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APPLICATION OF BACTERIAL LEACHING IN THE PROCESSING OF WASTES FROM INCINERATION PLANT FROM PROSTĚJOV

Summary. The objective of this research work was to measure and evaluate the suitability of bacterial leaching for extracting heavy metais out of the wastes two kinds of waste were tested on bacterial leaching:

- A sample from a sludgepress
- A sample of waste from an ashpan

ZASTOSOWANIE ŁUGOWANIA BAKTERYJNEGO W PRZERÓBCE ODPADÓW ZE SPALARNI W PROSTEJOWIE

Streszczenie. Przedmiotem referowanej pracy badawczej była ocena możliwości zastosowania ługowania bakteryjnego w celu wyługowania metali ciężkich obecnych w odpadach ze spalarni w Prostejowie. Spalarnia ta wytwarza odpady dwojakiego rodzaju: stałe - popioły i ciekłe - szlamy. Te właśnie oba rodzaje odpadów reprezentowanie przez próbkę z osadnika szlamu i próbkę z popielnika poddano bakteryjnemu ługowaniu.

The method of bacterial leaching

The bacterial leaching was performed in sterilised Erlenmeyer conical flasks filled with 10 grams of respective waste samples,180 millilitres of 9K medium without $FeSO_4$, and 20 mililitres of the solution containing bacteria Thiobacillus ferrooxidans. The pure cultures of Thiobacillus ferrooxidans provided by the Mining Institute of the Slovak Academy of Sciences in Košice were used for the experiments. Acidobasic reaction of the environment was measured by means of the laboratory pH-meter Radelkis (Hungary). All the time during the experiment lasting 28 days, the pH value has been being kept at the optimal level between 1.8

up to 2.0 to eliminate the forming of unwanted mineral jarosite. The temperature during leaching was in the range between 26 up to 30 degrees centigrade.

Mineralogical and chemical analyses were performed at the Research and Development Institute of Nová Hut' steel works, Ostrava. The whole range chemical analysis was done by means of energy-dispersing spectrometre EDAX9900 with the PVQUAN software using the standards. The separate grains analysis was done by the same way, in this case without standards. The analysis of heavy metals, namely Fe, As, Cd, Mn, Cu, Zn, Pb, Ag, Cr, Ni, Ti, Al and Hg was performed at the Central Analytical Laboratory of VŠB-Technical University of Ostrava, using ICP.

The MPN method

This method, invented by Meynell and Meynell in 1969, was adjusted at DMT Essen, Germany, and applied to special experiments. According to this method, the number of bacteria in 1 mililitre of solution is calculated as so called "most probable number" (MPN) which determines the concentration of Fe^{2+} ions oxidized by bacteria. 27.5 microlitres of mineral suspension is mixed with 250 microlitres of medium in five parallel arrays. Every series is then diluted separately in ten steps in the ratio of 1:10. The dilution is performed on microtitration plates which are subsequently closed and incubated for two weeks in thermostat with the ambient temperature 30 degrees centigrade. The growth of bacteria to the final dilution is evaluated according to the change of colour caused by the forming $Fe_2(SO_4)_3$. The statistic evaluation based on the standard tables is then performed.

The sample from the sludgepress

It is a sample which was taken on 12. 5. 1995 at 10.00 a.m. This waste was created by combustion of following kinds of wastes (according to Czech classification of wastes):

97101: specific waste for medical institutions

31441: polluted construction rubble and excavation earth

59906: industrial trash (especially dangerous waste)

54703: sludge from oil separators (especially dangerous waste)

Mineralogical studies have shown that this sample is represented mostly by various types of oxidic minerals and besides them there are also silicones in the sample. There were identified these kinds of mineral phases in the sample: Fe_2O_3, $Ca_3Si_2O_7$, $Mg(SiO_4)_2$, NaCl, and $NaAlSi_3O_8$. Morfology of the sludge grains before washing is shown on the Fig. 1. There were identified grains with a big content of Bi (87,21%) in the amount. This grain is shown on the Fig. 2.

The character of the sample after a month of leaching is shown on the Fig. 3. After a month of leaching there can be seen an increased content of needle-like formations in the sample which correspond, as far as their composition, to $CaSO_4.2H_2O$. After a month of leaching there were identified phases containing $PbSO_4$ (Fig. 4), and $BaSO_4$ (Fig. 5). The following mineral phases were identified in the sample by a phases X-ray analysis: SiO_2, Fe_2O_3, and $CaHPO_4.2H_2O$. It was assumed from the analysis that the chlorides were washed out after a month of leaching, where the decrease was the biggest.

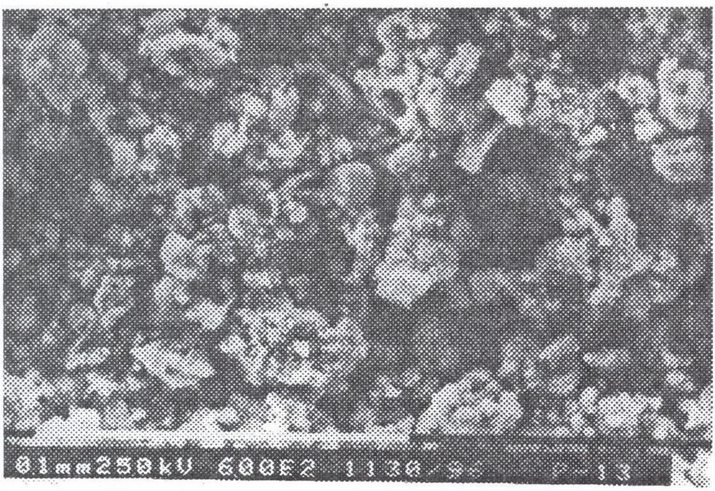

Fig.1.

Rys.1.

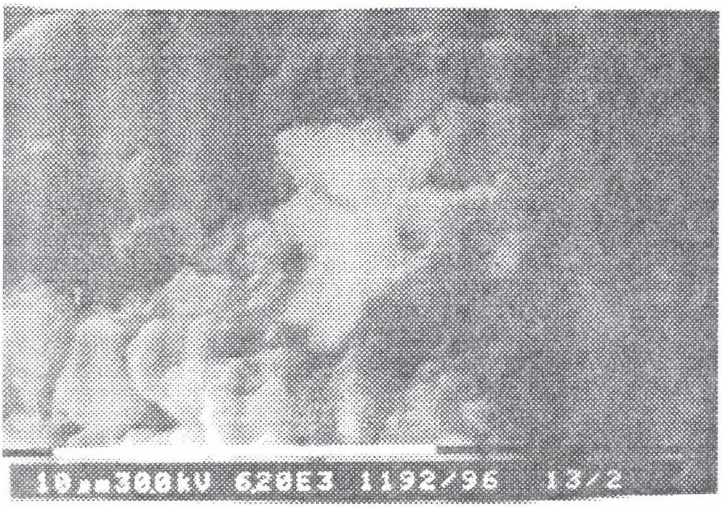

Fig.2.

Rys.2.

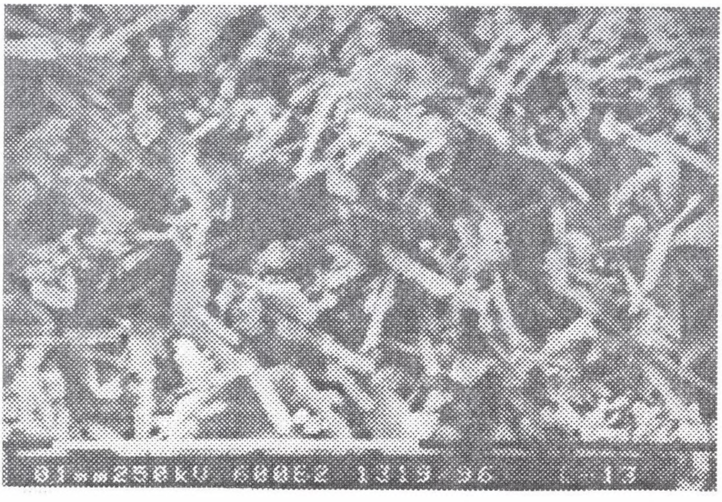

Fig.3.

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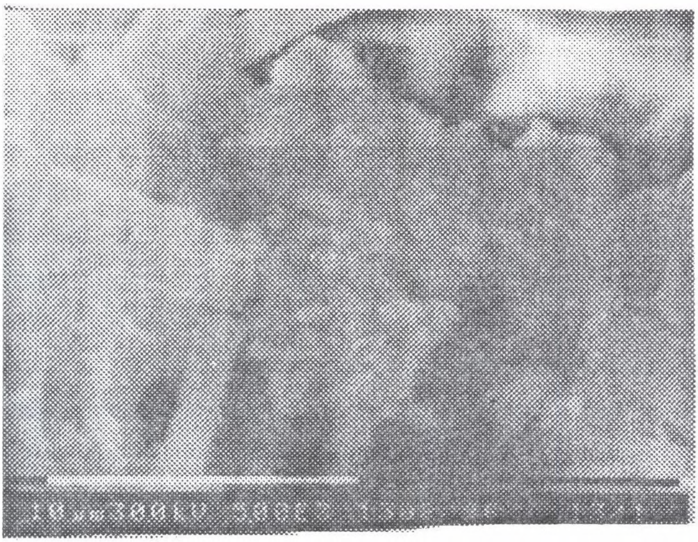

Fig.4.

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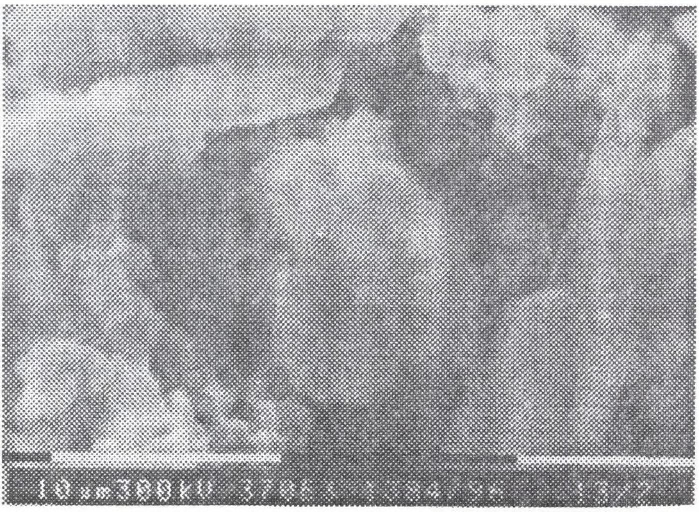

Fig.5.

Rys.5.

The results of the bacterial leaching are shown inthe Tables No 1 and No 2. From the point of view of the hard metals As, Cu, and Zn are those which are the most washed out ones. After a month of leaching occures a gathering of Ti and Al in a solid phase which is caused especially by the fact that these elements are quite hard to wash out and by washing out of soluble, especially chloride phases, the content of these elements in a solid phase is increasing. Hg is being leach off quite easily but its content in the sample is a very small one. As far as the observation of the biomass, it could be said that the bacteria adapt themselves slowly but gradualy to this sample and after a month of leaching, when the experiment was finished, the bacteria reach actually the maximum concentration of 10^9 and even after a month it is possible to observe a considerable reduction in number of ferritic ions. This means that the chosen washing period is not sufficient and that the process of bacterial leaching starts actually after the month. It would be possible to shorten the leaching period by using adapted bacterial cultures.

Table 1

Results of bacterial leaching

Content of elements before leaching /%/						
As	Ag	Cr	Zn	Cd	Pb	Ni
0.0140	0.0008	0.248	1.757	0.00040	1.367	0.106
Content of elements after leaching /%/						
0.0012	0.0013	0.190	1.001	0.00025	1.224	0.071
Recovery of elements into leachate /%/						
91.43		23.39	43.03	37.50	10.46	33.03

Content of elements before leaching /%/					
Mn	Cu	Fe	Ti	Al	Hg
0.105	0.143	11.013	0.479	1.278	0.0005
Content of elements after leaching /%/					
0.089	0.080	9.783	1.371	2.030	0.0001
Recovery of elements into leachate /%/					
15.23	44.06	11.17			80.00

Table 2

Growth of biomass determined by the MPN method and content of Fe^{2+} ions in the solution

Duration of leaching	Fe^{2+}(mg/l)	Number of bacteria in 1ml
first week	1926.2	6.10^3
second week	603.1	5.10^5
third week	502.5	4.10^8
fourth week	485.7	40.10^9

The sample from the ashpan

This sample was taken on 12. 5. 1995 at 10.00 a.m. It is a sample which was created by combustion of following kinds of waste materials :

97101: specific waste for medical institutions

31441: polluted construction rubble and excavation eartth

59906: industrial trash (especially dangerous waste)

35106: containers from ferritic metals with remaining containt of polution

54703: sludge from oil separators (especially dangerous waste)

The sample mostly contains $BaCl_2$ from the mineralogical point of view. Further the following mineral phases were identified in the sample: $Ca_3Cr_2(SiO)_3$, Fe_2O_3, SiO_2, NaCl, $Ca_{12}Al_{14}O_{33}$, $CaSO_4$, and $FeCl_3.CaSO_4$, $FeCl_3$. The sample character before the application of adjusting processes is shown on the Fig. 6. A typical $BaCl_2$ grain is shown on the Fig. 7.

The sample character after a month is shown on the Fig. 8. It is obvious, as well as in the previous case, that after a month of leaching there occur needle-like formations formed mostly by $CaSO_4.2H_2O$. In case of this sample decreases the amount of chloeide ions as well and the amount of sulphur and and phosphorus ions is increasing. There were identified the following mineral phases in the sample: SiO_2, $CaSO_4.2H_2O$, Fe_2O_3, $CaHPO_4.2H_2O$. By the study of individual grains has turned out that the sample shows a bigger content of grains containing Cr than in the previous case. (Fig. 9 with the content of 28,11% of Cr).

From the bacterial leaching results (Table 3 and 4) that this kind of waste is perfectly washable and in the contrary to the previous sample almost every observed element is being considerably washed out (except for Ag and Al).

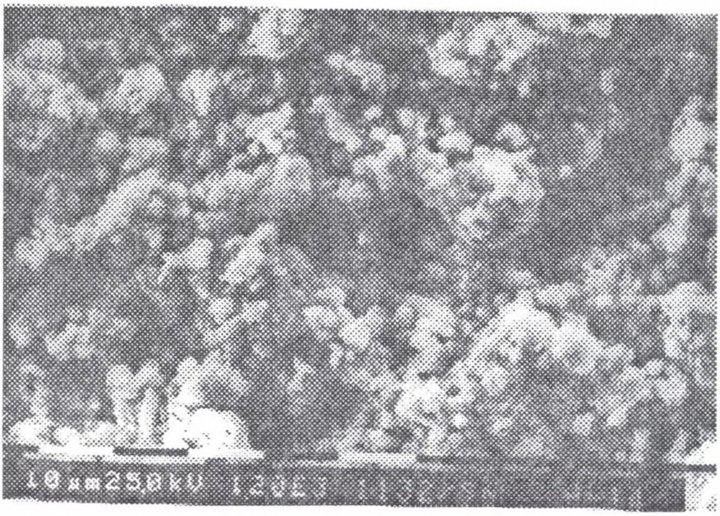

Fig.6.

Rys.6.

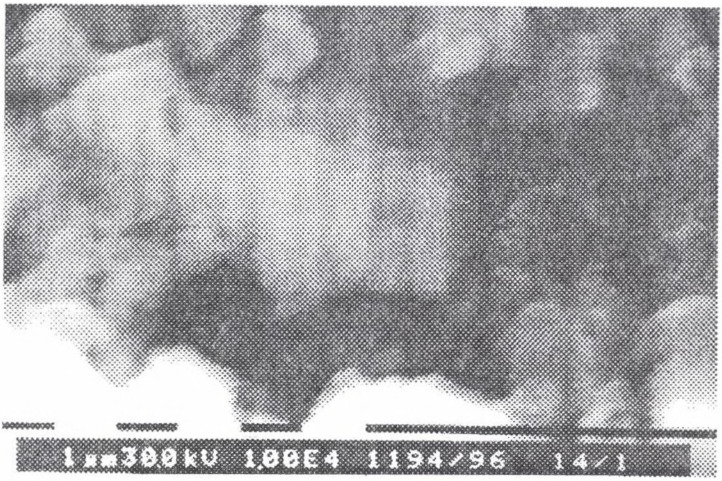

Fig.7.

Rys.7.

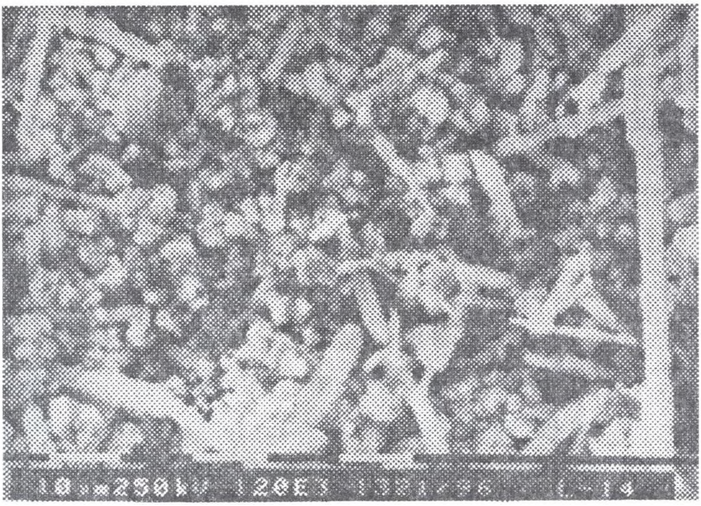

Fig.8.

Rys.8.

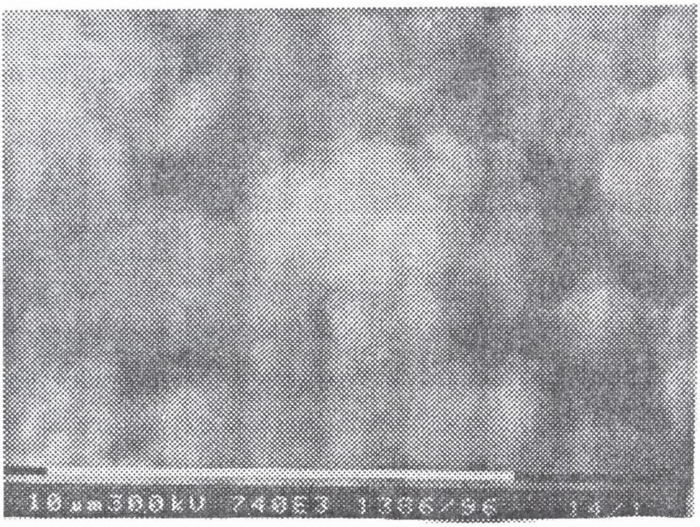

Fig.9.

Rys.9.

Table 3

Results of bacterial leaching

Content of elements before leaching /%/						
As	Ag	Cr	Zn	Cd	Pb	Ni
0.0068	0.00067	0.526	2.263	22.10^{-7}	0.178	0.126
Content of elements after leaching /%/						
0.0012	0.00300	0.346	0.052	18.10^{-7}	0.008	0.064
Recovery of elements into leachate /%/						
82.35		34.22	97.70	18.18	95.50	49.20

Content of elements before leaching /%/					
Mn	Cu	Fe	Ti	Al	Hg
0.085	0.260	15.851	5.144	2.183	0.0005
Content of elements after leaching /%/					
0.007	0.057	6.036	1.440	3.367	0.0001
Recovery of elements into leachate /%/					
91.76	78.07	61.83	71.76		80.00

Table 4

Growth of biomass determined by the MPN method and content of Fe^{2+} ions in the solution

Duration of leaching	Fe^{2+}(mg/l)	Number of bacteria in 1ml
first week	418.8	35.10^{5}
second week	167.5	24.10^{6}
third week	67.1	14.10^{7}
fourth week	51.2	12.10^{9}

The sample shows very good results as far as the bacteria adaptability. Already after a week of leaching there was reached a high concentration of bacteria in 1 ml of the solution (10^5), and this concentration was significantly increasing every week. A similar situation applies to Fe^{2+} whose concentration is continuously decreasing in the suspension. Even if there were reached much better results in this case than in case of the first sample, even here it would be needed to extend the washing period.

Conclusion

The results of bacterial leaching of the wastes from the incinerator of Prostějov (sludge and ash) have shown that both of these samples are suitable for the application of bacterial leaching. After a month of leaching the sample of ash is better washed out than the sample of sludge. The results have further shown that even better results can be reached if there were not applied clear bacterial cultures of Thiobacillus ferrooxidans but if there were used a beforehand adapted cultures. This way the leaching period could be significantly shortened and the leaching of individual metals would also improve. Considering the fact that these wastes are being stored at dumping grounds, where a contact with the mentioned bacteria is possible, we can expect these bacteria to be washed out into the ground waters after a longer time period (even a few years). By this, of course, can the environment be endangered.

REFERENCES

1. Fečko P., Bundzel B., Stahovcová A., Bouchal T.: Bakteriálne lúhovanie popolov zo spaľovne Prostějov. Proceedings 5th Internationales EIPOS-Kolloquium Umweltwissenschaften, VŠB Ostrava 1996, s.320-329.
2. Kušnierová M.: Prognosis of the stability of arsenit in the biotop of brown coal dump. Journal of hazardous materials, 37, 1994 pp.27-31.
3. Michalíková F., Búgel M., Zeleňák F.: Úpravnické metody používané pri získavaní úžitkových zložiek z popolčekov. Proceedings Environment and Mineral processing, VŠB-Ostrava 1992.

4. Virčíková E., Reitznerová E.: Determination of the arsenic phases in the flue dust from cooper production, Metalurgia , Vol 31, No.4, 1994, pp.131-135.

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Streszczenie

Nieustanne gromadzenie odpadów pochodzących z różnych dziedzin przemysłu oraz ich niepożądane oddziaływanie na środowisko naturalne prowadzi do rozwijania się nowych, postępowych metod, które są w stanie przeciwdziałać tym szkodliwym dla środowiska skutkom.

Przedmiotem referowanej pracy badawczej była ocena możliwości zastosowania ługowania bakteryjnego w celu wyługowania metali ciężkich obecnych w odpadach ze spalarni w Prostejowie. Spalarnia ta wytwarza odpady dwojakiego rodzaju: stałe - popioły i ciężkie - szlamy. Te właśnie oba rodzaje odpadów, reprezentowane przez próbkę z osadnika szlamu i próbkę z popielnika, poddano bakteryjnemu ługowaniu.

Ługowanie bakteryjne prowadzono wykorzystując do tego celu kultury bakteryjne Th. ferrooxidans. Przebieg ługowania oceniano poprzez pomiar pH, które w ciągu 28 dni eksperymentu utrzymywało się na optymalnym poziomie 1,8 - 2,0 (uniemożliwiając tym sposobem tworzenie się niepożądanego minerału: jarozytu), oraz wyniki analiz mineralogicznych i chemicznych: ze względu na zachowanie się występujących w odpadach metali, takich jak: Fe, As, Zn, Pb, Ag, Hg i in. Biochemizm procesu określono poprzez najbardziej prawdopodobną liczbę bakterii w 1 cm^3 roztworu (MPN- „most probable number"), którą określa stężenie jonów Fe^{+2} utlenionych przez bakterie Th.ferrooxidans.

Wyniki badań nad ługowaniem bakteryjnym odpadów pochodzących ze spalarni w Prestejowie wykazały, że dla obu rodzajów próbek zastosowanie tego rodzaju ługowania jest możliwe, jednak po miesiącu ługowania okazało się, że próbka popiołu jest bardziej podatna na ługowanie (wyższy stopień wypłukania metali) niż próbka szlamu. Wykazana została wyższa przydatność w procesie ługowania kultury Th.Ferrooxidans wstępnie adaptowanej w

porównaniu z kulturą czystą. Tym sposobem czas ługowania może być znacznie skrócony, a wyługowanie poszczególnych metali może być wyższe. Ten fakt należy mieć na uwadze, jeśli tego rodzaju odpady miałyby być gromadzone na składowiskach ziemnych, w których kontakt z omawianymi bakteriami jest możliwy. Niepożądanym efektem tego spontanicznego, wieloletniego nawet ługowania może być zanieczyszczenie wód podziemnych, a więc degradacja środowiska naturalnego.