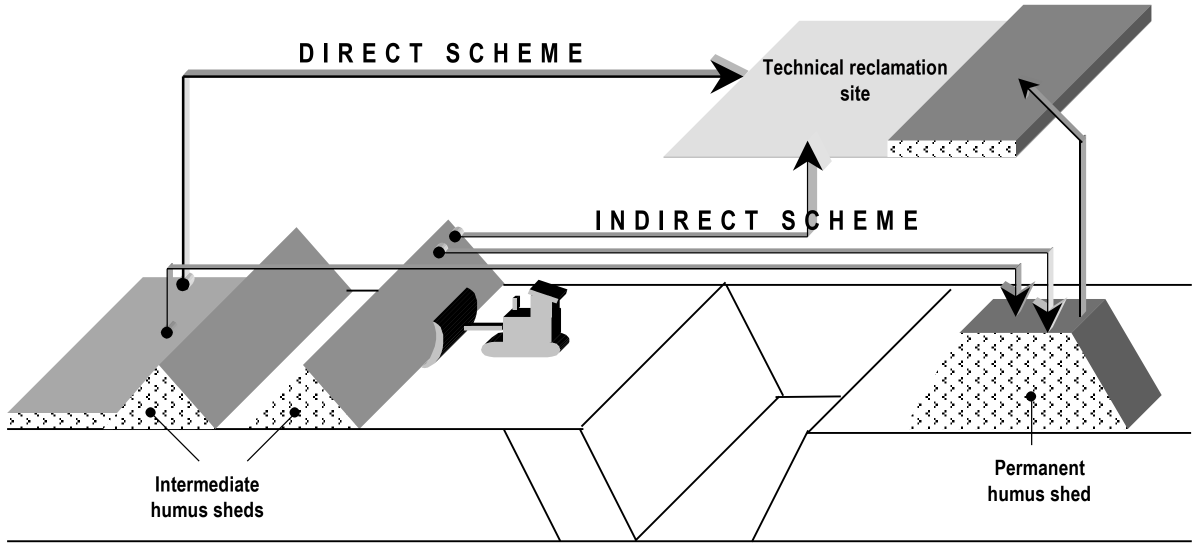

Figure 2. Direct and indirect schemes of technical reclamation

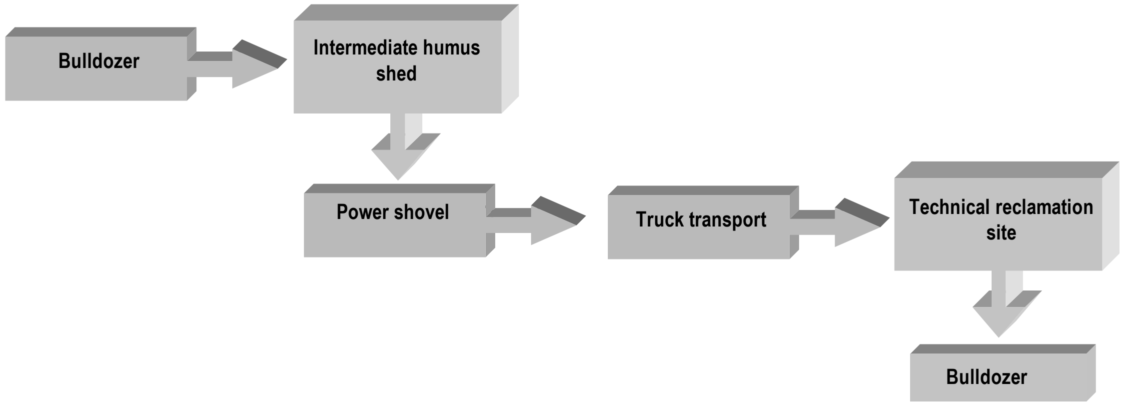

Figure 3. Integrated mechanization structure with establishing intermediate humus sheds for the indirect reclamation scheme

The efficiency of excavation, dumping and reclamation works decreases when using tractor mechanization with increasing the transport distances to the reclaimed areas. This problem has been identified particularly in reclaiming the disturbed ground of Maritsa East mines. Its solution is based on using mining mechanization for removing the humus layer. As a result, specific integrated mechanization structures have been drawn up for those conditions (Figs. 3 and 4).

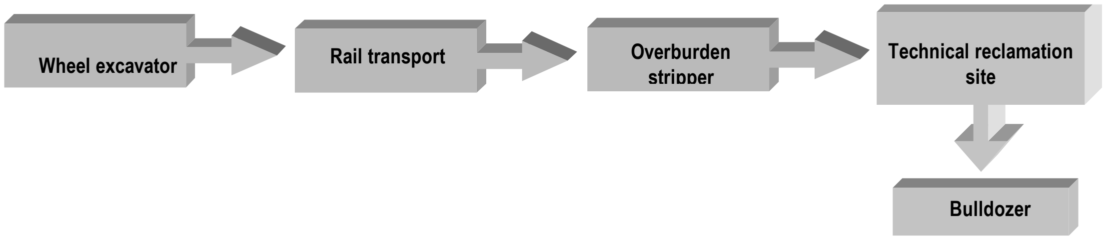

Figure 4. Integrated mechanization structure using basic mining machines and railway transport

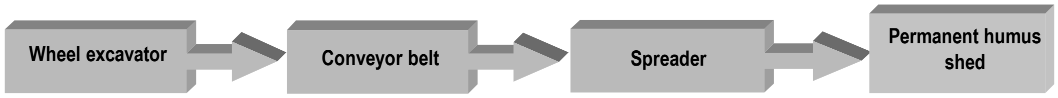

Figure 5. Integrated mechanization structure using basic mining machines and conveyor transport

Serious problems for the reclamation works are the irregular distribution of the potentially fertile and fertile soil volumes in time and the lack of lands ready to be reclaimed. During the first coal mine development stage the humus removed is maximum in volume. At that stage there are no conditions for implementing and completing the whole set of reclamation works. This circumstance calls for the need to build temporary humus sheds (indirect scheme – Fig.1), which determines the formation of new integrated mechanization structures. They involve both ancillary and basic mining mechanization depending on the particular conditions (Fig. 5).

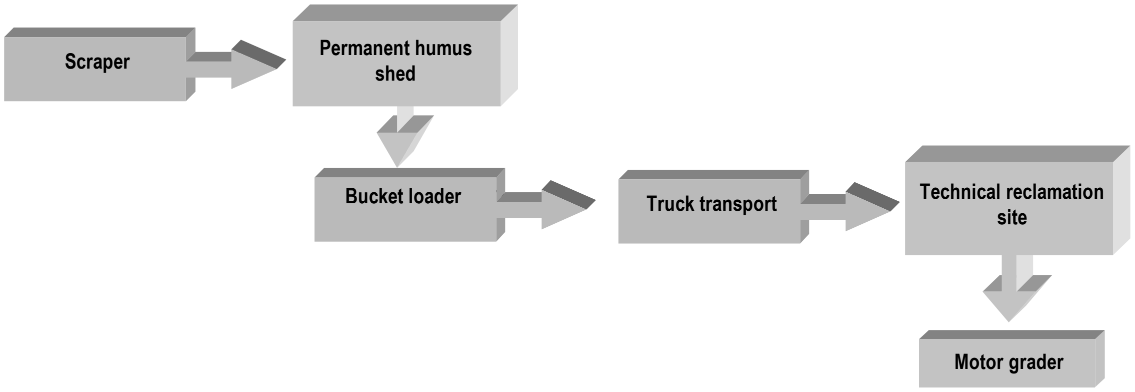

Figure 6. Integrated mechanization structure with establishing temporary humus sheds for the indirect scheme of land reclamation at Maritsa East mines

The proposed systematization of the integrated mechanization structures comprises the existing and prospective combinations of machines for performing basic operations in humus layer removal and technical land reclamation. Its can be used both for drawing up new integrated mechanization structures and for analyzing and comparing the existing ones, by observing the following sequence:

- during the first stage of humus layer removal are included those structures that can be used depending on the technical, technological or natural factors and conditions;
- the variants of integrated mechanization structures are compared in terms of price, output, relative capital costs and energy consumption;
- a feasibility study of the integrated mechanization structures is carried out for the whole technical reclamation stage with rational qualitative combination and quantitative correlation of machines designed for removal, loading, transportation and utilization of the humus material; the most efficient variant is selected.

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GENERATION OF POLLUTED DRAINAGE WATERS FROM SLAG AND SLIME DUMPS IN A STEEL – MAKING PLANT

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ABSTRACT

Slag and slime dumps constructed in the Kremikovzi steel-making plant, Western Bulgaria, after rainfalls were as source of heavily polluted drainage waters. The dumps were characterized by high content of several heavy metals (Fe, Pb, Zn, Cd, Cu) and arsenic. Significant portions of these components were present in forms amenable to biological and / or chemical leaching under aerobic and / or anaerobic conditions. Different chemolithotrophic and heterotrophic microorganisms inhabited the dumps. Some sulfate, oxide and carbonate minerals of the above-mentioned metals and arsenic were leached by secreted microbial metabolites, mainly organic acids. Iron oxide minerals were solubilized also by enzymatic microbial reduction of the ferric iron. Sulfide minerals were oxidized, although at low rates, by some chemolithotrophic bacteria.

The relatively low rates of pollutants solubilization in the dumps were due mainly to the low content of carbon and energy sources and nutrients (mainly N and P) for indigenous microorganisms.

Key words: waste , mobilization, toxicity

INTRODUCTION

The steel-making plant “Kremikovzi” is situated in Sofia valley, 18-km northwest from Sofia City. The plant has been built on the south slope of the Balkan Mountain and its total area is about 830 ha. This area is characterized by continental climate (the average annual temperature is 9.9° C, the average annual fall is 640 l/m^2).

The technogenic wastes generated from different operations have been deposited in three 3 dumps:

1. The slag dump is situated northeast from the plant at a 1-km distance. The slags are from steel-making units, and their transportation is by trucks.
2. The slime dump is situated southeast from the plant. The pulp has been produced from different sources: a coke-oven, a steel making, a blast furnace processing and a cold rolling unit. It has been transported to the slime dump by hydro-transport. The effluents from the slime dump are treating by means of a local clean-up operation and then are returned to the relevant processing units.
3. The tailing dump is situated southwest from the plant and consists of slurryies from an Agglomeration processing unit.

The purpose of this study was the risk assessment by means of some modern methods for characterization of the materials deposited in the dumps as a result of the processing in steel-making plant “Kremikovzi”. These data will reveal the main mechanisms for metal mobilization from the technogenic wastes and the quality of the generated drainage waters.

MATERIALS AND METHODS

A detailed sampling procedure was used to characterize the wastes and drainage waters from slime and slag dumps. The concentration of dissolved metals were determined by ICP, the concentration of cyanides, phenols and ammonium were determined by suitable spectrofotometric methods (DIN 38405, DIN 38409, DIN 38406 relevance). The concentration of dissolved oilproducts were determinated by spectrophotometer Horiba at λ = 262 μm after a preliminary extraction with chloroform. The solid samples taken from the slime and slag dumps were characterized by a high content of heavy metals and toxic elements (Table 1).

Table 1. Data about the content of heavy metals and toxic elements in technogenic wastes from the steel-making plant

Elements	Type of wastes	
	Slag	Slime
Pb, mg/kg	23,7	29500,0
Zn, mg/kg	35,1	13200,0
Cu, mg/kg	20,2	333,0
Ni, mg/kg	47,8	93,6
Fe, %	1,20	28,3
Mn, mg/kg	356,0	8885,0
As, mg/kg	17,4	26,1
Co, mg/kg	1,6	11,3
Cd, mg/kg	< 1,0	103,0

These materials were characterized by neutral to slightly-alkaline pH (7,76 for materials from the slime dump and 8,65 for materials from the slag dump), which was a result from their acid-neutralization properties (Table 2).

The biogeochemical forms of heavy metals and arsenic in solid samples, were determined by means of a sequential extraction procedure (Tessier et al., 1979).

Table2. Data about the acid-neutralization properties of the wastes

Parameter	Type of wastes	
	Slag	Slime
Carbonate content$^-$, %	6,38	10,2
S total, mg/kg	297,0	6312,0
S sulphidic mg/kg	200,0	5411,0
Acid generation potential, kg $CaCO_3$/t	0,625	16,91
Neutralization potential, kg $CaCO_3$/t	78,11	210,45
Net neutralization potential, kg $CaCO_3$/t	77,45	193,50

The role of microorganisms in the processes of mobilization of the different elements was studied by means of laboratory tests. These tests were as follows:

1. Control test - material from technogenic wastes and distilled water;
2. As test 1 plus addition of assimilable forms of N, P, K;
3. As test 2 plus addition of easily assimilable carbon and energy source for heterotrophic microorganisms (0.25 % glucose + 0.25 % peptone);
4. As test 2 plus addition of easily assimilable forms of carbon and energy source for heterotrophic microorganisms (0.5 % glucose + 0.5 % peptone);
5. As test 2 plus addition of easily assimilable forms of energy source for chemolithotrophic microorganisms (2 % $S_2O_3^{2-}$).

These tests were carried out in 500 ml flasks, at a pulp density of 5 %, room temperature (25 °C) and a permanently agitation (150 rpm). Their duration was 7 days, and after this period the liquid phase was separated by centrifugation. The concentration of dissolved metals was determined after solid removal.

The characteristics of the generated drainage waters from the dumps was done by the EPA Toxicity Characteristics Leaching Procedure (US EPA 1990).

RESULTS AND DISCUSSION

The water samples from the slime dumps were characterized by a nearly alkaline pH, which was a result of the carbonate-bicarbonate buffering system and of the high content of dissolved ammonium ions. The oilproducts, phenols, and cyanide and ammonium ions were in concentrations higher than the relevant permissible levels (Table 3).

These compounds are powerful complexing agents, and as a result of that, the concentration of dissolved iron was 74.3 mg/l, although the pH was alkaline (8.67). On the other hand, these results showed that the concentrations of heavy metals and toxic elements are below the permissible levels for industrial waters. The data about the effluents from the treatment plant revealed that the concentrations of dissolved phenols, cyanides, oilproducts, ammonium and iron were higher than the permissible levels. The clear differences in the concentrations of these compounds had an effect on the processes of biological oxidation, which were carried out by different groups of microorganisms. For example, the oxidation of organic compounds was connected with the formation of organic acids, which solubilized heavy metals from the technogenic wastes and formed stable complexes with the relevant metal ions. As a result of this, their concentrations were slightly increased in the treatment plant effluents.

Table 3. Data about the properties of water samples from steel-making plant

Parameter	Pregnant water to the slime dump	Pregnant water from the slime dump
1. pH	8.67	8.42
2. Eh, mV	+57	+132
3. t°, C°	30.2	31.2
4. Total dissolved solids, mg/ l	1100	970
5.Slime particles, mg/l	2100	67.3
6. $KMnO_4$ oxidativity, mgO_2/l	256	65.6
7. Hardness, meq/l	5.3	6.8
8. Alkalinity, mmol/l	9.8	7.5
9. SO_4^{2-}, mg/l	121	223
10.Cl^-, mg/l	14.8	14.3
11.CN^-, mg/l	12.7	3.6
12.Phenols, mg/l	0.38	0.2
13.Oilproducts, mg/l	36.4	9.3
14. NH_4, mg/l	42.3	19.5
15. Ca, mg/l	543,0	609,0
16. Mg, mg/l	42,0	56,3
17. Pb, mg	0,13	0,18
18. Zn, mg	3.6	5.3
19. Cu, mg/l	0,26	0,34
20. Ni, mg/l	0,004	0,006
21. Fe, mg/l	74.3	3.7
22. Mn, mg/l	0,270	0,12
23. Cd, mg/l	0,004	0,004
24. K, mg/l	11,3	11,3

The results from the sequential extraction procedure revealed that the distribution of heavy metals and arsenic into different fractions, depended on the mechanism of formation of the relevant technogenic waste, the element specificity and the conditions during the storage of wastes. (Table 4).

The basic forms of lead at the slag formation are galena (PbS), PbO_2 and complexes with residual organic compounds. As a result of the processes of oxidation, secondary minerals as Pb $(OH)_2$ and $PbCO_3$ are formed. They are dissolved at high concentrations of non-organic (exchangeable fraction) or organic (carbonate fraction) ligands in the solution. On the other hand, the high temperature during the formation of coke led to entrapping of the Pb in the slime, mainly as an inert and a reducible fractions. The reducible fraction of heavy metals and toxic elements is associated mainly with oxide – hydroxide minerals of iron and manganese.

Table 4. Data about the forms of lead, zinc and copper determinate by means of a sequential extraction procedure

Pb	Type of waste			
	Slag		Slime	
Fractions	mg/kg	%	mg/kg	%
exchangeable	0.02	0.1	19,01	0,24
carbonate	2.94	12.4	2,50	0,03
reducible	2.98	12.56	3051,6	38,05
oxidizing	14,80	62,46	57,72	0,72
inert	2,96	12,48	4890,2	60,96
total	23,70	100,	8020	100,0

Zn	Type of waste			
	Slag		Slime	
Fraction	mg/kg	%	mg/kg	%
Exchangeable	2.04	5.81	16.54	0.65
Carbonate	7.13	20.32	6.59	0.26
Reducible	7.93	22.59	631.07	24.87
Oxidizing	3.17	9.02	65.74	2.59
Inert	14.83	42.26	1819.5	71.63
Total	35.10	100,00	2540.0	100,00

The zinc is presented in the samples under study mainly as an inert and a reducible fractions. The metals associated in the inert fraction are compounds with a silicate mineral structure and for their solubilization was the longest period of time necessary. A relatively high content of Zn in the slag is presented as ZnO and $ZnCO_3$ (carbonate fraction) and as ZnS (oxidizing fraction). The exchangeable and carbonate fractions are mobilized for shorter period of time with comparison to the other fractions.

The microbiological analysis showed the presence of different groups of heterotrophic microorganisms (bacteria, fungi, streptomycetes), catalyzing oxidation of the organic compounds under aerobic and anaerobic conditions. Chemolithotrophic bacteria oxidizing the reducible forms of sulfur, iron and nitrogen were also present.

The results from the biogeochemical tests revealed that the relative mobilization of heavy metals and arsenic depended on their mineral forms, the activity of the indigenous microflora, and the levels of limiting factors of the environment (Table 5). The water soluble forms of these elements are average 6 – 10 time higher in the slag in comparison with slime wastes (test 1). The microbial activity increases as a result of the addition of easily assimilable forms of potassium, nitrogen and phosphorous in the solution. On the other hand, the relatively high concentrations of dissolved potassium and nitrogen in the effluents from the slime dump showed that these elements had no effect on the microbial activity. As a result of this, a high increase in the mobilization of these metals (test 2), in comparison with the previous test, was not observed.

An addition of easily assimilated organic compounds stimulated the activity of the heterotrophic microorganisms (test 3 and 4) and accelerated the leaching processes. The organic compounds were mineralized, which led to liberation of the metals complexed by these compounds. As a result of this their mobility in the environment was increased. These processes are more intensive under aerobic condition and for this reason the element parts susceptible tor such transformation are grouped also in the oxidizing fraction. High concentrations of organic compounds were degraded, which was connected with the consumption of dissolved molecular oxygen. As a result of this, the conditions in the environment changed to anaerobic, which stimulated the relevant heterotrophic microorganisms. These processes, led to a low level of redox potential, reduction and solubilization of the oxide forms of iron and manganese. This was connected with the liberation of the heavy metals and toxic elements. The presence of these elements in dissolved forms depends on the concentrations of complexing agents in the environment. These processes was intensive in the slime dump, where the humidity of deposited materials was high and the effluents contained high concentrations of complexing agents – oilproducts, phenols, and cyanides and etc.. The processes of mineralization of the organic compounds were connected with the formation of organic acids, which solubilized the heavy metals.

Table 5. Data about the relative role of the main mechanisms of mobilization of heavy metals and As from the wastes produced by the steel-making plant

TEST	Slag				Slime			
	Percent of leaching, %							
	Pb	Cu	Zn	As	Pb	Cu	Zn	As
1.	3.7	0.4	0.4	2.9	0.4	0.2	03	0.2
2.	3.8	2.2	14.3	5.1	0.7	0.3	0.5	0.64
3.	8.44	18.9	16.6	10.3	1.33	1.7	1.8	0.2
4.	13.9	32.8	25.6	13.4	1.8	3.1	2.5	0.3
5.	37.6	68.0	66.7	64.1	0.4	0.3	5.7	5.3

These results show that the relative role of the heterotrophic microorganisms in the processes of mobilization of heavy metals and arsenic depends on the initial concentration of the easily assimilated organic compounds.

An addition of easily assimilated source of energy as $S_2O_3^{2-}$, stimulated the activity of the basophilic chemolithotrophic microorganisms, which oxidized the reducible forms of sulfur in the wastes (test 5). The acidity generated during this process was neutralized by the high content of carbonates. The efficiency results of metal leaching depended on the geochemical characteristics of the relevant elements. For example, the low concentration of dissolved lead was result from the formation of $PbSO_4$. On the other hand, the high zinc extraction was a result from the formation of well soluble products. The relative role of chemolithotrophic micro-organisms in the filed conditions depends on the penetration of oxygen in to the depth of the deposited materials.

These results showed that the combination of some environmental factors (temperature, humidity, forms and concentrations of the energy and carbon source), lead to leaching of the heavy metals and arsenic from the deposited technogenic wastes in the dumps. For this reason, the generated drainage waters possess a potential toxicity to the environment.

The results from TCLP test reflect the dissolution of the heavy metals and arsenic from the slime and slag and the possibilities for a secondary contamination of other components of the environment. The technogenic wastes were characterized as toxic due to the high concentrations of the dissolved pollutants, including of the most toxic of them (As, Cd, Pb) in the pregnant solutions (Table 6).

Table 6. Data about the toxicity of wastes produced from steel-making plant

Component	Type of waste	
	Slag	Slime
	Concentration of pollutants in the pregnant solutions, mg/ l	
Pb	6,20	44,0
Zn	5,10	26,0
Cu	0,32	2,3
Ni	0,27	0,17
As	2,61	0,05
Co	0,28	0,15
Cd	< 0,04	0,24
Fe	7,59	0,77
Mn	8,80	97,20

The relatively high humidity of wastes in the slime dump determinated the generation of drainage water with high concentrations of dissolved metals during the whole year. For example, the concentration of dissolved lead was 9 times above the permissible level accepted for the toxicity test. The slag from the blast furnace processing generated drainage waters only in spring and winter due to the low humidity of the deposited materials during the other seasons. These waters contain dissolved lead and arsenic above the permissible level too.

The main mechanisms for mobilization of these metals in the drainage waters are the formation of soluble complexes between the heavy metals and the ligands, contained in the effluents. The preliminary enzymatic or non-enzymatic reduction (mainly by organic acids) of the oxide forms of iron and manganese from the deposited materials was also essential.

The results of this study revealed the appearance of natural biogeochemical processes connected with the mobilization of the heavy metals and arsenic from the "Kremikovzi" deposited technogenic wastes. As a result of this, secondary processes of contamination of the surface and groundwater, and the soils in local area occured. (Borisov& Chuldzian, 1991).

CONCLUSIONS

The investigation of the technogenic wastes generated from the "Kremikovzi" steel-making plant, showed the presence of different geochemical forms of the heavy metals and arsenic. These forms were characterized by a different mobility depending on the environmental factors and the element specificity. The indigenous microflora participated by means of direct and non direct mechanisms in the processes of transformation of the heavy metals and arsenic. As a result of this, drainage waters with a high toxicity, were generated in this plant.

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TWO-STAGE MICROBIAL LEACHING OF COPPER AND PRECIOUS METALS FROM A SULPHIDE ORE

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ABSTRACT
A rich-in-pyrite copper ore containing also gold and silver as valuable components was treated by a two-stage microbial leaching. The leaching was carried out in a percolation PVC column containing 30 kg of ore crushed to minus 10 mm. The ore was firstly leached by means of acidophilic chemolithotrophic bacteria and 68.0% of the copper was solubilized in this way within 10 months. At the same time, a considerable portion of the precious metals which initially were finely disseminated in sulphide minerals was liberated from the sulphide matrix as a result of the bacterial oxidation. The dissolved copper was precipitated from the pregnant solutions by cementation with metallic iron. The oxidized ore was then leached by means of alkaline solutions containing amino acids of microbial origin and thiosulphate to solubilize the precious metals. 77.7% of the gold and 55.4% of the silver were solubilize in this way within 25 days. The pregnant solutions were treated by cementation with metallic zinc to precipitate the precious metals as mixed gold-silver concentrates.

INTRODUCTION

Different acidophilic chemolithotrophic bacteria are able to oxidize sulphide minerals to the relevant soluble sulphates (1-2). Such oxidation is used commercially to leach non-ferrous metals and uranium from mineral raw materials (ores and concentrates) and to liberate gold, which is finely disseminated in sulphide minerals (3-5). The liberated gold is then leached by different chemical reagents (mainly by cyanides) and or microbial metabolites. A very efficient leaching of gold from different mineral raw materials has been achieved by means of solutions containing amino acids of microbial origin and thiosulphate ions as gold-complexing agents (4-7). Leaching with such solutions is characterized by increased rates of gold and silver solubilization compared to these obtained by cyanidation. The final extraction of these metals by both methods are similar. However, the reagents used in this combined chemico-biological method are not toxic and the method as a whole is economically more attractive than cyanidation.

In this study a rich-in-pyrite copper sulphide ore containing gold encapsulated in sulphide minerals was initially treated by acidophilic chemolithotrophic bacteria to leach copper and to liberate the gold. The ore was then leached by solutions containing microbial amino acids and thiosulphate to solubilize the gold.

MATERIALS AND METHODS

Data about the chemical and mineralogical composition of the ore used in this study are shown in Table 1. Chalcopyrite was the main copper-bearing mineral in the ore but secondary copper sulphides such as covellite and bornite were also present. The ore was rich in pyrite and the total content of sulphides was about 10%. Most of the gold was finely disseminated in pyrite and chalcopyrite. The main portion of the gold particles was less than 1 micron. Quartz was the main mineral of the host rock.

The bacterial oxidative pretreatment and subsequent chemico-biological leaching of the ore were carried out in a PVC percolation column with an effective length of 800 mm and a 95 mm internal diameter. The column was charged with 30 kg of ore crushed to minus 10 mm.

Solutions containing acidophilic chemolithotrophic bacteria, iron ions (mainly in the trivalent state), some essential nutrients (mainly ammonium and phosphate ions), essential nutrients (mainly ammonium and phosphate ions), sulphuric acid and dissolved oxygen were pumped to the top of the column at a rate of 100 l/ton ore per 24 h. The pH of the columns effluents was adjusted to values in the range of 1.7 – 1.9 by addition of sulphuric acid. $(MN_4)_2SO_4$ and KH_2PO_4 were added to produce final solutions concentrations of about 0.50 and 0.10 g/l, respectively/ The column effluents were treated in BACFOX units (8) in which the bacteria oxidized the ferrous ions to the ferric state under conditions of intensive aeration. The solutions were then recycled to the top of the column and were circulated continuously in this way allowing copper, iron and sulphate to accumulate. The pregnant column effluents were treated by cementation with metallic iron when their copper content exceeded 250 mg/l. The cementation was carried out in a reactor with mechanical stirring using iron shavings to precipitate the copper. The progress of the bacterial pretreatment of the ore was followed by analysis of the circulating solution for ferrous, ferric and total iron species, copper and sulphate ions, pH, Eh and number of iron-oxidizing chemolithotrophic bacteria.

Table 1. Data about the chemical and mineralogical analysis of the ore used in this study

Component	Content	Component	Content
Copper	0.32 %	Silver	9.1 g/t
Total sulphur	5.0%	Gold	4.2 g/t
Sulphide sulphur	4.7%	Gold phases (in % from the total gold content):	
Sulphate sulphur	0,3%	- free gold	0.5%
Iron	6.3%	- gold encapsulated in iron hydroxides and oxides	12.2%
Sulphide minerals:		- gold finely disseminated in sulphides	84.8%
- pyrite	8.5%	- gold finely disseminated in silicates	2.5%
- chalcopyrite	1.0%		
- other sulphides	0.5%		
		Total	100.0%

After the sulphide oxidation and the copper leaching the ore was washed several times with fresh water and then was treated with solutions containing microbial protein hydrolisate – 1.0 g/l, thiosulphate ions (added as ammonium thiosulphate) – 15 g/l, copper ions (added as copper sulphate) – 0.5 g/l and sulphite ions – 0,5 g/l. The pH of the solutions was maintained in the range of the 9.5 – 10.0 by addition of ammonia. The protein hydrolysate was a mixture consisting of protein hydrolysates from waste biomass of three different microbial species. The hydrolysates contained different gold-complexing amino acids and were mixed together in suitable proportions.

The leach solutions were pumped to the top of the column as a rate of 200 l/ton ore per 24 h. The solutions percolated through the ore mass and dissolved gold and silver. The column effluents were treated by cementation with metallic zinc to precipitate the dissolved precious metals. The cementation was carried out in a fluidized-bed cementator which worked under continuous-flow conditions. The depleted solutions from the cementation unit were collected in a regeneration vessels where make up water and reagents were added to the desired levels. The leach solutions adjusted in this way were then recycled to the column.

RESULTS AND DISCUSSION

The treatment of the ore by means of the acidophilic chemolithotrophic bacteria was very efficient. Within a few days following initiation of the treatment, the column was densely populated with such bacteria. Acidithiobacillus ferrooxidans and Leptospirillum ferrooxidans were the prevalent microorganisms in the leach system. The total number of these bacteria in the circulating solutions was higher than 10^8 cells/ml. However, most of the bacteria were firmly attached to the ore and their number exceeded 10^9 cells/g ore in the upper ore layers.

68.0% of the copper was leached from the ore within 10 months of treatment (Figure 1). The treatment of the copper-bearing pregnant column effluents by cementation was also efficient and cement copper concentrates containing about 80-82% copper were obtained in this way. The consumption of metallic iron during the cementation amounted to about 2.0 – 2.5 kg iron/kg copper.

The content of sulphidic sulphur in the ore at the end of the period of copper leaching was lowered to 2.1% and this reflected a degree of sulphide oxidation of about 55% (Figure 1). Preliminary experiments in small percolation columns (with 10 kg of ore each) revealed that this degree of sulphide oxidation was sufficient to liberate most of the gold from the sulphide matrix. This was probably to the fact that in the pyrite and chalcopyrite specimens present in this ore, like in many other similar cases, the gold was located mainly in the deffect sites of the sulphide crystal lattice and these sites were preferentially attacked by the chemolithotrophic bacteria (3). During the above-mentioned preliminary experiments it was found that the gold extraction from such pretreated ore samples exceeded 85%, while the extraction from the original, non-pretreated ore was less than 15%. It was also found that the rates of gold and silver solubilization obtained by the combined chemical and biological leaching were much higher those obtained by cyanidation, although the final extractions obtained by the both methods were similar.

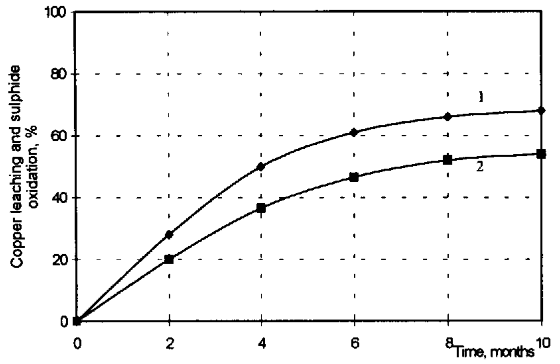

Figure 1. Leaching of copper (1) and degree of sulphide oxidation (2) by the chemolithtropic bacteria

The subsequent leaching of precious metals from the pretreated ore was also very efficient (Figure 2). 77.7% of the gold and 55.4% of the silver were solubilized in this way within 25 days. The number of undesired microbial contaminants growing at the expense of the thiosulphate or of the amino acids in the leach system was low due to its relatively high pH.

The products from the cementation of the pregnant column effluents by Zn^o were mixed gold-silver concentrated which contained also copper and zinc as valuable components. These concentrates can be processed by the well-known conventional methods for recovering pure gold and silver.

The consumption of reagents during the leaching and cementation of the precious metals amounted to 4.1 kg ammonium thiosulphate, 0.25 kg protein hydrolysate, 0.8 kg copper sulphate and 0.14 kg metallic zinc per ton of ore.

The results from this study revealed that the subsequent leaching of copper and precious metals from rich-in-pyrite ores by means of microorganisms and non-toxic reagents is technically feasible and environmentally safe way to process such ores.

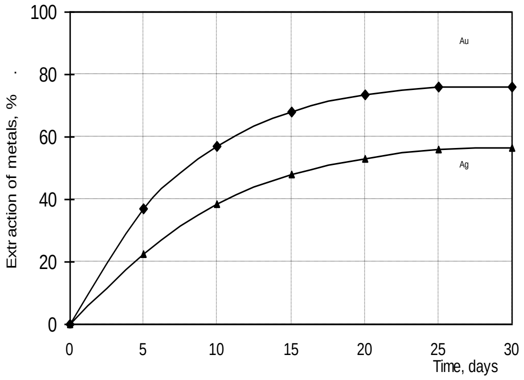

Figure 2. Leaching of precious metals from the pretreated ore

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