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Possibilities of recovery of dispersed metals occurring in black shale using microorganisms*

Some shales formations situated within Poland contain an increased amount of several metals. These metals are, however, widely dissipated, as well as occurring in homogenous forms, therefore, their recovery requires the application of non-conventional methods. We made preliminary investigations of the utilization of microbiological methods for this purpose. In research into the recovery of U, V, Mo, Zn and Pb from the black shale, bacteria of the genus *Thiobacillus ferrooxidans* were utilized. During experiments of 7 months duration with periodic exchanges of the leaching solution the following recoveries were obtained: Zn — 95%, Pb — 55%, U — 75%, Mo — 60% and V — 47%. These results give a good prognosis for further applications of microbiological methods in the recovery of metals dissipated in shale material.

INTRODUCTION

In the world processing industry bituminous shales are exploited mainly as a valuable raw material for the recovery of bituminous substances contained in them. The shales contain, moreover, numerous elements — mainly metallic — in trace amounts. However, these elements are dispersed to such a degree that they cannot have any essential industrial significance, especially in the case of existence of other richer sources (A. Anderson, O. Gunnar, 1975; A. P. Zefirov *et al.*, 1971). Polish shales do not have an organic phase content significant enough to merit industrial processing to obtain bituminous substances, but their metal content is of some interest. We do not possess any significant resources of many economically important metals, such as U, V and Mo. The shales are a poor, but widely spread source, indicated by results of geological studies. Recovery of metals by classical methods from such type of raw material is possible but too costly and complicated (K. Pinkas, 1977). Therefore, we decided to use a process of chemical leaching supported by the action of microorganisms (S. I. Polkin, G. I. Karavayko, 1975) as an alternative, or at least a supplementary operation in the total processing of shales. Such kinds of processes are applied throught the world for various types of mineral raw materials and wastes (G. I. Karavayko, 1970, A. E. Torma, 1978).

METHODOLOGICAL ASSUMPTIONS

Black shales from the Podlasie Region, being the most metalliferous form of shales met in Poland, were used in research on recovery technology of metals occurring irn shales in trace amounts. Shale samples originated from exploratory drilling performed by the Polish Geological Institute in Warsaw. The investigated black shales are characterized by a prevalent proportion of aluminosilicate and organic substances, and a minimal content of carbonate (basic) substances with a significant content of pyrite (about 3.5%). Several metals werealso found in trace amounts (10^{-1}–10^{-3}%): Ni, Cu, Zn, Co, U, Mo, V, Ti, Pb and Re. Mineralogical investigations showed that these metals were not in homogenous mineral forms. They occurred both in sulphide and oxidized forms scattered in organic substances and clayey minerals, and also in pyrite concentrations. Detailed evaluation of mineralogical metalliferous properties of the investigated bituminous shales was presented in our earlier studies on perspectives of industrial utilization (K. Sztaba, E. Konopka, 1988). In the analysis of the metalliferous properties of the investigated black shales we chose metals of interest, both from the point of view of their economic importance and their concentration in the investigated material. The ratio (E) of average concentration to clark was chosen as an arbitrary criterion. The values are given below (clark and concentration in ppm):

uranium	$E = 65.0$	(conc. = 130, clark = 2)
vanadium	$E = 10.9$	(conc. = 1469, clark = 135)
molybdenum	$E = 62.0$	(conc. = 93, clark = 1.5)
copper	$E = 5.2$	(conc. = 288, clark = 55)
zinc	$E = 71.1$	(conc. = 4978, clark = 70)
lead	$E = 38.5$	(conc. = 481, clark = 12.5)
nickel	$E = 3.6$	(conc. = 348, clark = 75)
cobalt	$E = 2.1$	(conc. = 52, clark = 25)

This permits arrangement the elements in the sequence: zinc, uranium, molybdenum, lead, vanadium, copper, nickel, cobalt. In a similar arbitrary way, taking the relative concentration $E = 10$ as the limiting value, we recognized the first five elements of the sequence to be of interest, i.e. in addition to U, Mo and V also Zn and Pb.

The process of metal leaching considered as a direct result of microorganism action, especially on scale bigger than that of the laboratory, is based on the use of thionic bacteria (G. I. Karavayko, 1970; T. V. Kovalenko, T. E. Dudarieva, 1986; K. Sztaba, E. Konopka, 1988). Thionic bacteria are the most commonly met in natural geochemical processes. Considering the above discussed environmental conditions of the studied shales it was most appropriate to use *Thiobacillus ferrooxidans* in our research on metal recovery. For the growth of this kind of bacteria, significant acidity of their habitat is favourable, i.e., pH = 1.5–3.5, at which most of the metals form soluble compounds. The process of oxidation of practically all metal sulphides is a source of energy determining growth of *Th. ferrooxidans*.

This also includes oxidation of FeS_2, and bivalent ferrous ions; in special cases they oxidize ferrous sulphate to ferric sulphate, the solution of which is, in the presence of sulphuric acid, an effective leaching medium for a number of metals.

Preliminary investigations on possibilities of the application of *Thiobacillus ferrooxidans* in chemical-biological leaching of the mentioned metals, scattered in the black shale (E. Konopka, E. Kisielowska, 1988), showed that the natural environment of the shale deposits is favourable for the essential chemical and biochemical processes assumed. Thus, we undertook multivariant investigations concerned with methods of intensifying this process, the practical purpose being determination of the optimal conditions of leaching. We were especially interested in finding extreme conditions for estimation, of the limits of leaching for the particular metals, during the shortest possible period of time. It was also important to determine factors which could decrease the efficiency of the process. Sumarizing — we tried to obtain exact information about the influence on the leaching process of some conditions which can be controlled and modified according to actual situation.

METHOD APPLIED

Leaching was carried out using black shale samples of grain size 0.5–2 mm and mass of 10 g. They were sterilized with absolute alcohol (except for samples which were leached under natural conditions and the bacterial suspension was not introduced). Average contents of metals in the samples studied were as follows: U — 130 g/t, V — 1050 g/t, Mo — 200 g/t, Zn — 7160 g/t, Pb — 700 g/t.

The volume of the leaching solution was, in each case, equal to 100 cm^3 and was made up of bacterial suspension together with nutrient medium in various proportions. *Thiobacillus ferrooxidans* cells used in the experiments were isolated from the natural habitat and adapted to conditions of increasing shale content. The applied bacterial suspension contained 10^6 cells/cm^3. A standard liquid nutrient medium 9K was used as the leaching solution. All experiments in this series were set at the same time. The experiment plan considered the following important parameters influencing the process of leaching:

DURATION OF THE PROCESS

The experiments lasted 7 months. Every 4 weeks it was possible to check several parameters describing the leaching process including pH, volume of bacterial suspension, U, V, Mo, Zn and Pb, recovery of U, V, Mo, Zn and Pb, surface changers, and mineral composition. We used this opportunity on a limited scale.

LEACHING SOLUTION EXCHANGE OPTIONS

The experiments were planned as follows:
a — without exchange of the leaching solution;
b — exchanging half of the volume of the leaching solution;
c — exchanging the whole volume of the leaching solution.

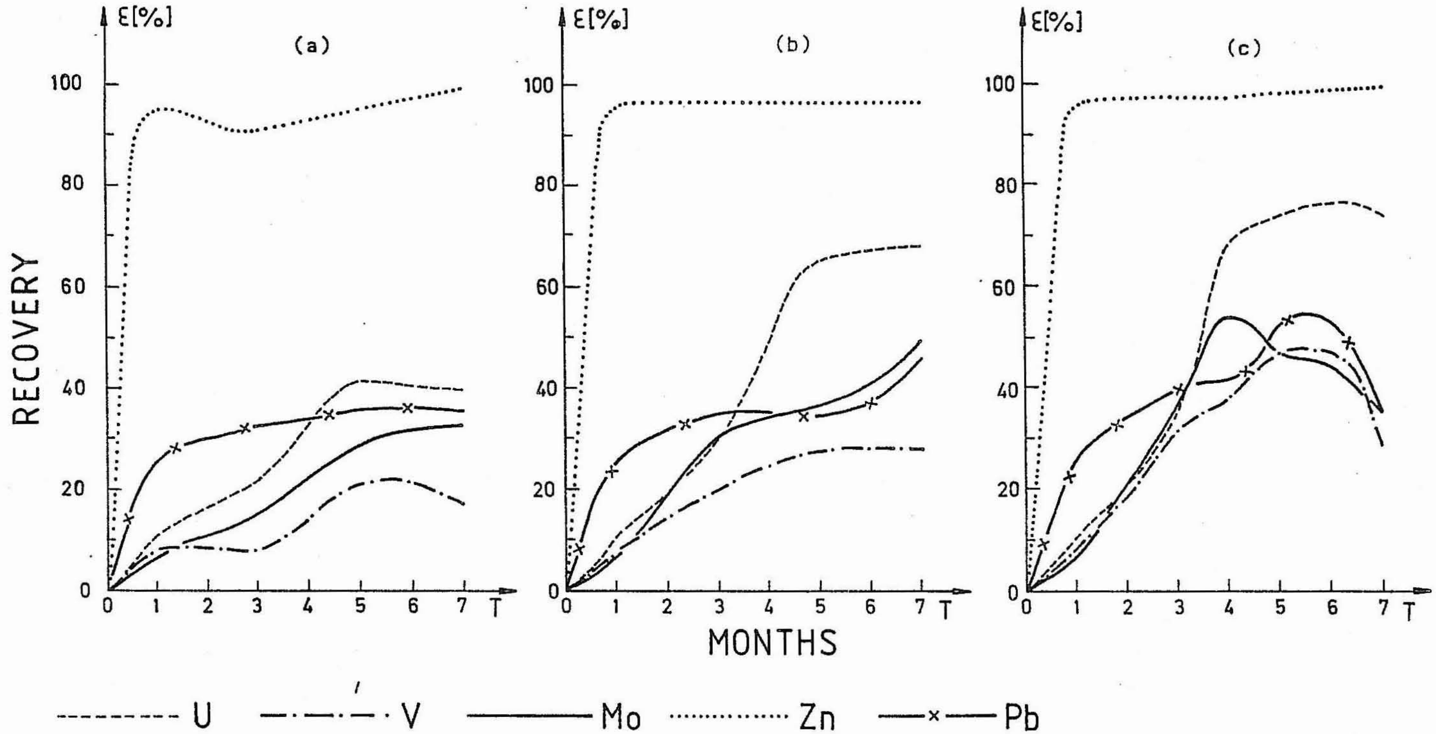

Fig. 1. Effectiveness of bacterial leaching of U, V, Mo, Zn and Pb in experiments: a — without exchange of the leaching solution, b — with periodical exchange of half volume of the leaching solution, c — with periodical exchange of the whole volume of the leaching solution

Efektywność bakteryjnego ługowania U, V, Mo, Zn i Pb w doświadczeniach prowadzonych: a — bez wymiany roztworu ługującego, b — z okresową wymianą połowy objętości roztworu ługującego, c — z okresową wymianą całej objętości roztworu ługującego

VOLUME OF BACTERIAL SUSPENSION

Applied volume of bacterial suspension was 20, 10 or 0 cm^3 (the suspension was not introduced).

In this paper we present only a portion of the results of an extensive program of investigations concerning the effectiveness of bacterial leaching of U, V, Mo, Zn and Pb under conditions of additional periodic inoculations — every 4 weeks — with 10 cm^3 of bacteria suspension, depending on degree of exchange of the leaching solution. Effectiveness is expressed in percentage recovery (ε) of metal leached from the solid phase (Fig. 1).

DISCUSSION OF RESULTS

The results of investigations of the leaching process, the product of 7-month experiments in different environmental conditions, clearly show some regularities occurring in this process. They also allow some conclusions to be drawn concerning possibilities of modelling of the process.

Analysing behaviour of the particular metals in the experiments one can find essential differences in their reaction to the biological processes, occurring and also in the resulting physico-chemical changes of the environment. Zinc and lead behaved in such way that the biological process were only of secondary significance. About 90% of Zn was already leached in the initial experimental period. However, a barely reduced effect was observed in experiments without bacteria. Lead behaved in a quantitatively similar way, but the recovery was significantly lower. Nevertheless, the effectiveness of lead leaching increased during the process. It was estimated at 55% and was correlated with the ratio of exchanges of the leaching solution.

Relations between biochemical processes and the recovery of metals were the most clearly seen for uranium, for each set of parameters. Where experiments were performed without exchange of nutrient medium (not taking into account a partial "exchange" while introducing the bacterial suspension) the increase in recovery was proportional to the volume of introduced bacterial suspension. It was, however, little differentiated during the initial period (up to 3 months). Exchange of the leaching solution (bacterial suspension + nutrient medium) advantageously influenced the effectiveness of uranium leaching. Total exchange of the leaching solution significantly accelerated the final effect. It also clearly highlighted disadvantageous effects which could be expected after long leaching periods and could negatively influence the final results. While the effectiveness of uranium leaching was increasing up to month 6 of the experiment, reaching 75% it tended to decrease after that period. This could be explained by investigation of the structure and mineral composition of the leached material. Exchange of half of the leaching solution significantly inhibited the process; after 7 months of leaching the results received were similar to those after 4 months when the whole volume of the leaching solution was exchanged.

Similar relations were observed for the leaching processs of vanadium and molybdenum. Generally they leached less effectively during the discussed period of time, although the effects were clearly positive in comparison with experiments performed under sterile conditions. In the initial period of the experiments molybdenum leached better, though the differences were not apparent when the whole leaching solution was exchanged. Just in these series of experiments, maximum recovery was equal to about 60% for molybdenum and 47% for vanadium. The effectiveness of leaching of these metals showed an increase during the first 4–5 months of the experiments, later the occurrence of some disadvantageous phenomena lowering the effectiveness were observed.

Generally, one can say that the results received give a good prognosis for the further application of biotechnological methods for the recovery of some metals dissipated in materials such as black shales.

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MOŻLIWOŚĆ ODZYSKU ROZPROSZONYCH METALI WYSTĘPUJĄCYCH W CZARNYM ŁUPKU Z WYKORZYSTANIEM MIKROORGANIZMÓW

Streszczenie

Występujące w Polsce formacje niektórych czarnych łupków zawierają podwyższone (w stosunku do średniej zawartości w skorupie ziemskiej) ilości licznych metali. Ponieważ metale te występują w znacznym rozproszeniu, jak również nie mają jednoznacznie określonych form mineralnych, odzysk ich wymaga zastosowania metod niekonwencjonalnych. Przeprowadzono prace rozpoznawcze nad wykorzystaniem do tego celu metod mikrobiologicznych.

W badaniach nad odzyskiem metali: U, V, Mo, Zn i Pb występujących w czarnym łupku były wykorzystane bakterie *Thiobacillus ferrooxidans*. Podczas siedmiu miesięcy trwania eksperymentu z okresową wymianą roztworu ługującego osiągnięto uzyski: Zn — 95%, Pb — 55%, U — 75%, Mo — 60% i V — 45%. Wyniki te dobrze rokują dla możliwości stosowania w przyszłości metod mikrobiologicznych do odzyskiwania metali rozproszonych w różnego rodzaju łupkach.