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THE INFLUENCE OF BACTERIA AND PARTICLE SIZE OF COAL PYRITES ON THE YIELD OF METALS BIOEXTRACTION

The influence of bacteria and break-up of the material leached on the effectiveness of metals extraction from coal pyrites was studied. T.ferrooxidans and T.thiooxidans strains isolated from underground mine waters and from leached coal pyrites caused a greater yield than the almost unidentified mixture of autochthonous Thiobacillus bacteria, but results were not considerably different. Results point to the possibility of conducting leaching processes using "raw" coal pyrites, not subjected to additional breaking up.

INTRODUCTION

Utilization of wastes which degrade natural environment has become an urgent problem in a large number of countries [1-3]. The technologies of utilizing and detoxificating waste substances applied nowadays are, however, in many cases, too expensive and rather ineffective. As a result, new methods enabling possibly complex and least expensive waste management are being searched for. One of the most effective methods of managing wastes seems to be the one employing bacterial leaching. Investigations into the use of Thiobacillus sulphur bacteria, and especially Thiobacillus ferrooxidans species, are being conducted with a view to utilizing various metalliferous wastes [3-6].

An attempt has been also made to use these bacteria to render the so-called coal pyrites harmless. They constitute one of the most onerous power station wastes containing considerable amount of sulphur in the form of metal sulphides. The atmospheric oxygen and rain water interact with the dumping grounds causing oxidation of sulphides. As a result of this process, a considerable amount of sulphuric acid is formed, which causes strong acidification of soil and underground waters. Equally unfavorable phenomenon is the penetration into waters and soil of a large number of metals including heavy metals, which accumulate in plants grown in surrounding fields. Consequently, multidirectional investigations are conducted aiming at utilization of these wastes which entails their simultaneous detoxification. This was also the objective of experiments carried out with regard to bacterial leaching of coal pyrites [7-9].

The paper presents the effect of bacteria and break-up of the material leached on the yield of the leaching process.

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MATERIALS AND METHODS

Investigated were coal pyrites from the Siersza Power Station in Poland. Leaching processes were conducted at the presence of active museum (model) strains of F26-77 T.ferrooxidans and T29-77 T.thiooxidans isolated from underground mine waters and adapted to the material leached [9], T.ferrooxidans strain isolated from the material leached [7], and also in the presence of mixture of autochthonous sulphur bacteria of the genus Thiobacillus. A modified 5K nutrient medium according to Silverman and Lundgren [10] with reduced Fe^{2+} ion content (from 9.0 to 5.0 g/dm^3) was used. Coal pyrites fractions: <0.3mm, 0.5-0.31mm, 5.0-0.51mm and 10.0-5.1mm were applied in the experiments. Prior to the leaching process, the pyrite samples were sterilized in a drier at temp. of 100°C for one hour for three consecutive days.

The experiments were conducted in three parallel series in Erlenmeyer flasks during 30 days. The density of the pulp used was 5% by weight and volume. The systems were inoculated with bacteria until the number of 10^6 of cells in $1cm^3$ of the leaching liquid was obtained. At the same time, leaching was conducted in sterilized systems without bacteria and with thymol as a bacteriostatic substance. Mineralogical analysis was carried out by use of Rigaku X-ray diffractometer, employing the rays $\lambda Cu,K_\alpha$ and nickel filter. The metals content in coal pyrites and leaching solutions was determined by absorption atomic spectroscopy method using Carl Zeiss-Jena spectrophotometer AAS-3. Total iron content in the solutions was determined by colorimetric method with rhodanate. Measurements of pH were carried out using MERA-ELWRO pH-meter N-517 with combined electrode.

RESULTS

Mineralogical analysis of the leached coal pyrites has shown that the material discussed contains pyrite FeS_2 with admixture of marcasite of the same chemical formula but different structure, sphalerite ZnS, quartz SiO_2 and inconsiderable amount of kaolinite $Al_4[Si_4O_{10}](OH)_8$ (Fig.1). The results of the chemical analysis point to much greater complexity of this matarial. Other components occurr, however, in smaller amounts, as shown in table 1. Except sulphur, iron, silicon, aluminum and magnesium, the remaining analyzed elements do not appear in the leached materials in amount greater than 1%.

The analysis of acidity changes in distilled water and 5K liquid during the process of chemical leaching demonstrated that the coal pyrites under investigation were of acid nature. This was first of all proved by the drop of pH (from pH 6.1 to pH 4.97) in the system containing wastes and distilled water (Fig.2). They can then be utilized as raw material in the processes of acid bacterial leaching.

The results of the investigations of the effect of the break-up on the effectiveness of leaching coal pyrites are shown in table 2 as a percentage leached of chosen metals from wastes of different break-up.

Table 1. Content of selected elements in coal pyrites

Element	Content in material [g/kg]	
	range	mean value
Al	52.7 - 57.1	54.9
Cu	0.16 - 0.26	0.21
Fe	125.0 - 148.0	136.5
Mg	36.2 - 44.7	40.4
Mn	1.25 - 1.47	1.36
Mo	0.06 - 0.07	0.07
Pb	0.19 - 0.2	0.2
S	236.0 - 306.0	271.0
Si	83.3 - 97.7	90.5
Zn	1.7 - 2.1	1.9
ash, %		72.3

Pi - pyrite
Ma - marcasite
Sf - sphalerite
Q - quartz
Ka - kaolinite

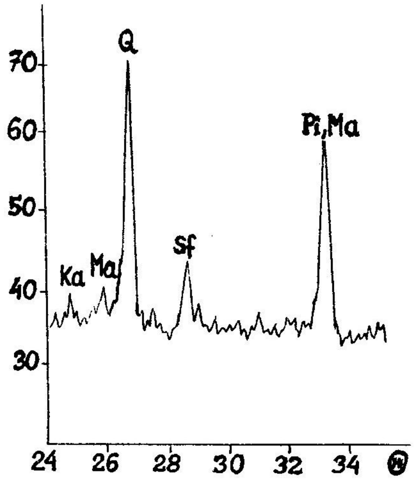
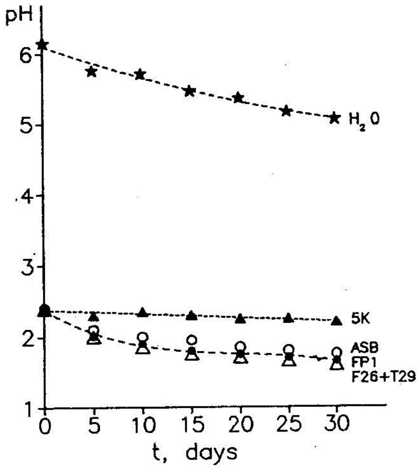


Fig.1. Mineral composition of coal pyrites

Fig.2. pH changes during chemical and bacterial leaching of coal pyrites: 5K - sterile 5K solution (control) without bacteria; F26 + T29 - 5K inoculated with mixture (1:1) of bacteria T. ferrooxidans F26-77 and T.thiooxidans T29-77; FP1 - 5K inoculated with T.ferrooxidans FP1-87; H_2O - distilled water.



It was found that extraction yields of particular metals in both chemical and bacterial leaching processes were considerably diversified. In the leaching processes occurring in control 5K solutions without bacteria, the leaching of metals from pyrites was slightly affected by the break-up. The greatest efficiency was found at <0,3mm size. In bacterial leaching with the presence of mixture (1:1) of F26-77 T.ferrooxidans

Table 2. The effect of the break-up on the effectiveness of leaching metals from coal pyrites

Metal	Percent of metals leached from coal pyrites							
Break-up	< 0,3 mm		0,5 - 0,31 mm		5,0 - 0,51 mm		10,0 - 5,1 mm	
Bacteria	-*	F26+T29	-*	F26+T29	-*	F26+T29	-*	F26+T29
Zn	14.0	55.0	10.0	45.0	8.0	44.0	8.0	41.0
Al	24.0	64.0	23.0	32.0	27.0	31.0	27.0	41.0
Mn	11.0	100.0	11.0	93.0	11.0	68.0	10.0	40.0
Cu	30.0	60.0	31.0	63.0	30.0	61.0	29.0	50.0
Mo	10.0	90.0	9.0	77.0	9.0	75.0	7.0	62.0
Pb	16.0	32.0	14.0	26.0	12.0	19.0	12.0	22.0
Fe	10.0	58.0	7.0	46.0	7.0	45.0	8.0	45.0

where: * - sterile control without bacteria;
F26 + T29 - mixture (1:1) of bacteria T.ferrooxidans F26-77 and T.thiooxidans T29-77

Table 3. The effect of bacteria on the effectiveness of metals leaching from coal pyrites

Metal	Yield of leaching of metals in solutions [%]			
	Sterile 5K (control)	5K+F26-77 +T29-77	5K + ASB	5K + FP1-87
Fe	14.5	60.0	58.9	59.1
Al	22.1	64.8	66.1	67.0
Zn	8.0	57.2	56.1	58.0
Mo	10.0	96.1	74.1	86.0
pH_o=2,4	2.2	1.60	1.75	1.65

where: 5K - modified nutrient medium 9K, with reduced Fe^{2+} content (from 9,0 to 5,0 g/dm^3);
F26-77 and FP1-87 - T.ferrooxidans strains;
T29-77 - T.thiooxidans strain;
ASB - autochthonous sulphur bacteria

and T29-77 T.thiooxidans model strains, the effect of break-up on the metal bio-extraction was evident. Also in this case, the greatest leaching yield was found to occur at <0.3mm size, the effect being however multiplied by the presence of the bacteria (table 2).

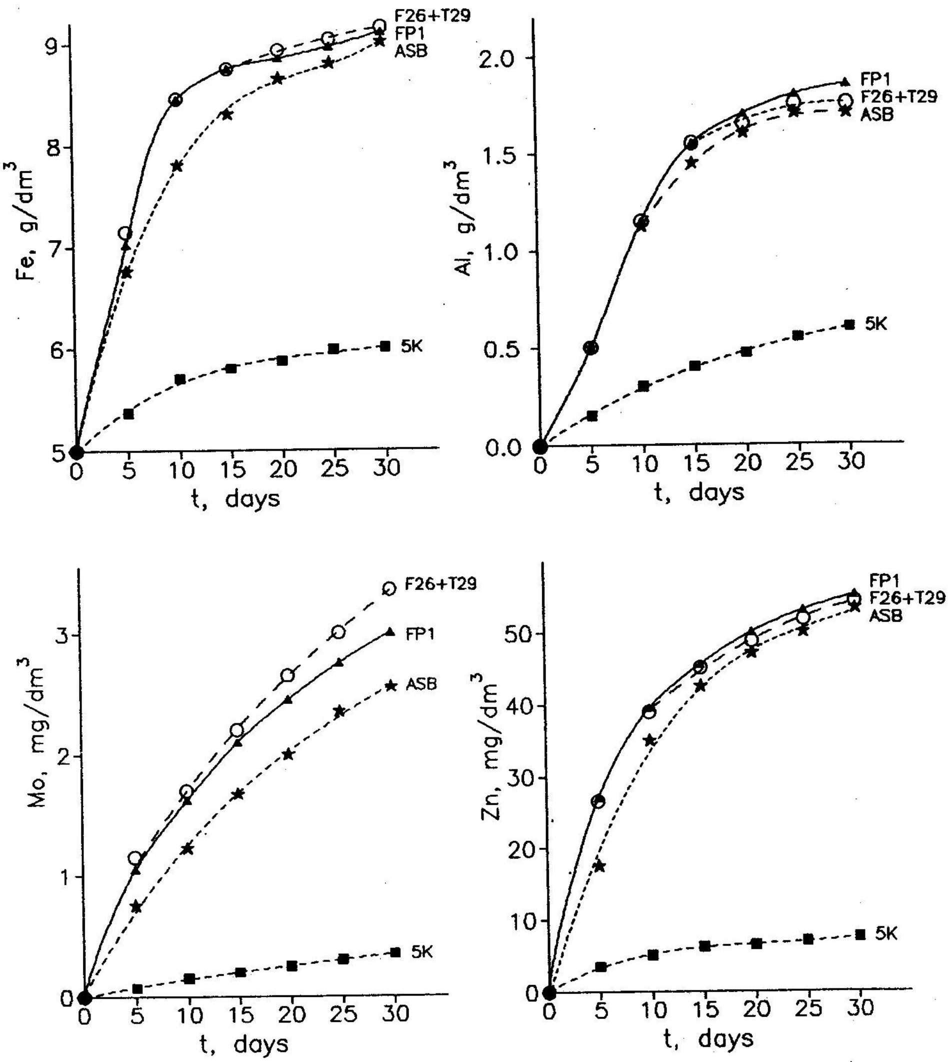


Fig. 3. Concentration of metals in leaching solutions during chemical and bacterial leaching of coal pyrites: 5K - sterile 5K solution (control) without bacteria; F26+T29 - 5K inoculated with mixture (1:1) of bacteria T.ferrooxidans F26-77 and T.thiooxidans T29-77; FP1 - 5K inoculated with T.ferrooxidans FP1-87.

The investigation results of the influence of various bacteria strains on the pH changes in leaching solutions as well as on the dynamics of leaching metals from coal pyrites are presented in figures 2 and 3. The bioextraction yields of iron, aluminium, zinc and molybdenum during the processes occurring in a sterile 5K solution and solutions inoculated with bacteria were compared in table 3. The latter solutions contained: autochthonous FP1-87 T.ferrooxidans strain, mixture (1:1) of model strains F26-77 T.ferrooxidans and T29-77 T.thiooxidans and mixture of Thiobacillus autochthonous bacteria. Clear intensification of the process in the presence of the aforesaid bacteria was found, but the differences in the effectiveness of leaching particular metals with their help were not considerable. Autochthonous FP1-87 T.ferrooxidans strain makes it possible to attain process yield approximating that obtained in the presence of F26-77 T.ferrooxidans and T29-77 T.thiooxidans model species mixture. In both systems the process was carried on with a slightly greater effectiveness than in the presence of almost unidentified mixture of autochthonous Thiobacillus bacteria. The above observations confirm the changes in pH of leaching solutions, the drop of pH in the system containing the latter being the least.

DISCUSSION

The origin and development of biohydrometallurgy are connected with the shortage of non-ferrous metals in a large number of countries [4]. The possibility of utilization of Thiobacillus bacteria, mainly T.ferrooxidans species, for the purpose of recovering metals from different sulphur minerals and other materials in which metal content is often lower than 1%, is one of the more interesting trends in the development of methods concerned with processing poor metalliferous raw materials and wastes containing metals [1-6]. T.ferrooxidans is especially suitable for this type of processes due to its considerable ability to adapt to environment conditions, especially to high concentration of metals [4,6,11-13]. However, it was found that the data concerning the toxicity of the same metal with regard to T.ferrooxidans are considerably differentiated. This is due to the fact that the adapting ability of the particular bacteria species is conditioned by their former existence or even by the prehistory of their existence [4,11,12]. Deriving energy from oxidizing ferrous ions as well as sulphur and its inorganic compounds T.ferrooxidans exist, first of all, in environments containing sulphides, mainly pyrite. The differentiation in the chemical nature of these habitats is the reason of the occurrence in natural environment of a large number of mutants of this species, essentially differing in biological activity. Due to this fact as well as chemical differentiation in the materials subjected to leaching, parameters of each new process are selected for it separately, basing on the results of laboratory tests. This applies also to the choice of microorganisms useful in the process.

The results of leaching metals from waste coal pyrites by means of model strains of F26-77 T.ferrooxidans and T29-77 T.thiooxidans sulphur bacteria, subjected to the process of adaptation to material leached, as well as FP1-87 T.ferrooxidans strain isolated from coal pyrites, and also by a mixture of autochthonous Thiobacillus bacteria, have demonstrated that the effects obtained in these experiments were not as differentiated as was the case during the leaching of wastes resulting from mine extraction and burning brown coal [14]. In the latter investigations autochthonous T. ferrooxidans and T. thiooxidans strains readapted to the material leached and made it possible to attain higher yields of metal bioextraction than the model strains subjected to adaptation process. From the data obtained in this paper it follows that it is not advisable to give priority to autochthonous bacteria over model ones in leaching coal pyrites. This may be due to the fact that model bacteria strains were isolated from underground mine waters, which, when flowing through geological formations of rock mass, must have come across inclusions of pyrite and other sulphides accompanying carbon deposits.

It is widely known that important increase in leaching yield can be reached by the reduction of particle size of material being leached, especially when there is a material of low porosity [4, 6]. This effect is due to spreading of surface area which is submitted to biodegradation processes.

Data obtained from the investigations of the effect of break-up on the bioextraction yield of metals from leached wastes point to the possibility of its increase by applying materials of considerable size reduction (<0.3mm). It was likewise found that the process can be also quite effective in the event of grain being larger (to 10 mm), which suggests the possibility of conducting it using "raw" pyrites, not subjected to additional break-up. Relatively high efficiency of leaching under this conditions could be connected with high porosity of material leached [7].

Although it is not possible, at the present stage of knowledge of the analysed process, to draw any further conclusions concerning its application, the literature data available now, pointing to the growing interest in the possibility of utilizing the biometallurgical processes to recover metals from various waste materials [1-6, 15-17], suggest usefulness of further investigations in this field. Nevertheless, the application of bacterial leaching is justifiable if there is an utilization both for solid residues and the solutions formed in the leaching processes.

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Badano wpływ bakterii i rozdrobnienia materiału ługowanego na efektywność ekstrakcji metali z pirytów węglowych. Wydajność ługowania była wyższa w obecności szczepów T.ferrooxidans i T.thiooxidans wyizolowanych z dołowych wód kopalnianych i z ługowanych pirytów węglowych niż w obecności bliżej nie zidentyfikowanej mieszaniny autochtonicznych bakterii rodzaju Thiobacillus. Uzyskane dane wskazują na możliwość prowadzenia procesów ługowania przy wykorzystaniu "surowych" pirytów węglowych, nie poddanych dodatkowemu rozdrabnianiu.