

STUDIES ON THE SELECTIVITY AND FINANCIAL IMPROVEMENT IN THE PROCESS OF TIN FLOTATION BY CHANGES OF THE pH, FLOTATION TIME AND CONCENTRATION OF COLLECTOR

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ABSTRACT

The main purpose of the present investigation is determining in which order the test results concerning the adsorption mechanism of the Aerosol 22 on the oxides could be used in tin flotation practice. Tests were performed with tin hematite, tourmaline and quartz. The minerals are studied separately in respect to their behavior in the flotation process in conditions of pH change, concentrations of the collector and slurry temperature. Differing from the ferrous minerals, hematite and tourmaline tin shows strong flotation properties at pH 2. From their own hand, the tourmaline and the hematite show a good flotation at pH 6. It was established that the increasing is the collector consumption the increasing monotonically is the mineral recovery. These results could be proved only by flotation tests of mineral mixtures to be found whether the selectivity is influenced as a result of an interaction among the minerals. The difference in the adsorption at different slurry temperatures is studied additionally. The calculations for financial profit show that the increase of the Sn recovery on the base of the reagents used will lead to a nominal profitability of 1,2 DM per annum in a case of plant productivity 300 t/d.

Key words: flotation, selectivity, temperature, pH, collector.

INTRODUCTION

The primary tin ore flotation attain more and more significance as a result of the increasing complexity of the ore mined and the related to it necessity of a further ore grinding.

In spite of the intensive research activity in the last years, a general flotation method has not been found yet (Arbiter, 1977; Wottgen, 1980). It concerns most of all the type of the collectors used. For example, in Bolivia - the greatest producer of primary tin ores they use Aerosol 22 in all their flotation plants (Savvidis, 1997, 2001). The infrared spectroscopy studies (Berger, 1980) of the Aerosol 22 deposition on the tin and the other by-minerals such as hematite, tourmaline and quartz have been used as an explanation of the adsorption mechanism of those reagents on the oxidized mineral surfaces. An attempt by using of appropriate reagent regimes was made aiming a flotation process selectivity improvement (Savvidis, 1997, 2001). Some directions regarding the optimal conditions of the collector accumulation were obtained as a result of those investigations which however do not fit totally with the values obtained in the flotation practice.

It should be found in the frame of the investigation performed in which order the results of the qualitative and quantitative studies of the adsorption mechanism are applicable to the tin flotation. Using different minerals performed the flotation tests. A priority in our investigations was the tin flotation improvement by founding an appropriate and most of all selective reagent collectors. The main aim is prevented in some order by the following factors:

1. Mineralogical content of the tin ore in the different deposits is highly variable;

2. A big amount of the by-products manifest similar flotation abilities;

3. The facts characterizing the region and most of all the very high concentration of the metal ions disturbs strongly the tin flotation process.

The carboxylates used in the past act unselectively and react very sensitively in respect to the ions in the slurry (Siebert, 1977). A relative improvement is observed by Siebert (1971) and Serano (1975) in the case of a substitution of mono-, di- and polycarbonic acids with brome. The last one leads to an improvement of the selectivity.

The phosphoric and the arsenic acids have showed good parameters as specifically operating collectors when they were used for a flotation of the Althenberg ores and for the tin ores in Tasmania. They dissolve fully the carboxylates. It should be noted that they are not so appropriate for the flotation of the Bolivian tin ore. The both type acids react in a poor acid media with the tin and ferrous minerals by a hemi-sorption (Dietze, 1975). The reason for the proportionate high selectivity take place in the fact that the adsorption on the tin minerals is considerably faster than on the other rock minerals.

EXPERIMENT SETTINGS

Tin flotation with Aerosol 22

After introducing of the sulposuccinamates as a collector for the tin ore (Arbiter, 1977) a reagent was found by which even in a case of a presence of large amount of alien ions good flotation results could be achieved. In the case of Aerosol 22 the matter goes to the tetrasodium N – (1, 2 dicarboxylethyl – N – octadecylsulphosuccinamate – a product of the

American company Cyanamid. The structural formula of that reagent is shown in the Figure 1.

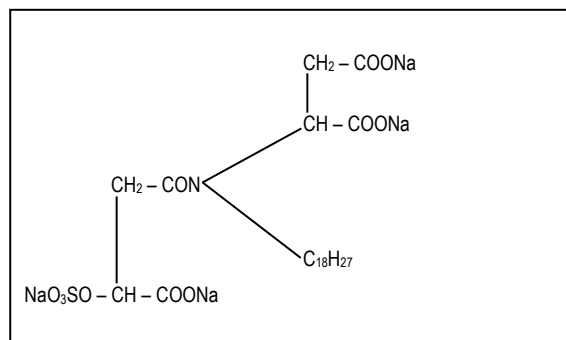


Figure 1. Structural formula of the Aerosol 22

Berger (1981) has an essential contribution to the clarification of the adsorption mechanism of the Aerosol 22 on the mineral surface. According to the quantitative adsorption measurements the following suitable flotation conditions are obtained: An adsorption minimum is obtained in the case of the ordinary for the practice concentrates as of 10^{-4} mol/l. A higher quantity of the collector is adsorbed at a slurry temperature of 35°C than at temperatures of 20°C . Analogically, an increased collector adsorption is observed when the hydrogen ion concentration and the activity increase as well as with the polyvalent metal ion concentration increase. It should be noted that the influence of the collector concentration, pH as well as the temperature have to be studied in some flotation experiments as well.

Description of the material studied

In the present experimental study tin ore, hematite, tourmaline and quartz were used. The sample of tin ore was prepared as a tin concentrate from a secondary deposit in Spain located near by Malaga. It has a content of 69% of Sn and about 2% of Fe. The rest ore impurities are quartz and some other silicates.

The hematite is extracted from the ore body of Minas Gerais and has a content of Fe as of 66%. The ore contains also a small quantity of impurities of quartz, magnetite and limonite. The shorl that is also well-known as "elzen-tourmaline" has coarse accretions with the quartz. The material is extracted from Kaatiala in Finland and has a Fe content of 9,9%.

The quartz is extracted from the Frechen quartz deposits and contains 99,9% of silica as well as small quantities of iron impurities.

The flotation experiments were carried out in a pneumatic micro flotation cell of 100 ccm. The slurry solid content in the process of the agitation was 100 g/l and at the beginning of the flotation process it was 50 g/l. The agitation time was 5 min. The foam product is carried out in 4 concentrates. The times of the separate flotation processes for obtaining of the respective concentrates are e 1; 1,5; 3 and 5 min respectively. The Sn and Fe contents were determined by the Quantitative X-ray Fluorescent Analysis.

Influence of the pH values

It is well-known from the flotation practice as well as from a number of investigations that the Aerosol 22 shows best collector properties in respect to the tin minerals when the process is carried out in the strongly acid area at pH 2,5 (Breuer, 1960; Barbery et al., 1977; Savvidis, 1997).

That fact is confirmed also on the base of some experiments which are graphically expressed in the Figure 2a.

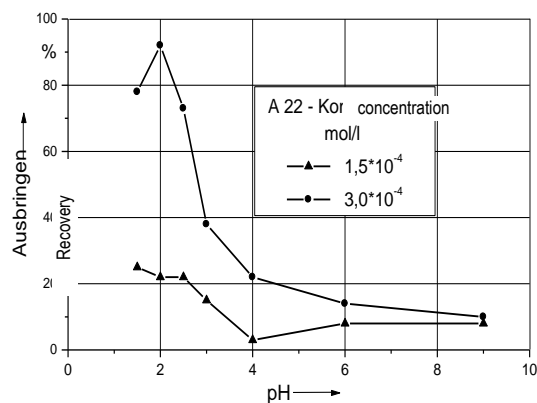


Figure 2a. Tin recovery depending on pH.

Herein, the tin recovery is presented at two different collector concentrations and depending on pH. The chosen concentrations of $1,5$ и $3,0 \cdot 10^{-4}$ mol/l correspond to the most used ones in the practice. Recovery maximums are obtained for the both collector concentrations at pH values of $1,5$ и $2,5$ respectively. The quite high pH values decrease strongly the recovery and it decreases with more than 10%. The amount of the recovery is highest, i.e. - 90% at collector concentrations as of $3 \cdot 10^{-4}$ mol/l and pH 2. There is a waste product with 78% at pH 1,5. The investigation of the collector concentration influence is considered once more in the further investigations. The flotation behavior of the rest of the minerals in the same conditions is shown in the Figures 2b, 2c and 2d.

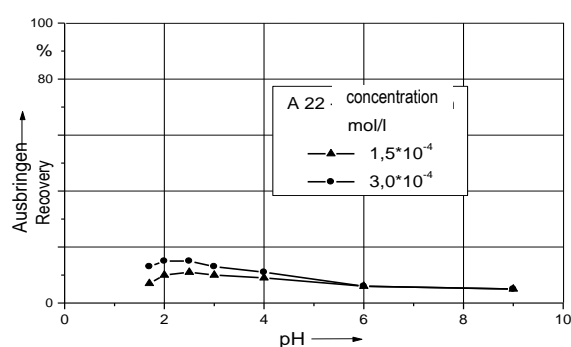


Figure 2b. Recovery results depending on pH.
e) regarding the quartz;

FLOTATION EXPERIMENT RESULTS

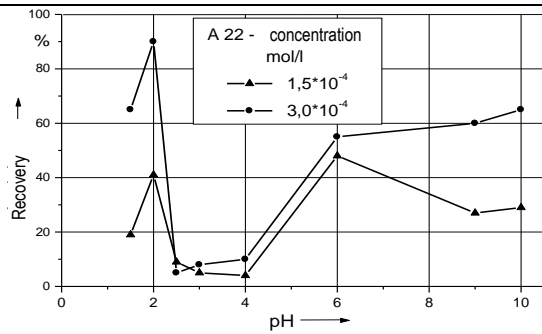


Figure 2c. Recovery results depending on pH.
c) regarding the hematite

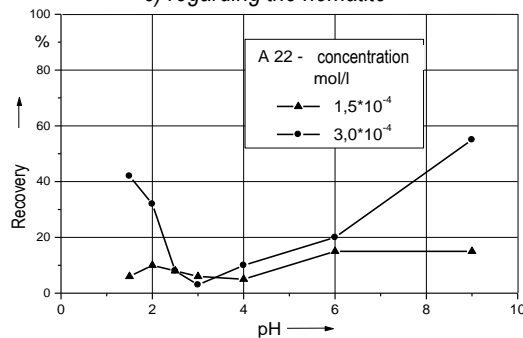


Figure 2d. Recovery results depending on pH.
d) regarding the tourmaline

The quartz recovery in the whole pH area and for the both concentrations was not more than 20%. A slight increase was found in the pH acidic area between 1,5 and 3,0. That could be explained by the increased quantity of the physically attached collector. A hemi-sorption on the clear quartz is not possible to be observed. The tourmaline and the hematite showed a similar behavior in the whole pH area. The hematite showed a good recovery of about 90% at pH 2 and its recovery at pH 1,5 and 2,5 decreases rapidly.

The recovery of the four minerals depending on the flotation time at pH 2,5 is shown in Figure 5.

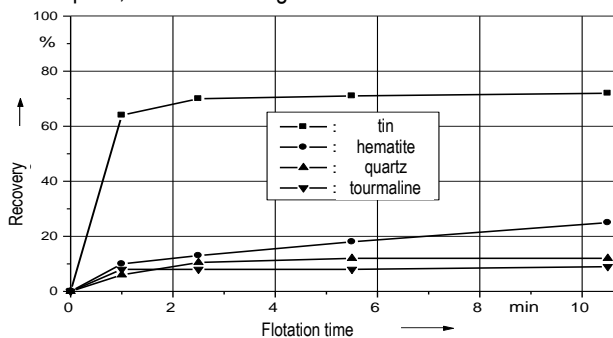


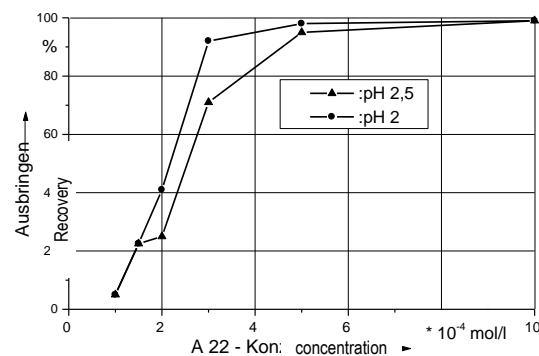
Figure 5. Recovery of the tin, hematite, quartz and the tourmaline depending on the flotation time at pH 2,5

The hematite showed extremely bad flotation properties in that pH area. The tourmaline and hematite recovery increased slightly of about 10% at pH 4 and at pH 6 decreased to 50% and the tourmaline one – to 20%. In that case, the iron fragments in the minerals react in a hemi-sorption manner with the carboxylate groups of the collector. Most probably, hydrate compounds are formed in that pH area. The solubility of the iron composing the tourmaline and the hematite increases with the pH decrease and that leads to an additional influence on the flotation results.

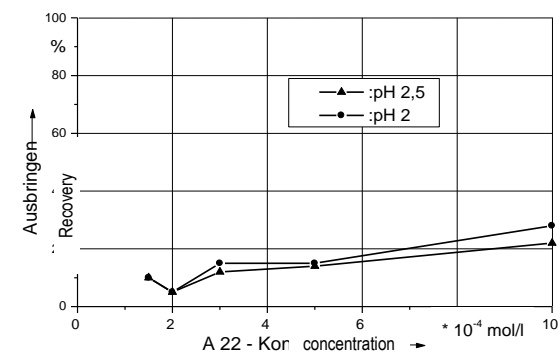
Influence of the collector concentration

The Aerosol 22 consumption varies between 500 and 1000 g/t. The last one corresponds to a collector molar solution from 1,53 up to 3,06 10^{-4} mol/l at a slurry density of 200 g/l. As a result of the Berger's (1980) investigations it was found a decrease of the collector quantity taken by the adsorption in the range from 10^{-4} up to 10^{-3} mol/l. The flotation behavior of the four minerals depending on the Aerosol 22 concentration in the range from 10^{-4} up to 10^{-3} mol/l is shown in Figures 3a, 3b, 3c and 3d. The experiments were performed at pH 2 and 2,5.

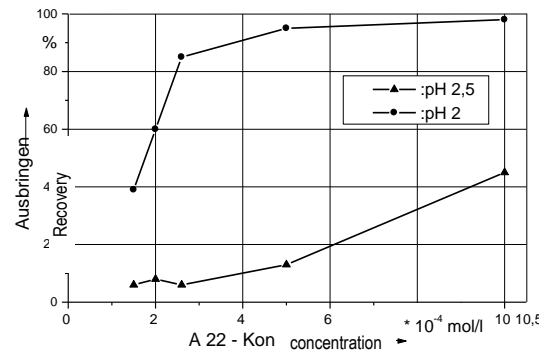
In the tin flotation case it is observed a recovery increase for the both pH values and the highest recovery is found at a concentration of $5 \cdot 10^{-4}$ mol/l. The tin flotation in conditions of an increasing collector concentration could be seen in the Figure 3b. A maximum recovery of 22% is achieved at pH 2 and a collector concentration of 10^{-3} mol/l.



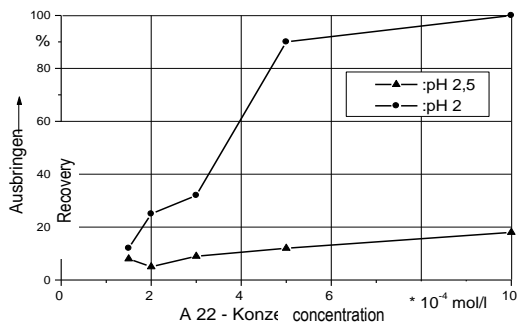
(a)



(b)



(c)



(d)

Figure 3. Recovery results depending on the collector concentration

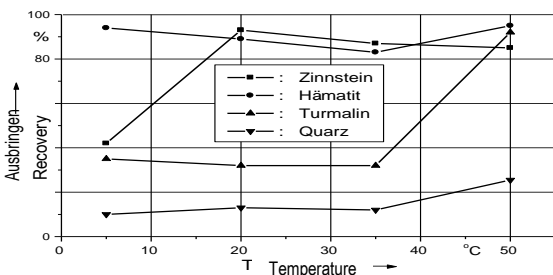
a) regarding the tin; e) regarding the quartz; c regarding the hematite; d) regarding the tourmaline;

A low recovery is observed in a similar way at a high collector concentration and relatively worst rates of the linkages between the collector molecules and the mineral surface. Most probably, a collector physical accumulation is observed depending on the concentration as well as its adsorption on defects of the crystal lattice. Similar flotation results are found for the tourmaline and the hematite. The both minerals are undergone to a full flotation at pH 2 and $5 \cdot 10^{-4}$ mol/l. A slight recovery increase is observed at pH 2,5 as well as at 10^{-3} mol/l. Surprisingly, the adsorbate decrease described by Berger (1980) do not influence negatively on the flotation behavior of the four minerals. Most probably, there are an existing relation between the dimer formation described by him and the flotation results. There is an increase of the quantity of the adsorbed collector on the base of the higher potential of the collision between the minerals and the collector dimer molecules and in the same time the layered molecules strengthen the hydrophobic properties. That effect of the increasing collector hydrophobic ability properties could be compared to the action of the long-chained non-polar molecules.

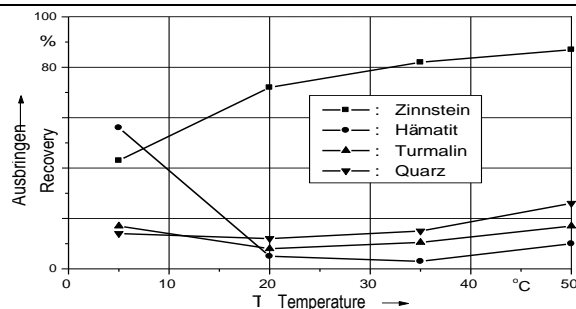
As a consequence of the results described it could be concluded that the selective tin flotation can pass at pH 2,5. The additional experiments are carried out at a collector concentration of 10^{-4} mol/l.

Influence of the slurry temperature

There is a well-known relation of the adsorption processes from the slurry temperature. It could be seen in the Figures 4a and 4b that in all of the cases the temperature influence on the flotation results. The four minerals recovery is shown depending on the temperature and at pH 2, 2,5, 4 and 6

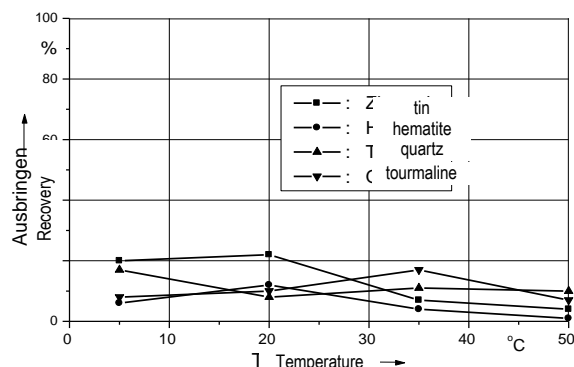


(a)

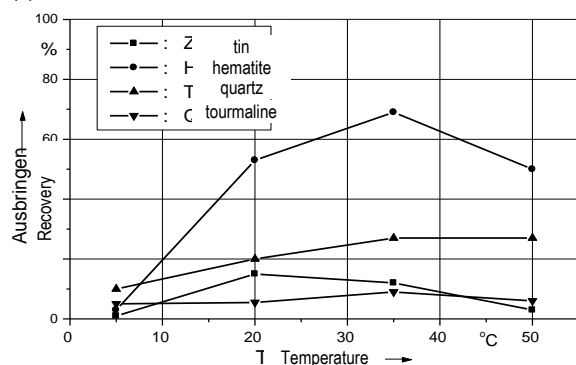


(b)

The agitation tank and the flotation cell were set in an additional tank full with water to regulate their temperature. The water temperature regulation was done by a thermostat. The cooling of the water to 5°C was based on the same principle. The water was cooled to 1 - 2°C by ice bits in such way that a temperature of 5°C was achieved in the volumes of the cell or Becker glass. The results show that a selective separation of the tin minerals from the ferrous ones in the acid pH range and especially at a pH 2,5 is possible by a temperature regulation. As it could be seen in the Figure 4b, the tin minerals recovery increases monotonically with the temperature increase. Improved flotation results for the rest of the minerals are found only at 1m of the temperature range from 35 up to 50°C. An entire activation as a result from the high temperatures is observed probably in the acid pH range. There are negative results observed as it is shown in the Figure 4d at higher pH values and a temperature increase of 50°C.



(c)



(d)

Figure 4. Recovery results depending on the temperature.

a) at pH 2 ; e) at pH 2,5; c) at pH 4; d) at pH 6

Most probably, the collector-mineral link is destroyed at high temperatures and in the same pH range. The tin minerals

recovery at temperatures of 5, 20, 35 and 50°C as well as at pH from 2 up to 6 is presented in the Figure 6.

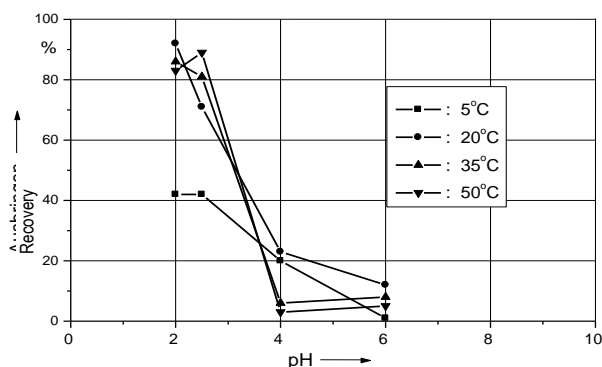


Figure 6. Recovery results depending on the pH at 5, 20, 35 u 50 °C.

The effect of the increasing temperature on the type of the collector accumulation is shown in the figure. The recovery is low (42%) at temperature 5°C and pH 2 and pH 2,5. As it is shown in the Figure 6 the results are worst at pH 6 and a maintaining of the same other conditions. Most probably, the chemical activity is not enough for a hemi-sorption on the tin minerals surface at the low temperatures. In that case, the physical adsorption mechanisms are more strongly expressed and in that way the linkages stability is not enough.

The tin minerals flotation behavior at 20°C is similar to that at 5°C. It could be noted here that usually a reaction behavior activation of the mineral surface and or collector molecules are aimed by the temperature increase. It is expressed by a double increase of the recovery at pH 2 and 20°C in a comparison with that at 5°C. The high recovery values are identical to those in the conditions of tourmaline and hematite flotation as it could be seen in the Figures 7 and 8.

A considerable increase of the Aerosol 22 selective accumulation on the tin minerals is possible at 35°C and pH 2,5. There is even a slight 10% increase of the tin recovery found at that temperature and at pH 6. That effect could be explained by tin hydroxide ion activation.

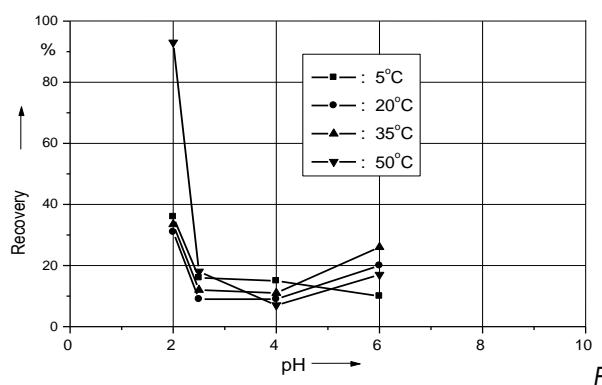


Figure 7. Recovery of tourmaline depending on pH at 5, 20, 35 and 50 °C.

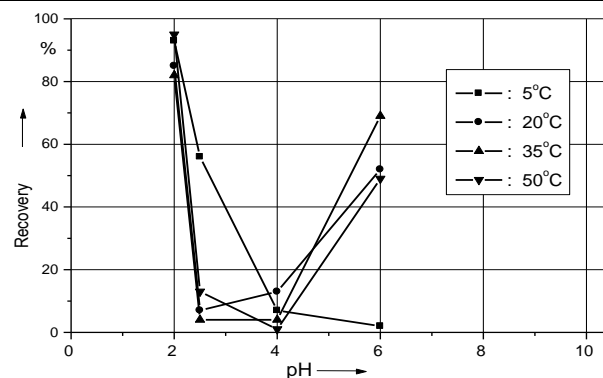


Figure 8. Recovery of hematite depending on pH at 5, 20, 35 u 50 °C.

The results of the flotation of the tourmaline and hematite shown in the Figures 7 and 8 are similar. The flotation of the both minerals is good at pH 2 and pH 6. Activation by increasing the temperature is aimed in the acid range of the pH and a temperature at 35 °C. It is obviously seen especially at pH 6 at which we have activation by a ferrous oxide formation. It is not valid in conditions of low temperatures as it could be seen from the tourmaline and hematite curves. The temperature influences slightly on the quartz flotation behavior and there is an increase of 37% observed only at very high temperatures (about 50°C) and an acid pH.

Consideration of the financial profit

An attempt is made for a calculation of the nominal profit by a calculation of the additional profit in the case of an increased productivity of the tin flotation with 5% of a recovery processing of the slimes of a grind size less than 20 µm

Bases of the calculation

- Initial ore material: 300 t/d
 - Sn content – 0,75%
 - Concentrate price: 3,25 US \$/lb, or 18 DM/kg
 - Price of the reagent Aerosol 22: 6,75 DM/kg
 - Additional costs for reagents:
300 g/t Aerosol 22: 2,025 DM/t or 607,5 DM/d
 - Nominal profit following from the extraction increase: 5%
 - Съдържание на Sn в концентрата: 20%
- Additional concentrate quantity: 0,5625 t/d
- Tin content: 0,1125 t
- Nominal profit: 4.214,25 DM/d
 - Nominal profit – reagent costs: 4.214,25 - 607,5 = 3.516,75 (300 work days/a: 1.237,275 DM/a)

DISCUSSIONN OF RESULTS

A surfactant reagent was investigated by the Aerosol 22, which thanks to its complex molecular structure and its four polar groups finds a large-scale application in the practice.

The ferrous minerals as hematite and tourmaline have a highly reduced flotation properties at pH 2,5 in compared to the tin minerals. The ferrous minerals have good flotation ability at pH6. It is a consequence of the high affinity of the carboxylate group to the iron and it clearly proven by the adsorption

experiments. There is a recovery increase at pH 6 while there is not a difference in its value at pH 4. Most probably, the linkage between the ferrous hydroxide and the collector plays at pH 4 a high order role which one opposes to the strongly mechanic interactions in the flotation process in the higher pH ranges.

There is no found a strong relation between the concentration in the range 10^{-4} - 10^{-3} mol/l and the adsorbed quantity of the collector. That could be compared to the increased collector consumption and the monotonic increase of the minerals recovery. It should be expected in the process of the tin flotation that the adsorption improvement and thus the valuable component content in the concentrate will be not achieved by the collector consumption increase. There are insignificant differences found in the adsorption at the different temperatures.

It could be seen from the economical evaluation that the increased recovery that is rendered in an account in the reagent usage would led to a nominal profit increase up to 1,2 millions of DM annually in the case of the operating of an plant with a productivity of 300 t per day.

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