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The Role of Microorganisms in Bioleaching of Lanthanum, Cerium and Neodymium from Phosphorus-Containing Wastes in the South of Kazakhstan

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ABSTRACT

In the South of Kazakhstan stockpiled more than 50.0 million tons of phosphor containing waste, threatening the region's environment. On the basis of the conducted research, refined mineralogical composition of phosphorus-containing wastes in the South Kazakhstan, represented by pseudowollastonite a-$CaOxSiO_2$, cuspidine $3CaOxCaF_2x2SiO_2$, ferrophosphorus Fe_2P, melilite - Ca_2 (Al, MgSi)Si_2O_7, akermanite-$Ca_2MgSi_2O_7$, rankinite $3CaOx2SiO_2$, fluorapatite $Ca_5(PO_4)_3F$, whitlockite NaF, fluorite CaF_2 and silica calcium $5CaOxP_2O_5xSiO_2$. In trace amounts discovered lanthanum, cerium and neodymium, found that the use of nitrifying bacteria *Nitrosomonas europaea Z2* effective for bioleaching of lanthanum and cerium, the yield in a solution exceeds the results without the use of microorganisms on 81, 88% and 119, 64%, respectively. Thionic bacteria *Acidithio bacillus. ferrooxidans Ach1* increase the extraction of neodymium by 7.45%, in comparison with the variant without the use of microorganisms.

INTRODUCTION

Currently, one of the most promising areas of extraction of metals is a bacterial-chemical leaching, which is environmentally friendly and does not require large material and energy costs (Qu Y. B. and Lian, 2013). Bacteria promising for bio-geotechnologies purposes are widely distributed in nature where the oxidation of iron or sulfide minerals (Kaibin F *et al*., 2014, Wang J *et al.*, 2014, Jahani S. *et al.*, 2015). The main microorganisms oxidizing Fe^{2+}, S^0, and sulfide minerals are *Acidithiobacillus* ferrooxidans, *A. thiooxidans*, *Sulfobacillus thermosulfidooxidans, Leptospirillum ferrooxidans, Sulfolobus acidocaldarius, S. solfataricus, Acidianus brierleyi, A. infernus* (Haragobinda S. *et al.*, 2013, Wang J. *et al.*, 2014). In addition to *A. ferrooxidans,* also known *Leptospirillum ferrooxidans (*Breed A.W. *et al.*, 1999) first oxidize sulfide and sulfite ions, ferrous iron, and various sulfide minerals. In the course of a number of studies found that some heterotrophic microorganisms are also capable of destroying rocks with the allocation of organic products – organic acids, polysaccharides; source of energy and carbon for different organisms are organic matter. Active destructors of silicates are also fungi representatives of the genera *Aspergillus niger, Penicillium notatum* and others (Mulligan C. N *et al.*, 2004). In the works of a number of researchers have examined the role of denitrifying bacteria in biosorption of metals from solutions. These microorganisms, being facultative anaerobes, used as electron acceptor nitrogen oxides (NO^{3-}, NO^{2-}, N_2O) or oxygen and electron donors can serve many different organic compounds, hydrogen, the recovered sulfur compounds.

Known research related to the development of the technology for REE extraction of phosphogypsum *in situ* (M. Haschke *et al.*, 2016).

On the territory of South Kazakhstan region stockpiled more than 50.0 million of phosphorus-containing waste, which identified a number of REE, pose a serious threat to the region's environment. Therefore, the problem of their recycling is one of the important environmental problems in the region. At the same time, the role of rare earth elements in the development of equipment and technologies for a new generation of definite (Pazand K, 2014).

The aim of the study was to conduct a comparative analysis of the results of the leaching of lanthanum, cerium and neodymium from phosphorus-containing wastes in the South of Kazakhstan.

MATERIALS AND METHODS

The chemical composition of the waste was determined by 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). Determination of Fe^{+2} and Fe^{+3} were conducted trigonometric eskimi volumetric method in the technical solutions, which was distributed to measure the iron content in solution in the range from 0.1-10 g/l.

Physico-chemical study was done 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).

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 semiquantitative 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 clean diffraction patterns of impurities and minerals. For the main phase were carried out the calculation of content. Possible impurities whose identification is not straightforward due to the low content and the presence of only 1-2 of the diffraction reflexes.

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 INCA Energy 350 firms OXFORD Instruments (United Kingdom) related to system structural analysis of polycrystalline objects HKL Basis.

In the experiments, we used strains of microorganisms: *Acidithiobacillus ferrooxidans Ach1, Nitrosomonas europaea Z2, Aspergillus niger Ach2* isolated from industrial waste in southern Kazakhstan.

For the cultivation of thiobacteria *Acidithiobacillus ferrooxidans* was used the Silverman and Lundgren nutrient medium (9K), g/l: $(NH_4)_2SO_4$ - 2,0; K_2HPO_4 - 1,0; $MgSO_4$ - 0,5; NaCl 0,2; $FeSO_4 \times 7H_2O$ – 44,2; pH 2,0; for *Nitrosomonas europeae* Vinogradsky medium, g/l: glucose - 20,0; K_2HP0_4 - 1,0; $MgS0_4 \times 7H_20$ - 0,5; $CaCO_3$ - 20.0; yeast extract-10; the solution of trace elements 1 ml; for *Aspergillus niger* the liquid and solid Chapek medium, g/l: sucrose or glucose - 20,0; $NaN0_3$-2,0; K_2HPO_4 - 1,0; $MgS0_4 x7H_20$ - 0,5; KCl - 0,5; $FeS0_4 \times 7H_20$ - 0,1.

In the preparation of the nutrient medium used scales "Scout Pro", and in a sterilization autoclave SPGA-100-1-NN.

The bacteria required for biological leaching, inoculated on elective medium and cultured at pH 2-2.5 with a temperature of 28-30ºC in the thermostat GS-1/80. Aeration was carried out using aerophon AP 1200.

Model experiments for the study of the biological leaching of rare earth elements with the active strains were carried out in laboratory percolators using a fraction of 0.25-0.5 cm phosphorus-containing waste. For laboratory experience, the samples were ground in a mortar. The samples were passed through sieves of different diameter, were averaged. Bioleaching in percolation installations was performed for the parameters: the ratio of S:L=1:3, temperature +22+24ºC, the exposure time of the experience-72 hours. As control was used a sulfuric acid (H_2SO_4 -3.0 g/l). Under model conditions the influence of the composition of the elective media and monoculture of microorganisms on the leaching of lanthanum, cerium and neodymium from phosphate waste heap mode. The experiment was conducted according to the scheme:

a. Silverman and Lundgren medium (9K);

a1. Silverman and Lundgren medium +*A. ferrooxidans Ach1* (9K+AF)

b. H_2SO_4 - 3.0 g/L

c. Chapek medium (CH)

c1. Chapek medium+ *Aspergillus niger Ach 2*(CH+AN)

d. Vinogradsky medium (VM)

d1. Vinogradsky medium + *Nitrosomonas europaea Z2* (VM+NE)

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" (Schabenberger O. *et al.*, 2002).

RESULTS AND DISCUSSION

Analysis of the composition of phosphorus slag showed the presence of the following components: P_2O_5 (0.63-3.40%), CaO (44,60-49,35%), SiO_2 (40,10 of 43.54%), Al_2O_3 (2,46- of 3.48%). In the samples detected silicoborate ($5CaO \times P_2O_5 \times SiO_2$), pseudowollastonite (a-$CaO \times SiO_2$), rankinite ($3CaO \times 2SiO_2$), fluorapatite –($Ca_5(PO_4)_3F$) and calcite granules ($CaCO_3$). The fluoride discovered in the amount of 2-3%. In small quantities discovered akermanite-$Ca_2MgSi_2O_7$, galenite -$Ca_2Al_2SiO_7$. In trace amounts identified REE, wt.%: La 5,6-10,5; Ce 5,8 – 10,7; Nd 5,0 – 9,4.

It was found that the use of elective media along with the microorganisms increases the yield of the desired metals into a productive solution in comparison with the control variant, where was used only elective medium. So when using the strain *A. ferrooxidans Ach1* with the medium 9K yield increases lantana extraction on 0,00023 wt.% or 2.38% of total output; cerium - 0,00097 wt.% or of 9.48%, neodymium - 0,00051 wt.% or was 7.45% (**Figure 1**). The extraction of lanthanum and neodymium by using *Aspergillus niger Ach2* in the liquid medium of Chapek, a reduction in the output elements into a productive solution by 11.58% and 10.64%, respectively. The highest yield of lanthanum and cerium in the solution as noted in the option of using *Nitrosomonas europaea Z2* -81,88% and 119, 64%, respectively.

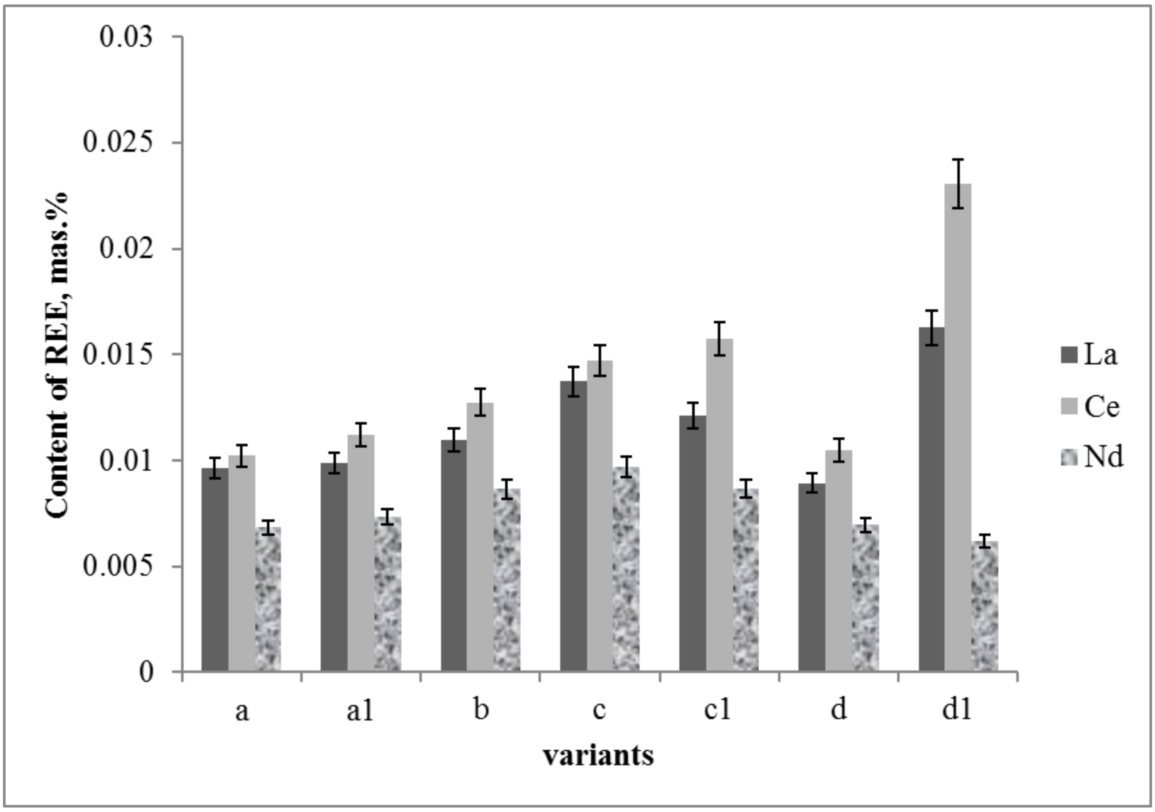

Figure 1. The effect of elective environments and microorganisms on the extraction of lanthanum, cerium and neodymium from phosphate waste

CONCLUSION

On the basis of the conducted research, refined mineralogical composition of phosphorus-containing wastes in the South of Kazakhstan, represented by pseudowollastonite, cuspidine, ferrophosphorus, melilite, akermanite, rankinite, fluorapatite, whitlockite, fluorite and silica calcium. In trace amounts discovered lanthanum, cerium and neodymium.

Found that the use of nitrifying bacteria *Nitrosomonas europaea Z2* effective for bioleaching of lanthanum and cerium, the yield in a solution exceeds results without the use of microorganisms on 81,88% and 119, 64%, respectively. Thionic bacteria *Acidithiobacillus. ferrooxidans Ach1* increase the extraction of neodymium by 7.45%, in comparison with the variant without the use of microorganisms.

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