

**University of Belgrade
Technical Faculty in Bor and
Mining and Metallurgy Institute Bor**



**43rd International
October Conference
on Mining and Metallurgy**

IOCM 2011
PROCEEDINGS

Editors:
Desimir Marković
Dragana Živković
Svetlana Nestorović

October 12 - 15, 2011
Kladovo, Serbia

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Technical Editors:

Ljubiša Balanović, PhD student

University of Belgrade - Technical Faculty in Bor

Mr Ivana Marković

University of Belgrade - Technical Faculty in Bor

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ACIDIC AND BACTERIAL LEACHING OF THE FLY ASH- ENVIRONMENTAL PROTECTION TECHNOLOGY

Jelena Avdalović¹, Vladimir Beškoski², Srđan Miletić², Mila Ilić², Miroslav Vrvic³

¹*Institute for Technology of Nuclear and Other Mineral Raw Materials, 11000 Belgrade, Franche d'Eperea 86, P.f. 390*

²*Department of Chemistry IChTM, 11001 Belgrade, Njegoševa 12, P.f. 473*

³*Faculty of Chemistry, University of Belgrade, 11158 Belgrade, Studentski trg 12-16, P.f. 51, Serbia*

Abstract

In this study, the possibility of acid and microbiological ash leaching, has been investigated in order to minimize the concentration of toxic ash elements. Acid leaching experiment was carried out by H₂SO₄, and lasted for two days. Microbiological leaching experiment was carried out with bacterial strain of the Acidithiobacillus ferrooxidans (Origin: Bor copper deposit) and lasted for two weeks. Total leaching effects were as follow: Mn-54.74; Cu-37.92; Zn-35.25; Cd-31.88; Ni-19.42; Cr-14.53 and Pb-14.07%. In this way, leaching of metals from fly ash is in same time process (my be potential technology) for valorization of this waste and environment protection.

Keywords: leaching, fly ash *Acidithiobacillus ferrooxidans*

1. INTRODUCTION

In the coal combustion process, the organic compounds are completely burnt, white the inorganic coal components and hence many potentially dangerous metals are concentrated in the ash. This can cause serious consequences when the ash reaches the open-air landfills, where it is exposed to many different impacts of the ecosystem. Some recent investigations confirmed that significant quantities of heavy metals, cumulated after combustion and during the cooling process, were present in the surface layer of coal particles, with a size of only a few microns[1-4].

In this study, the possibility acidic and microbiological ash leaching, was investigated in order to minimize the concentration of toxic ash elements. The first phase of the experiment is the acid leaching of ash with H₂SO₄, which is both a preparation of ash for the microbiological leaching, since at this stage leads to neutralization of the high content of alkaline components. The second phase is the microbiological leaching of ash, generated bacterial Fe₂(SO₄)₃ from pyrite.

2. EKSPERIMENTAL

2.1 Chemical analysis of ash and pyrite

Silicate analysis of the ash was conducted using the conventional method, by alkaline fusion with NaKCO₃ and dissolution in HCl[5-7]. From the filtrate, Fe, Al, Ti, Ca and Mg were determined while the residue was further treated with HF in order to obtain volatile SiF₄, from which the SiO₂ content was determined. The remaining precipitate was treated again as silicate material.

For the determination of alkaline metals and trace elements, the sample was decomposed with a mixture of HClO₄ and HF, while for the determination of phosphorus, the sample was decomposed with a mixture of aqua regia and HClO₄.

The alkaline metals were determined by atomic emission flame spectrophotometry, Fe, Al, Ti, Ca, Mg and trace metals by atomic absorption flame spectrophotometry, while phosphorus was determined spectrophotometrically as the yellow phosphomolybdate complex.

Sulphide sulphur from the pyrite concentrate was determined gravimetrically after oxidation with KClO_3 and HNO_3 followed by precipitation as BaSO_4 . Correction on sulphate sulphur from the pyrite concentrate was determined in the "soda-extract" (boiling solution of Na_2CO_3), as BaSO_4 .

Heavy metals from pyrite were determined in the same manner as employed for the ash.

2.2 Preparation of pyrite for the leaching experiments

The pyrite concentrate for the leaching experiments was prepared from commercial Bor concentrate by treating with a 0.5 mol/dm^3 sulphuric acid solution ($\text{pH} = 0.5$) (solid to liquid phase ratio 1:5 m/V), and mixing with mechanical stirrer at a room temperature overnight. Then, the solution was decanted, washed with deionised water and dried at 80°C to a constant mass.

2.3 Acidic leaching

Fly ash was dispersed in $0.05 \text{ M H}_2\text{SO}_4$ solution, shaken for 48 h, filtered from the solution, washed out with deionised water and dried at 110°C . Metals were determined from filtrate by atomic emission flame spectrophotometry.

2.4 Microbiological leaching

The microbiological leaching experiments were carried out with bacterium *A. ferrooxidans* B4 from the microorganism collection of the Department of Chemistry, ICTM, Belgrade. Experimental conditions were: leaching period of 14 d, 100 mL leaching solution (g/dm^3): $(\text{NH}_4)_2\text{SO}_4$ (3), K_2HPO_4 (0.5), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.5), KCl (0.1), $\text{Ca}(\text{NO}_3)_2$ (0.01), at a pH of 2.5 in 500 mL Erlenmeyer flasks at a pulp density of 10 % (m/V) (10 g leaching substrate in 100 mL solution). One half of the substrates pyrite and the other was fly ash. The initial number of microorganisms was 3.7×10^8 per mL, determined by the Most Probable Number method[8]. Experiment was realized on a horizontal shaker New Brunswick Scientific. The incubation temperature was 28°C and the rotation speed 100 rpm.

3. RESULTS AND DISCUSSION

Chemical analyses of fly ash are presented in Table 1. The obtained results show the presence of SiO_2 , Al_2O_3 , Fe_2O_3 and CaO as the dominant ash components.

Table 1. Chemical analysis of fly ash

SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	TiO_2 %	MnO %	Na_2O %	K_2O %	P_2O_5 %	SO_3 %	LOI %
53.25	21.73	6.43	7.86	2.03	1.02	0.068	0.230	1.28	0.053	0.793	5.20

Chemical analyses of pyrite are presented in Tables 2–3

Table 2. Chemical analysis of pyrite after preparation for the leaching experiments

	%
Fe	41
Sulphide S	44.6
Cu	0.21

Table 3. Content of heavy metals in pyrite after preparation for the leaching experiments

Sample	Mn ppm	Pb ppm	Cu ppm	Zn ppm	Cd ppm	Cr ppm	Ni ppm
Pyrite	7	45	2100	12	1	10	14

Chemical analyses of fly ash before leaching experiments, are presented in Table 4.

Table 4. Content of heavy metals in fly ash before and after acidic leaching experiments

Sample	Mn ppm	Pb ppm	Cu ppm	Zn ppm	Cd ppm	Cr ppm	Ni ppm
Fly ash before	600	60	82	85	3.5	175	185
Fly ash after	358	54	68.5	66.5	3	160	165

Percentage of metals leached after acidic leaching are as follows: 40.33% Mn, 10.00% Pb, 21.76% Zn, 16.46% Cu, 14.28% Cd, 10.81% Ni, 8.57% Cr.

The experiment of microbiological ash leaching was completed after 14 d with the same microorganism number as at the beginning, 3.7×10^8 per mL. This fact implicates that substrate did not have a toxic effect on the bacteria. During the experiment, 24 % of pyrite sulphur was dissolved and 1.67 $\text{Fe}_2(\text{SO}_4)_3$ produced.

The percentage of leached metals, resulting from the activity of *Acidithiobacillus ferrooxidans*, (i.e., the effective metals leaching) was calculated by subtraction of percentage metal leaching in the control suspension from that in the *Acidithiobacillus ferrooxidans* suspension, from which the amount of metals leached from pyrite has been subtracted. The obtained results are presented in Table 5.

Table 5. Percentage of metals leached after 14 days

	Mn	Cr	Cd	Ni	Zn	Pb	Cu
Suspensions with <i>A. ferrooxidans</i>	16.45	6.42	20.53	11.57	17.65	6.28	22.66
Control suspension	2.04	0.46	2.93	2.96	4.16	2.21	1.2
Effective leaching	14.41	5.96	17.60	8.61	13.49	4.07	21.46

4. CONCLUSION

The results of the effective metal leaching are as follows: Mn(54.74%) > Cu(37.92) > Zn(35.25%) > Cd(31.88%) > Ni(19.42%) > Cr(14.53%) > Pb(14.07%).

Electrofilter ash leaching before its final deposition in landfills, can be a useful way of minimizing the content of toxic elements in the ash. The most mobile metals which are a serious danger for the environment, should be leached out by $\text{Fe}_2(\text{SO}_4)_3$ and H_2SO_4 .

Since it was confirmed that the electrofilter ash is not toxic substrate for *A. ferrooxidans*, the conclusion is that the process of microbial leaching of ash can be combined with the process of microbiological leaching of sulphide mineral concentrates. The advantages of synergistic effects would be the following: 1) acid from sulphide minerals bioleaching process would be used to treat ash. 2) there would be a reduction in the need for limestone. 3) ions extracted from the ashes could be used into the stages of obtaining metals in bioleaching plants.

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