

BENEFICIATION OIL SHALE BY BACTERIAL DEPYRITIZATION AS POSSIBLE GREEN TECHNOLOGY: BIOPROCESSING ON LABORATORY SCALE

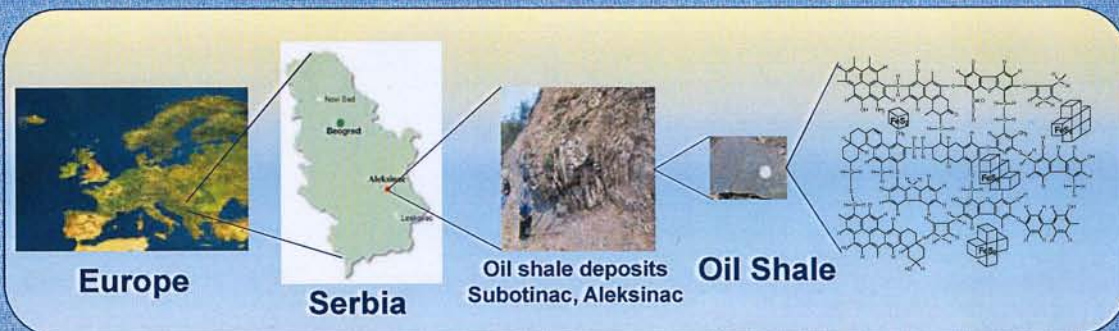
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INTRODUCTION

Amount of reserves of oil shale in Serbia are up to about 6 billion tons (estimated), while the largest deposit (approx. 1/3 of total quantity) for open-pit and underground exploitation is situated in the locality of Aleksinac in East Serbia (not exploited at the moment). Shale from Aleksinac is an immature Oligocene-Miocene lacustrine sediment. The average content of the organic substance in Aleksinac shale is about 20 %, with a dominant share of kerogen (the content of bitumen is less than 5 %). The mineral part comprises about 20 % carbonates, approximately 10 % pyrite and the rest are aluminosilicates.



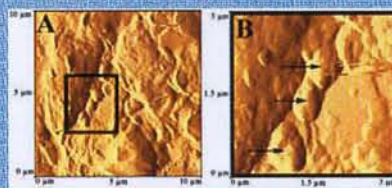
RESULTS AND DISCUSSION

In our lab researches relating to the "quality improvement" of raw shale from Aleksinac that have been made for near 30 years, for depyritization as "non-destructive reagents" we use strains of chemolithoautotrophic thionic bacteria *Acidithiobacillus ferrooxidans*. In a large number of experimental variations of the "shake flask test technique" the best results have been obtained for depyritization (more than 95%). Combining AFM surface imaging and leaching analysis following bacterial colonisation of oil shale layers demonstrates that an initial attachment to the surface is necessary for the leaching and that later on, once a sufficient concentration of Fe²⁺ ions in the solution is achieved, cells detach to become free cells, and leaching occurs primarily by the Fe³⁺ [1-6].

Table 1. Parameters determined at the beginning ("zero-time") and at the end of the three week's bioleaching

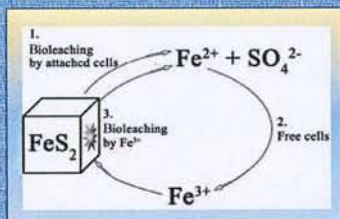
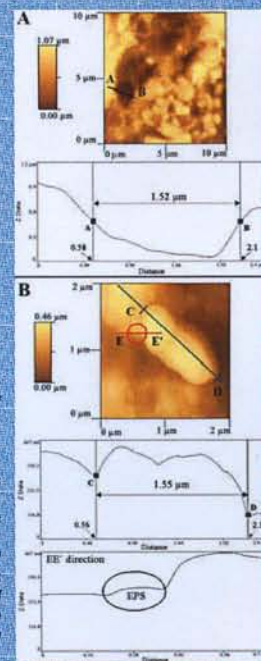
Duration of bioleaching (weeks)	Solid liquid ratio (the density of the pulp, % ²)					
	1:10 (100)		1:12 (8.3)		1:14 (7.1)	
	0	3	0	3	0	3
Parameters determined						
pH	2.58	1.29	2.46	1.28	2.42	2.42
Residual iron ³⁺ (% of initial pyrite)	197	197	197	197	197	197
Soluble iron ²⁺ (% of initial pyrite)	0.29	81.44	0.21	90.90	0.81	75.18
Pre-precipitated iron ³⁺ (% of initial pyrite)	4.81	6.37	5.38	4.44	2.78	7.49
Bioleached pyrite, cumulative ³ (% of initial pyrite)	4.94	87.61	3.83	38.82	3.61	81.07
Residual pyrite in the substrate (% of initial pyrite)	87.19	4.35	95.39	1.79	93.35	3.23
Efficiency of bioleaching process ⁴	1.2	8.4	1.2	6.4	1.1	5.4
Volume of leaching solution (cm ³) ⁵	100	100	100	100	100	100

¹All forms of iron were calculated as pyrite.
²Ratio of bioleached substrate and precipitated iron.
³Ratio of cumulative bioleached pyrite versus pyrite dissolved in the control run.

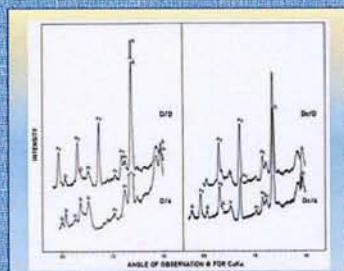


AFM images of *At. ferrooxidans* B cells: attached to oil shale cuttings after 48 h of incubation. Vertical deflection images of AFM scans acquired by contact made in air. Panel (A) shows an oil shale layer with cells attached to surface defects, and panel (B) represents a close-up view of one cutting, framed on panel (A). The cells are seen as convex ellipsoid shapes, such as the ones indicated by arrows in the topography image in panel (B).

AFM analysis of the oil shale surface after five days of incubation with *At. ferrooxidans*. Panel (A) shows a topographic AFM image of the oil shale with one of the pits measured (cross section AB). Panel (B) shows a topographic AFM image of a single *At. ferrooxidans* A cell with the cell width measurement (cross section CD). In addition, AFM analysis demonstrates the existence of EPS surrounding the cell (cross section EE).



Systematic overview of pyrite bacterial leaching. 1. In the first stage, cells attach to the surface and Fe²⁺ ions are leached into the solution. 2. In the second stage, the number of free cells increases due to the rise in Fe²⁺ levels in the solution. 3. In stage 3, biobleaching by Fe³⁺ ion as an oxidising agent predominates.



X-ray diffraction spectra of the Aleksinac oil shale HCl concentrate, substrates obtained in the experiment with solid to liquid ratio of 1:12. D/0 denotes the inoculated substrate at "zero-time", D/4 after the 4th week, Dc/0 denotes the substrate in control test at "zero-time", Dc/4 after the 4th week. Py-pyrite, Qz-quartz, Ill-illite, Plt-plagioclase.

CONCLUSION

Benefits of the bacterial depyritization are primarily in order to reduce aero pollution and corrosivity, and also this green process must be low cost green bio/technology for biobeneficiation of oil shale.

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