PROGNOSIS OF THE STABILITY OF ARSENIC IN THE BIOTOP OF THE BROWN-COAL DUMP

Mária Kušnierová
Institute of Geotechnology SAS, 043 53 Košice, Slovakia

ABSTRACT

In the nature there is a large number of various microorganisms which participate in the process of transformation of minerals and other materials, in their corrosion, disintegration decomposition or even formation of new components. Many of the microorganisms gain the energy for their metabolic processes trough oxidation of anorganic compounds. Interaction of microorganisms or their metabolites with deposited components, which may be toxid, can take place directly in the dump biotop. In fly-ashes produced by burning the Slovak brown coal a higher arsenic content is present, the arsenic in the original coal being bound in a very stable FeAsS compound (arsenopyrite). However this compound is decomposed by burning and so we were interested in the stability of newly formed arsenic compounds found in the fly-ash. Their stability was tested by leaching experiments in an environment of nutrient medium for bacteria Thiobacillus ferrooxidans 9KA (pH 1.5) at a concentration of cells $7x10^7$ ml^{-1} and simultaneously also without bacterial culture at the same condition. Apart from this, the extraction of arsenic from fly-ash was monitored also in the environment of metabolites of fungi Aspergillus niger (citric acid) at pH 1.8.

INTRODUCTION

Speaking of wastes, we should mention fly-ashes from electricity works, whose per capita and per km^2 production in Slovakia is among the highest in thhe world [1]. At present, this

0304-3894/94/$07.00
SSDI 0304-3894(94)00022-9

material is considered to be a waste with a low degree of reuse and is normally deposited on dumps.

High porosity and thhus low density make it possible to use this material for production of light building materials with relatively good thermal-insulating properties. From this point of view arsenic may be considered as qualitatively dangerous and therefore unwanted component of fly-ashes. Decisive danger factors are mainly the form and the properties of arsenic compounds in fly-ashes, in relation to the existing exogenetic influences in the biotop of the dump. Because fly-ashes are the product of the coal heat treatment, it may be assumed that arsenic compounds will be not very stable nor resistent against various exogenetic influences.

This is also due to the fact that in nature a large quantity of various microorganisms exists which participate in the process of transformation of minerals and other anorganic materials, in their corrosion, disintegration, decomposition, but also in the formation of new compounds and their deposits (Table 1). Many of these microorganisms gain energy for their metabolic processes by oxidation or reduction of anorganic compounds. These so-called chemolithotrophic aerobic microorganisms are specific in that they can be active even in extreme conditions, such as in very acid (pH 2) or hot ($60^{o}C$) environments. One of the most widespread bacteria found in biotops of deposits and waste dumps are the thion bacteria *Thiobacillus ferrooxidans* which pump energy for their metabolic processes from oxidation processes in which they participate in electron transport from donors (Fe^{2+}) to acceptors (O_2) thus catalyzing the whole process [2].

RESULTS

The influence of this type of bacteria in the biotop of a fly-ash dump may be estimated from results of a leaching test whose results are documented in Fig. 1. Catalytic action of bacteria is manifested only after 23 days of leaching (curve 1). It is important that the As extraction was very apparent right from the start also in a blank experiment without bacteria (curve 2) indicating that arsenic extraction is influenced by the acidic

medium. It should be noted that prolonged presence and activity of *Thiobacillus ferrooxidans* in deposits and waste biotops containing substrates favouring the growth of these bacteria leads to the production of $Fe_2(SO_4)_3$ and H_2SO_4 which in turn leads to a pH decrease of infiltration waters.

The influence of an acidic medium on the extraction of As was confirmed also by experimentally verifying the contamination of metabolites of fungi *Aspergillus niger* (their product is citric acid) on the chemistry of fly-ashes. Results are in Table 2.

Table 1 Survey of microorganisms able to leach elements from various forms of materials in nature

Element	Form of occuremces	Microorganism capable of leaching
Si	bauxite	*Silicated bacterium, Aspergillus niger, B, mucilaginosis, B.circulans*
As	sulfide	*Thiobacillus ferrooxidans, Thiobacillus thiooxidans, Leptospirillum*
	other As^{3+} compounds	*Pseudomonas putida, Alcaligenes eutrophus, Pseudomonas arsenooxidans*
Al	silicate	*Aspergillus niger, Penicillium glaucum, Penicillium brevicaule*
Fe	Fe^{2+} in silicate	*Thiobacillus ferrooxidans, Aspergillus niger, B. polymyxa, B. circulans, Penicillium species, Penicillium glaucum, Pseudomonas*

It follows from these results that due to the influence of the citric acid solution a substantial reduction of the As (by 71.9 %), S (by 70.2 %), CaO (by 55.9 %), MgO (by 15.6 %) was obtained, while the content of SiO_2 and Al_2O_3 has increased. It is remarkable to note that the Fe content remained practically unchanged and the TiO_2 content decreased only slightly, since it is well known [3,4] that the citric acid is used for deferrization

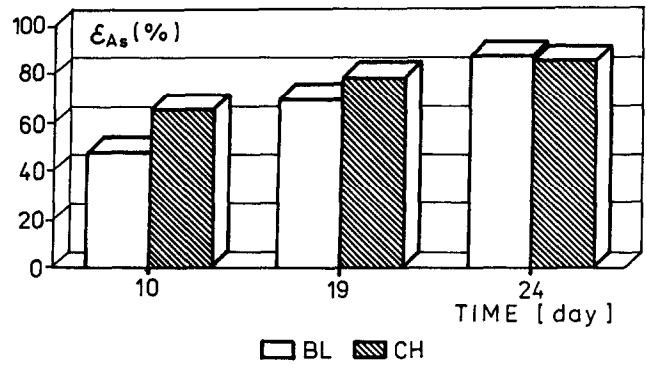

Fig. 1 Relation between the duration of the bacterial extraction of fly-ashes and arsenic extraction into the solution
BL: Leaching test with bacteria *Thiobacillus ferrooxidans* pH, 1.5
CH: Controle of nutrient medium 9K part A, pH 1.5

of silicates and that relatively good results were obtained in the extraction of Ti from fly-ashes of the Opatovice electrical works [5].

Table 2 Results of a leaching test of fly-ashes

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	TiO_2	As	S
Initial sample	51.8	11.5	7.8	1.0	1.4	1.3	0.4	0.24	2.2
Sample after leaching	55.0	13.7	7.75	0.45	1.2	1.3	0.3	0.06	0.65

Leaching agent: citric acid; pH 1.7; suspension density 20 %

The chemistry of fly-ashes in the dump biotop may be influenced, within reasonably long time, also by silicate bacteria (such as *Bacillus circulans*) as well as various other toxonomic groups of microorganisms which are present in soils and are able to destruct silicates and aluminosilicates [6], and whose activity may lead to changes in pcm range of Al and Si.

CONCLUSION

It may be concluded from the obtained results that the influence of metabolites of investigated microorganisms is positive in that the As content in fly-ashes is decreased. However, this process can have a negative influence on the ecology of the biotop of a fly-ashes dump and, moreover, we will be probably not able to control it. On the other hand negative influence of similar character may be caused also by acid rains which are no more exceptional.

This work was supported, in part by Slovak Grant Agency for Science SAS (grant N 6-138).

REFERENCES

[1] F. Michalíková, M. Bugel, F. Zeleňák: Úpravnícke metódy používané pri získavaní úžitkových zložiek z popolčekov. Environment and Mineral Processing, Ostrava, 1992, p. 68.

[2] G.M. Wenberg: Trend 4 (1984) 21.

[3] S. Groudev, V. Groudeva: Microbial removal of silicon from mineral raw materials. Int. Symp. on Biohydrometallurgy, Košice 1987.

[4] N. Števulová, K. Tkáčová, E. Pastíriková, I. Hocmanová: Modelovanie biodeferitizácie mechanicky aktivovaných práškov kremeňa. Biohydrometalurgia II., Košice (Slovakia) 1992, p. 58.

[5] P. Fečko, H. Ráclavská, K. Ráclavský, P. Horklová: Možnosti získavania titánu z popolčekov elektrárne Opatovice. Environment and Mineral Processing, Ostrava 1992, p. 172.

[6] G.I. Karavajko, G. Rossi, A.D. Agate, S.N. Groudev, Z.A. Avakyan: Biotechnology of Metals, CFIP-GNKNT, Moskva 1988.