

The Influence of the Lead-Zinc Slags Fractional Composition and the Type of Microorganisms for the Processes of Metals Bioleaching

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Abstract Shymkent is one of the largest industrial cities of Kazakhstan with a lot of industrial wastes. These include lead-zinc slag, which has a strong anthropogenic stress on the environment. On the other hand, there is a large number of components concentrated in the waste. The possibility of using different groups of microorganisms for the recovery of valuable metals from a variety fraction of lead-zinc waste was investigated. It is found that the bioleaching of zinc-lead wastes of valuable components depends not only on the species of microorganisms, but also on the fractional composition of the waste.

Keywords Zinc-lead slags, Bioleaching, Fractional composition

1. Introduction

The high rate of production and processing of mineral raw materials has led to the formation of a large number of mining and industrial wastes. At the enterprises of mining production in Kazakhstan are dumps and tailings of more than 20 billion tons of man-made mineral formations, with annual accumulation of about 1 billion tons of new wastes (Karimova Z. et al., 2002).

Waste concentrators and metallurgical plants are unstable and non-uniform composition. In a joint storage of wide types of rocks and ores, differentiating them by chemical composition and physical-mechanical properties, their agitation, oxidation and leaching during prolonged storage, make them undergo significant changes. Waste occupy large areas of land and are the source of dust and gas emissions and toxic entities, that pollute the atmosphere, soil, surface water and groundwater thus having a negative impact on the environment.

Biotechnological methods to extract valuable metals of various types of ores and metal waste are known (Acevedo F., 2002). For example, the possibilities of microbial recovery of copper from chalcopyrite was investigated (Kutschke S. et al., 2015). Also the role of the salt-resistant types of metals

bioleaching microorganisms with a high content of sodium and magnesium salts in solution are known (Rea S.M. et al., 2015). Identified limiting pH value on the life of thiobacteria *Acidithiobacillus ferrooxidans* (Ngoma E. et al., 2015) has been documented. According to Mitsunobu S. et al. (2016) the mechanisms underlying the contact leaching process in pyrite bioleaching by *Acidithiobacillus ferrooxidans* using scanning transmission X-ray microscopy (STXM) -based C and Fe near edge X-ray absorption fine structure (NEXAFS) analyses has been investigated. Attached *A. ferrooxidans* produces polysaccharide-abundant extracellular polymeric substances (EPS) at the cell-pyrite interface. A key role of Fe (III) in EPS is enhancing pyrite dissolution has been determined. Pretreatment of pyrite with the phospholipid, [1,2-bis (10,12-tricosadiynoyl) -sn-glycero-3-phosphocholine, to form an adsorbed organic layer reduced the amount of pyrite oxidation in the absence of bacteria and in the presence of *A. ferrooxidans* (Hao J. et al., 2009). In Murad A et al. (2003) and Ghorbani Y. et al. (2007) investigations, the biological leaching of aluminum by isolated fungi *Aspergillus niger* and *Penicillium notatum* from low grade bauxite (<50% Al₂O₃) was studied. It is reported that fungi are involved in metal bioleaching processes indirectly by producing citric and oxalic acid, dissolving the crystal lattice of minerals. The bioleaching behavior of rock phosphate was studied using different strains of *Aspergillus niger* (Saeed et al., 2002) and analysis revealed the presence of fluorapatite [Ca₂(PO₄)₃F] as the main source of phosphorus. Ahn H.-J. et al. (2013)

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investigated various factors, such as organic acid generation with fungi type, pH of the culture and pulp density. However, the influence of various groups of microorganisms to extract valuable metals from different fractions of man-made waste is insufficiently studied.

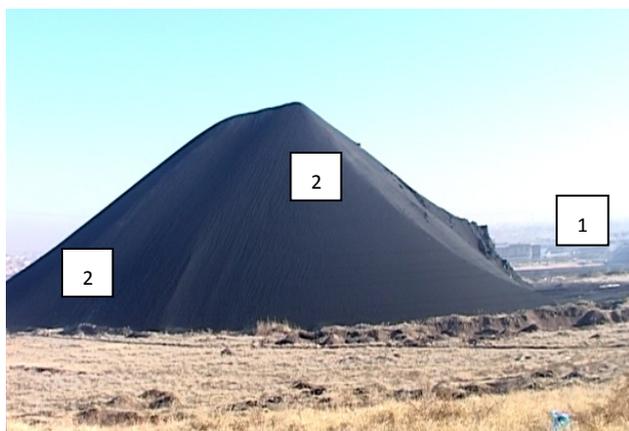
In this regard, the purpose of this study was to investigate the ability of microorganisms to extract valuable components from various fractions of lead - zinc waste.

2. Materials and Methods

2.1 As the object of study, we used lead-zinc slags, located in the amount of a more than 2.0 million tons in the city of Shymkent in South Kazakhstan region (Figure 1). Wastes contain: Pb 0,01~2%, Zn 2~12%, Cu 0,8~11%, FeO36~40%, CaO12~14%, SiO₂ 24~26%.



a



b

1. residential neighborhoods, 2. lead-zinc waste
a. Remote sensing lead-zinc waste (www.googlemap.com), b. side view

Figure 1. Location of lead-zinc waste in Shymkent city

2.2. Microorganisms. For isolation of microorganisms samples of waste was ground in a mortar, were averaged. Selected 1 g waste, which was added to 100 g of sterile distilled water to make slurry. Next, 0, 2 ml of suspension

was deposited on the solid surface of fish-peptone agar (FPA) for heterotrophs, agar of Chapek for micromycetes and agar of Ashby for nitrogen-fixing microorganisms and distributed on the surface of the agar. The allocation of heterotrophs was carried out on the FPA, the following composition, g/l: Pancreatic hydrolysate sprat – 10, 05; NaCl-4, 95, agar-20, 0. The micromycetes were allocated on the Chapek medium following composition, on 1g/l of water: -30,0 sucrose or glucose - 20,0; NaNO₃-2,0; K₂HPO₄ - 1,0; MgSO₄×7H₂O - 0,5; KCl - 0,5; FeSO₄×7H₂O - 0,1. nitrogen-fixing microorganisms on the Ashby medium, g/l: mannite (15% solution) – 27 ml; K₂HPO₄ – 0,2; MgSO₄×7H₂O – 0,2; NaCl – 0,2; K₂SO₄ – 0,1; CaCO₃ – 5; agar– 20.

For the isolation of nitrifying and thiobacteria used the method limit tenfold dilutions on liquid nutrient medium, e.g. for isolation acidophilus iron oxidizing bacteria used the Silverman-Lundgren medium (9K), g/l H₂O: (NH₄)₂SO₄ – 3,0; KCl – 0,1; K₂HPO₄ – 0,5; MgSO₄×7H₂O – 0,5; Ca(NO₃)₂ – 0,01; FeSO₄×7H₂O – 44,2; 10n H₂SO₄ – 1ml; for nitrifying bacteria 1 phase – Vinogradskii medium, g/l H₂O: K₂ HPO₄ – 1,0; (NH₄)₂ SO₄ – 1,0; Mg SO₄×7H₂O – 0,5; NaCl – 0,5.

The liquid nutrient medium was transferred into another incubator at 28-32°C for 3-5 days. The accumulation of culture was placed in conditions of aeration in a rocking chair with amplitude of 180 rpm.

Identification and taxonomic affiliation of microorganisms was determined in accordance with Bergey's Manual (1985) on morphological, physiological and cytological characteristics of the colonies.

2.3. IRS analysis. Physic-chemical study was performed using infrared spectroscopy on the spectrophotometer SPECORD 75 IR spectrometer and inductively coupled plasma with mass spectrometric detection Varian-820 MS(Australia), elemental composition by atomic adsorption analysis on the AAnalyst 800 spectrometer (Perkin-Elmer) and high performance liquid chromatograph Varian-Pro (Netherlands).

2.4. X-ray diffractometry. Analysis was performed on an automated diffractometer DRON-4 with Cu Ka – radiation, β-filter. Conditions for recording of diffraction patterns: U=35kV; I=20 mA; scale: 2000 imp; time constant 2s; shooting Teta-2J; detector 2 deg/min. x-ray diffraction for semi quantitative basis diffractograms performed on powder samples using the method of equal portions and artificial mixtures. Determined quantitative ratios of the crystal phases. Interpretation of diffraction patterns was performed using the data of filing of ASTM Powder diffraction file and the diffraction patterns of pure from impurities of the minerals for the main phase were carried out and calculation of content determined.

2.5. Electron raster microscopy. A video recording of the material was carried out using the graphics card electron-raster microscope JSM 649LV manufactured by JEOL (Japan) with energy dispersive microanalysis system INCA Energy 350 OXFORD Instruments company (United Kingdom) related to system structural analysis of

polycrystalline objects HKL Basis.

2.6. Formulation of a model experiment. The study used a glass separating funnel with a volume of 250 ml in which were placed 50 g of slag. Averaged sample of slag is pre-sifted through aluminum sieves with the diameters cm: 0,01-0,25; 0,25-0,5; 0,5-1,0. Each fraction of slag was placed in a separate funnel where it was introduced 150 ml of bacterial suspension monoculture of microorganisms: *Acidithiobacillus ferrooxidans*, *Aspergillus niger*, *Nitrosomonas europaea* or solution of H_2SO_4 , i.e. the ratio of solid: liquid =1:3. The content of microorganisms in suspension amounted to 10^7 - 10^8 cells/ml. As a control, discussed options with the use of liquid culture media without the introduction of microorganisms. Exposure time-72 hours at temperature $+20\pm 22^\circ C$. After the time of the experiment, the solution was poured off and analyzed on the content of valuable components.

2.7. Statistical processing of the obtained results was performed by calculation of the arithmetic mean value and standard deviation. All definitions were carried out in 3-and 5-fold repetition. Data were processed using a personal computer IBM "Pentium" on the basis of packages of applied programs "Excel".

3. Results and Discussion

X-ray phase analysis of waste samples taken from depths of 0-10, 10-20, 20-30, 30-40 cm rather the same type, has a semi-amorphous structure and is represented wustite FeO , $d/n = 2,47-2,14-1,51 \text{ \AA}$, litharge PbO , $d/n = 3,48-2,96-1,74 \text{ \AA}$

and cosalite $Pb_2Bi_2S_5$, $d/n = 2,14-2,95-2,02-1,80 \text{ \AA}$.

As a result of researches it is established that the processes of leaching of valuable components from metal-containing wastes not only depend on the kind of used microorganisms, but also on the fractional composition of the waste. It is revealed that each group of microorganisms selectively remove metals. For example, when using nitrifying bacteria *Nitrosomonas europaea* for leaching manganese, nickel, selenium, strontium, cadmium and tellurium optimal size fraction of lead-zinc waste is 0.25-0.5 mm. Figure 2 shows the results of the leaching of manganese and strontium. Set, the fraction of 0.5-0.1 cm of manganese is extracted at 77,92% more than the control variant without the use of microorganisms. In an embodiment, a fraction of 0.25-0.5 cm exceeding the extraction of manganese is 85,61% in comparison with the control variant. The least amount recoverable manganese observed for a fraction of 0.01-0.25 cm, where the extraction of manganese with the use of nitrifying bacteria exceeded the control variant by 44.37%. In the extraction of strontium the use of microorganisms has allowed to extract the strontium from fractions 0,5-1,0; 0,25-0,5; 0,01-0,25 cm by 34,56; 52,72 and 29,01% higher than in the control samples. The reduction of particle size leads to a decrease in the extraction of metals from waste.

In the case of using the culture of micromycetes *Aspergillus niger* this fraction is optimal for the extraction of titanium, vanadium, strontium, silver, cadmium, tellurium, thallium. Thus, in variants with the use of micromycetes extraction of metals, on average, higher by 42.84% than in the control variants.

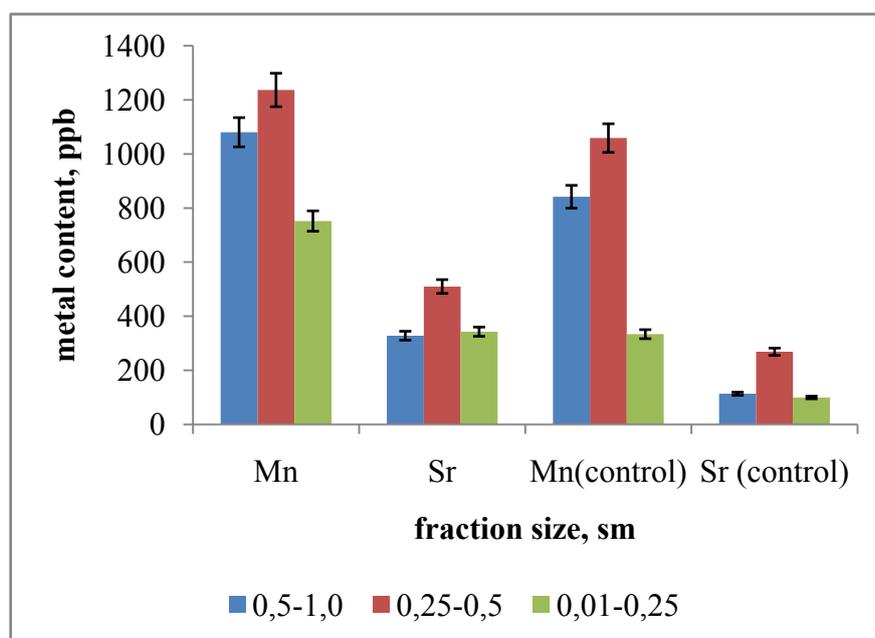


Figure 2. Influence of the fractional composition of waste at extraction of metals from lead-zinc slag using nitrifying bacteria

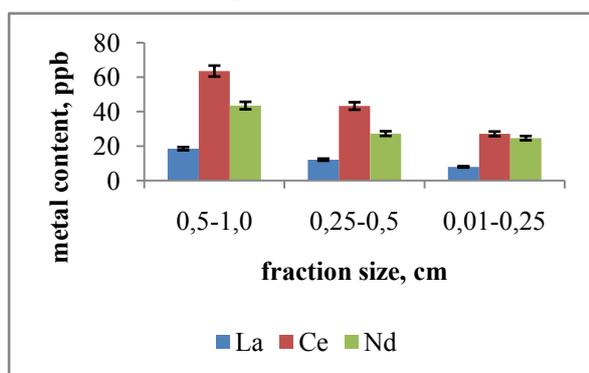
Table 1. Influence of the fractional composition of waste and the type of microorganism on REE extraction from lead -zinc slag

Element, ppb	<i>N. europaeae</i>			<i>A. niger</i>		
	0,5-1	0,25-0,5	0,01-0,25	0,5-1	0,25-0,5	0,01-0,25
La	0,085	0,092	0,128	0	0	0,021
La(control)	0,053	0,062	0,091	0	0	0
Ce	0,175	0,183	0,320	0	0	0,064
Ce(control)	0,077	0,102	0,192	0	0	0
Nd	0,054	0,058	0,111	0	0	0,021
Nd(control)	0,013	0,017	0,038	0	0	0

In contrast, a decrease in the fractional composition of waste contributes to the extraction solution of the lanthanum, cerium and neodymium (Table 1). The extraction of lanthanum with the use of micromycetes for each fraction was higher than the control group on 63,52; 67,81; 71,82%. For cerium the data on metal extraction in bioleaching exceed control characteristics by 44,21; 56,16; 60,19% in accordance with the size fractions. In the variant with the extraction of neodymium with the use of micromycetes metal recovery was higher by 25,37; 30,11; 34,43% compared to the control variants.

Bioleaching in acidic mediums with the use of acidophilic microorganisms *Acidithiobacillus ferrooxidans* showed the optimality of the use of fraction 0,5-1 mm for the extraction of valuable metals. For example, from fractions of slag 0.5-1.0 cm titanium is extracted in quantity, ppb: 57,966; from fraction of 0.25-0.5 cm - 37,302 and the least amount of metal leached from the fraction of 0.01-0.25 cm -28,095. This rule still holds for such elements as bismuth, arsenic, selenium, cadmium, tellurium, tin and cesium. The arsenic in the amount 71,391 ppb and tellurium in amounts 0,543 ppb is leached only from the fraction of 0.5-1.0 cm.

In the acidic medium with the use of thiobacteria from this fraction of lead-zinc waste extracted REE: lanthanum, cerium, neodymium (Figure 3).

**Figure 3.** The extraction of REE from the fraction 0.5-1 mm of lead-zinc waste

In all variants with the use of microorganisms marked by excess extraction of metals within 34,52-65,14 % compared to the control variants.

4. Conclusions

It is found that the bioleaching of zinc-lead waste of valuable components depends not only on the species of using microorganisms, but also on the fractional composition of the waste.

It revealed that using nitrifying bacteria *Nitrosomonas europaeae* for leaching manganese, nickel, selenium, strontium, cadmium and tellurium optimal size fraction of lead-zinc waste is 0.25-0.5 mm. The reduction of particle size leads to a decrease in the extraction of metals from waste.

The using the culture of micromycetes *Aspergillus niger* with the same fraction is optimal for the extraction of titanium, vanadium, strontium, silver, cadmium, tellurium, thallium. On the other hand, a decrease in the fractional composition of waste contributes to the extraction solution of the lanthanum, cerium and neodymium by both types of microorganisms.

It revealed that the using acidophilic microorganisms *Acidithiobacillus ferrooxidans* showed the optimality of the use of fraction 0,5-1 mm for the extraction of valuable metals, including REE from lead-zinc wastes in acidic medium.

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