

SHORT COMMUNICATION

**Bacterially generated $\text{Fe}_2(\text{SO}_4)_3$ from pyrite, as a leaching agent
for heavy metals from lignite ash**

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Abstract: Investigations of heavy metals from lignite ash, which is a coal combustion by-product, have for years been very interesting from different aspects of environmental protection. In this study, the possibility of microbiological ash leaching, with a strong oxidation agent, bacterially generated $\text{Fe}_2(\text{SO}_4)_3$ was investigated in order to minimize the concentration of toxic ash elements. Leaching experiment by the shake flask testing technique was performed during a period of 20 d at a temperature of 28 °C. The results obtained show 5- to 22-fold (for Cd and Ni approx. 5, Zn approx. 6, Mn approx. 8, Cr approx. 13 and Cu approx. 22) higher metal leaching efficiency in the suspension with bacterially generated $\text{Fe}_2(\text{SO}_4)_3$ than in the control suspension.

Keywords: *Acidithiobacillus ferrooxidans*, heavy metals, coal ash.

INTRODUCTION

It is well known that iron(III) sulphate, generated from pyrite by *Acidithiobacillus ferrooxidans*, is a good oxidant for many mineral substrates.^{1,2} The most typical example, with great economic importance, is the oxidation of uranium oxide (from uraninite $\text{UO}_2 \times 2\text{UO}_3$) into uranium sulphate. The subject of this paper is electrofilter ash (fly ash), a by-product of power plant coal combustion. In the European Union countries, more than 90 % of fly ash finds application in the cement industry,^{3–5} road construction,^{3,6} building industry,^{3,7} and in remediation.³ However, the situation in Serbia is very different. A very low percentage (2.5 %) of fly ash is used in the cement industry,⁸ while the rest is hydraulically transported and stored in landfills. Continuous accumulation and other negative environmental phenomena are the consequences of this action.

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In the coal combustion process, the organic compounds are completely burnt, while 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.^{9,10} In this study, the possibility of microbiological leaching of ash, as a non conventional biotechnological substrate, with bacterially generated $\text{Fe}_2(\text{SO}_4)_3$, in order to minimize the quantity of toxic elements, was investigated.

EXPERIMENTAL

Chemical analysis of ash and pyrite

Silicate analysis of the ash was conducted using the conventional method, by alkaline fusion with Na_2CO_3 and dissolution in HCl .¹¹ From the filtrate, Fe, Al, Ti, Ca and Mg were determined while the residue was further treated with HF in order to obtain volatile SiF_4 , from which the SiO_2 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 HClO_4 and HF , while for the determination of phosphorus, the sample was decomposed with a mixture of aqua regia and HClO_4 .

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.

Grain-size analysis of the ash

Samples were sieved through 37- μm sieves, type "Tyler", and analysed on a Coulter Multisizer particle sizing and counting analyser using a measuring tube with a 100 μm orifice.

Fly ash preparation for the leaching experiment

The presence of alkali components in fly ash is considered inconvenient for the reaction between the ash and the acidic iron(III) sulphate solution. Hence, it is necessary to neutralize the ash before adding the bacterial culture which would generate the oxidant. Before the leaching experiment, fly ash was dispersed in 0.05 M H_2SO_4 solution, shaken for 48 h, filtered from the solution, washed out with deionised water and dried at 110 °C.

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/dm³ sulphuric acid solution (pH \approx 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.

Leaching experiments

The leaching experiments were carried out with bacterium *Acidithiobacillus ferrooxidans* B4 from the microorganism collection of the Department of Chemistry, ICTM, Belgrade. Experimental conditions were: leaching period of 20 d, 100 ml leaching solution (g/dm³): $(\text{NH}_4)_2\text{SO}_4$ (3), K_2HPO_4 (0.5), $\text{MgSO}_4 \times 7\text{H}_2\text{O}$ (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 substrate was pyrite and the other was fly ash. The initial number of microorganisms was 8.5×10^8 per mL, determined by the Most Probable Number method.¹² The control suspension had the same chemical content and pH value as the suspension with *A. ferrooxidans*, but the *A. ferrooxidans* culture had been inactivated by sterilization.

Experiment was realized on a horizontal shaker New Brunswick Scientific. The incubation temperature was 28 °C and the rotation speed 100 rpm.

RESULTS

Chemical analyses of pyrite and fly ash after preparation for the leaching experiments, are presented in Tables I–III. The obtained results show the presence of SiO_2 , Al_2O_3 , Fe_2O_3 and CaO as the dominant ash components, while among the trace elements the most abundant was Mn, and the least Cd.

TABLE I. Chemical analysis of fly ash after preparation for the leaching experiments

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

TABLE II. Chemical analysis of pyrite after preparation for the leaching experiments

Component	%
Fe	41.00
Sulphide S	44.60
Cu	0.21

TABLE III. Content of heavy metals in fly ash and pyrite after preparation for the leaching experiments

Sample	Mn/ppm	Pb/ppm	Cu/ppm	Zn/ppm	Cd/ppm	Cr/ppm	Ni/ppm
Ash	600	60	82	85	3.5	175	185
Pyrite	7	45	2100	12	1	10	14

Results of grain-size ash analysis show the following size distribution:

- 7.87 % of ash particles less than 10 μm
- 17.10 % of ash particles 10–30 μm ,
- 11.94 % of ash particles 30–63 μm ,
- 16.15 % of ash particles 63–100 μm ,
- 46.84 % of ash particles more than 100 μm .

The experiment of microbiological ash leaching was completed after 20 d with the same microorganism number as at the beginning, 8.5×10^8 per ml. This fact implicates that substrate did not have a toxic effect on the bacteria. During the experiment, 40.25 % of pyrite sulphur was dissolved and 2.57 $\text{Fe}_2(\text{SO}_4)_3$ produced. The percentage of leached metals, resulting from the activity of *A. ferrooxidans*, (i.e., the effective metal leaching) was calculated by subtraction of percentage metal leaching in the control suspension from that in the *A. ferrooxidans* suspension, from which the amount of metals leached from pyrite has been subtracted. The obtained results are presented in Table IV.

TABLE IV. Percentage of metals leached after 20 d

	Mn leaching %	Cr leaching %	Cd leaching %	Ni leaching %	Zn leaching %	Pb leaching %	Cu leaching %
Suspensions with <i>A. ferrooxidans</i>	16.70	7.1	25.55	13.94	17.80	4.21	28.70
Control suspension	2.01	0.52	5.16	2.93	2.77	2.10	1.28
Efficiency of metal leaching	14.69	6.58	20.39	11.01	15.03	2.11	27.42

CONCLUSION

The results of the effective metal leaching are as follows: Cu (27.42 %) > Cd (20.39 %) > Zn (15.03 %) > Mn (14.69 %) > Ni (11.01 %) > Cr (6.58 %) > Pb (2.11 %).

The leached Cu came from the pyrite. The low percentage of Pb leached is the result of the production of low-solubility PbSO₄. The results obtained for Cd, Mn, Zn, Ni and Cr leaching are less than the published values for similar substrates.¹³ This can be explained by the fact that the smallest particles, the most suitable for leaching, were not dominant in the fly ash samples. Considering the quantity of produced Fe₂(SO₄)₃ and the content of pyrite sulphur in the leached substrate, it can be concluded that approx. 60 % of decomposed pyrite was present in the substrate after 20 d and that the leaching could be longer.

On the basis of the obtained results, investigation of ash bioleaching will be continued in the future, with a smaller size of fly ash granulation, a larger initial number of microorganisms and a longer duration of leaching. The leaching should be continued until all of the of pyrite had been decomposed.

Electrofilter ash bioleaching 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 Fe₂(SO₄)₃ and H₂SO₄.

Simultaneously with the process of microbiological ash leaching, significant quantities of Cu (from the pyrite) are solubilized which could be of interest not only from the viewpoint of environmental protection, but also for commercial aspect as well.

ИЗВОД

БАКТЕРИЈСКИ ГЕНЕРИСАНИ $\text{Fe}_2(\text{SO}_4)_3$ ИЗ ПИРИТА КАО АГЕНС ЗА
ЛУЖЕЊЕ ЕЛЕКТРОФИЛТЕРСКОГ ПЕПЕЛА ТЕРМОЕЛЕКТРАНЕ ИЗ
ПРОЦЕСА САГОРЕВАЊА ЛИГНИТА

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Тешки метали у пепелу, који настаје као споредни производ при сагоревању угља, већ годинама изазивају велику пажњу свих оних који су на било који начин повезани са заштитом животне средине. У овом раду је испитивана могућност микробиолошког лужења пепела, бактеријски генерисаним $\text{Fe}_2(\text{SO}_4)_3$, као јаким оксидационим средством, са циљем смањења концентрације токсичних елемената у пепелу. Изведен је експеримент лужења у ерленмајерима уз мућкање. Експеримент је трајао двадесет дана на температури од 28 °С. Добијени резултати показују да је ефикасност излужења метала од 5 до 22 пута већа у суспензији са бактеријски генерисаним $\text{Fe}_2(\text{SO}_4)_3$ него у контроли (за Cd и Ni око 5 пута, Zn око 6 пута, Mn око 8 пута, Cr око 13 пута и Cu око 22 пута).

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