

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/m²).

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 slurries 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 spectrophotometric methods (DIN 38405, DIN 38409, DIN 38406 relevance). The concentration of dissolved oilproducts were determined by spectrophotometer Horiba at $\lambda = 262 \mu\text{m}$ 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).

Table 2. 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 % S₂O₃²⁻).

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), PbO₂ and complexes with residual organic compounds. As a result of the processes of oxidation, secondary minerals as Pb (OH)₂ and PbCO₃ 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 ZnCO₃ (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 for 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

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

| produced by the slag-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 | 0.3 | 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 |

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.

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 S₂O₃²⁻, 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 PbSO₄. On the other hand, the high zinc extraction was a result from the formation of well soluble products. The relative role of chemolithotrophic microorganisms 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 determined 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 occurred. (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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