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INFLUENCE OF PHYSICAL AND CHEMICAL FACTORS ON ACID DIGESTION OF Zn-Pb FLOTATION TAILINGS

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The acid digestion of flotation tailings from Zn-Pb ore enrichment in the Boleslaw Mine and Metallurgical Plant was aimed at their initial chemical reusing by neutralization of alkaline components of gangue and potential recovery of magnesium compounds from filtrates after acid digestion. The nature of the research was explanatory and the obtained leaching residues will constitute a raw material in flotation tailings bioleaching in the presence of acidophilic microorganisms.

The article presents the results of the research regarding the influence of physicochemical factors (H_2SO_4 concentration, time, temperature, the ratio of solid phase to liquid phase) on the leaching rate of magnesium, zinc, cadmium, iron and lead by acid digestion of flotation tailings as well as the characteristics of solid leaching residues and magnesium compounds obtained by the concentration and crystallization of the filtrate.

Key words: Zn-Pb flotation tailing, digestion, magnesium recovery

INTRODUCTION

There are two zinc and lead ore processing plants in Poland. They belong to the Boleslaw Mine and Metallurgical Plant and the Trzebionka Mine Plant, where the process of ore enrichment produces a considerable amount of waste. Flotation tailings constitute around 60-70% of the ore processed for Zn concentrate production (Jarosiński and Natanek, 2005). At the current rate of ore processing at 2.6-2.7 teragrams (Tg) annually, around 1.5-1.6 Tg/y of flotation tailing is produced.

The subject of this research was the wastes storage area in the Boleslaw Mine and Metallurgical Plant situated in the Olkusz-Boleslaw region. This area contains sedimentation ponds, occupying the total area of approximately 110 ha. The current

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mining-processing activities, being conducted there for over 50 years, have caused the accumulation of flotation tailings in the amount of about 38 Tg in them (Pajor, 2005). The waste is the tailing of the flotation enrichment process of non-ferrous metal ores containing hazardous substances marked with symbol 01 03 80* (Rozp.Min.Śr., 2001) according to the Minister of the Environment Order of 27 September 2001 concerning the catalogue of waste.

Flotation tailings are produced from lead and zinc ores in the exit section of the processing line in the Boleslaw Mine and Metallurgical Plant, where the following materials (given in approximate percentages) are obtained from the extracted ore (Pajor, 2005):

- 8% of metals in the form of Zn and Pb concentrates and a bulk concentrate,
- 35% of dolomite stone,
- 57% of flotation tailings.

The mineralogical composition of the discussed waste contains mainly dolomite (77%) and marcasite (17%). There are also certain quantities of heavy metals, i.e., Fe, Zn, Pb, Cd, Mn and others (Pajor, 2005). The main source of contamination from surface storage of tailings are ions of metals and SO_4^{2-} ions which are leached by water flowing through an above-ground tailings storage facility, then infiltrated from over-sedimentary pond to underground waters. Metals, and their compounds, form dust emitted by the open surface of dry sedimentation ponds. Currently, there is not an explicit assessment of the influence of these ponds on the surroundings, but the restoration of the affected area to its appropriate utilization functions is connected with conducting detailed research and working out the method of their safe rehabilitation (Jarosiński and Natanek, 2005; Jarosiński, Żelazny, Nowak and Banach, 2005; Girczys and Sobik-Szołtysek, 1998; Łuszczkiewicz, 2007).

At present, the management of flotation tailings from the Boleslaw Mine and Metallurgical Plant mainly consists in utilizing them (about 60% of the mass of the produced wastes) in order to construct the embankment of an active sedimentation pond. The following directions of tailings recycling are still being investigated:

- as a component of hydraulic filling,
- as a reclamation material for levelling holes and strip pits in post-mining areas,
- in production of building materials,
- in recovery of metals by means of their re-enrichment.

The research into utilization of dolomite, the main component of similar waste from the Trzebionka Mine Plant, has been conducted (Jarosiński and Natanek, 2005; Jarosiński, Żelazny and Nowak, 2005; Jarosiński, Fela and Kozak, 2005; Jarosiński and Madejska, 2005). Dolomite has been investigated as a material for magnesium sulphate(VI) production, which is an important component used in many industrial processes in such industries as paper, textile, dyeing, tanning, building materials and metallurgy. Dolomite has also been examined as a component of artificial fertilizers (as so called magnesium sulphate heptahydrate - $MgSO_4{\cdot}7H_2O$- epsomite) (Jarosiński, Fela and Kozak, 2005; Jarosiński and Madejska, 2005).

The objective of research was to determine the conditions of acid digestion and neutralization of alkaline components of Zn-Pb flotation tailings from the point of the recovery of magnesium compounds. The influence of the following parameters on the degree of the metal transition in solutions was taken into account: the concentration of sulphuric acid(VI) solution, a ratio of solid phase to liquid phase, temperature, and time. The nature of the research was exploratory and the obtained results form the basis for further work on the possibility of recovery of useful components, for example zinc, from initially acidified flotation tailings, with the application of biometallurgy methods (Pacholewska, Cwalina, Cabała and Sozańska, 2007).

MATERIALS AND METHODS

The flotation tailings from the zinc and lead ores enrichment process from the Boleslaw Mine Plant were digested. The chemical composition of the examined tailings was as follows: 17.37% Fe; 5.13% Mg; 1.71% Zn; 1.63% Pb; and 0.0098% Cd.

The flotation tailings at the temperature of 333 K were dried and leached in glass flasks in the presence of 100 cm^3 of 1, 2 and 4 M solutions of H_2SO_4 with the corresponding amounts of tailings at a ratio of solid phase to liquid phase as 1:10, 1:5 and 1:2. The tailings were continuously stirred with a thermostatic shaker. After the sufficient leaching time, the solutions were filtered by means of a vacuum flask. The obtained filtrates were analysed quantitatively and the AAS method was used to determine the metal concentration of Zn, Pb, Cd, Fe and Mg. The phase composition of flotation tailings before and after leaching was determined by a pattern method with a Phillips PW 3710 X-ray diffractometer and X'Pert software.

RESULTS AND DISCUSSION

METAL LEACHING EFFICIENCY FROM Zn-Pb FLOTATION TAILINGS

The efficiency of metal leaching- *w* was calculated with the following formula:

$$w = \frac{V \dfrac{c_1}{1000}}{m_o \dfrac{c_o}{100}} 100\%$$

c_0 – the initial metal concentration in the tailings, %,
c_1 – the metal concentration in the solution after leaching, g/dm^3,
V – the volume of the solution after filtration, cm^3,
m_0 – the initial mass of the tailings, g.

INFLUENCE OF H_2SO_4 CONCENTRATION

The influence of H_2SO_4 concentration on the efficiency of leaching of Pb, Fe, Zn, Cd and Mg is shown in the Table 1 and in Figs 1 - 2. The values of the rate of metal leaching from flotation tailings during 3-hour digestion period at various H_2SO_4 concentrations are presented.

It was found that increasing H_2SO_4 concentration in leaching solutions caused a decrease in the rate of magnesium leaching from flotation tailings (Table 1). As a result, too high H_2SO_4 concentration limits digestion of magnesium compounds, which the results obtained in the research confirm (Jarosiński, Fela and Kozak, 2005).

Table 1. Rate of metal leaching at the ratio of phases 1:10, 3 hours

Exp. #	Concentration H_2SO_4 [mol/dm^3]	The efficiency of metal leaching, %				
		Mg	Zn	Cd	Pb	Fe
1	1	87.71	13.34	19.15	0.69	3.46
2	2	84.14	13.17	17.34	0.66	3.66
3	3	82.46	13.97	17.17	0.47	3.99

INFLUENCE OF TIME

In the course of flotation tailings leaching, both foaming of the solutions and emission of gases, connected with the neutralisation of dolomite in the H_2SO_4 solutions were observed.

With the increase in the time of digestion, the increase in the efficiency of metal leaching from flotation tailings was observed. A favourably high rate of magnesium leaching was obtained in particular after three hours of leaching (above 80% for the

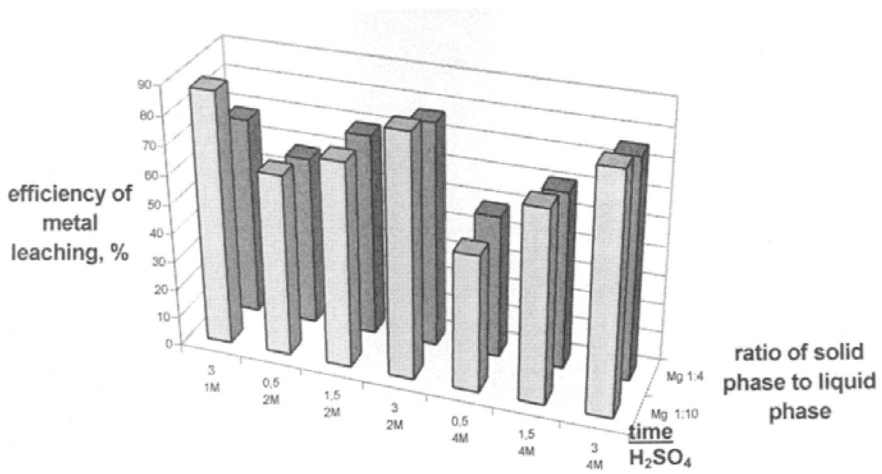

Fig. 1. Influence of time, H_2SO_4 concentration, solid phase to liquid phase on the efficiency of magnesium leaching from Zn-Pb flotation tailings

ratio of solid phase to liquid phase 1:10 and around 70% and more for the ratio of phases 1:4). Cd and Zn were also leached at a relatively high rate (13 – 15%), whereas the rate of leaching of Pb and Fe was lower (below 5%) (Figs 1- 2).

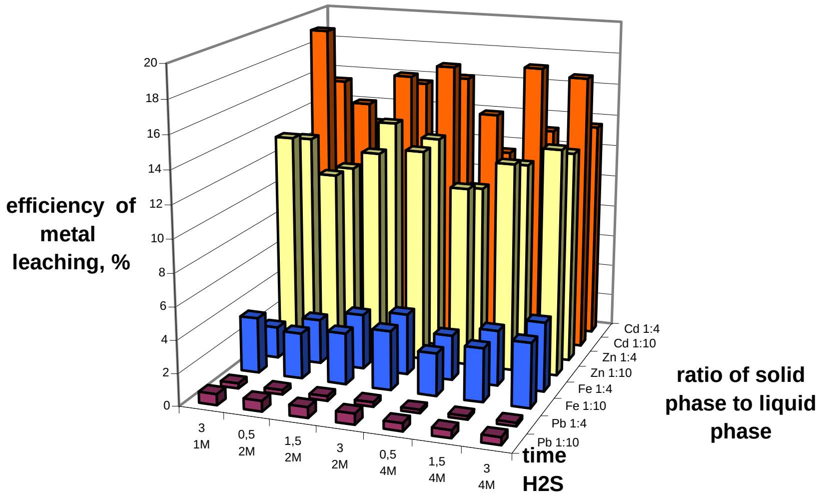

Fig. 2. Influence of time, H_2SO_4 concentration, solid phase to liquid phase on the efficiency of leaching of Cd, Fe, Pb and Zn from Zn-Pb flotation tailings

The metal concentrations (Mg, Zn, Cd, Pb, Fe) in the filtrates after leaching are presented in Table 2.

Table 2. The metal concentrations in solutions after leaching for the ratio of solid phase/liquid phase = 1:10 and 1:4, temperature 293 K

Exp. #	Concentration H_2SO_4, [mol/dm^3]	Time of leaching, [h]	Concentration of metals				
			Mg [g/dm^3]	Zn [g/dm^3]	Cd [mg/dm^3]	Pb [mg/dm^3]	Fe [g/dm^3]
	The ratio of phases 1:10						
1	1	3.0	5.36	0.27	2.23	5.21	0.71
2	2	0.5	3.81	0.22	1.68	4.98	0.58
3	2	3.0	5.08	0.26	1.99	4.89	0.75
4	4	0.5	2.76	0.21	1.61	3.51	0.52
5	4	3.0	5.04	0.28	2.00	3.54	0.83
	The ratio of phases 1:4						
6	1	3.0	10.52	0.64	4.48	6.34	1.01
7	2	0.5	8.85	0.55	3.67	5.19	1.41
8	2	3.0	11.70	0.67	4.64	5.45	1.93
9	4	0.5	7.20	0.51	3.18	3.91	1.37
10	4	3.0	11.65	0.66	3.95	4.14	2.21

INFLUENCE OF THE RATIO OF SOLID PHASE/LIQUID PHASE

The influence of the ratio change of the solid-to-liquid phases from 1:10, 1:4 and 1:2 on the metal concentration in the solutions after leaching was investigated. We used either 10g, 25g, 33g or 50g flotation tailings per 100cm^3 of H_2SO_4 during 3-hour period at 293 K. The obtained results of metals concentration in the filtrates are shown in Fig.3.

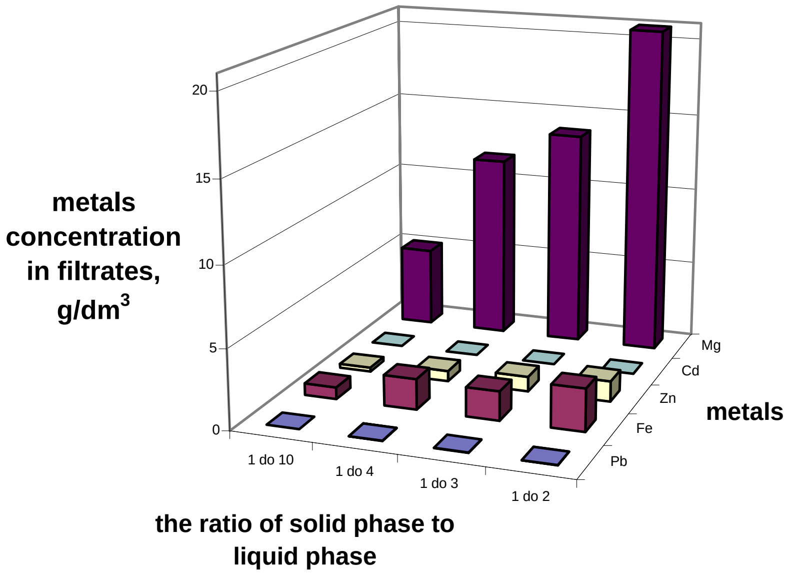

Fig. 3. Metal concentration in the solution at different solid/liquid phases ratios, the temperature of 293 K, 2 M H_2SO_4, 3 hours

It is apparent from the data presented in Fig. 3 that metal concentration in a filtrate increases with the increase in the mass of tailings proportionally to the amount of the leaching solution. The highest magnesium concentration at 20.93 g/dm^3 in solutions after the leaching process was observed at the ratio of solid-to-liquid phase 1:2. Under these conditions, Fe concentration was 2.67 g/dm^3, Zn concentration 1.31 g/dm^3, Pb concentration 12.70 mg/dm^3, and Cd concentration 8.99 mg/dm^3. It has been found that favourable high magnesium concentration equal to 11.70 g/dm^3 in the presence of 2M H_2SO_4 and after 3 hours of leaching was obtained at the ratio of the solid phase to the volume of the solution equal to 1:4 (25g/100cm^3). It corresponds with results obtained by Jarosiński et al. (2005) Using lower quantities of wastes, compared to the volume of solutions, does not provide sufficiently high magnesium concentration in the solution.

INFLUENCE OF STIRRING ON FLOTATION TAILINGS LEACHING

The experiment was repeated at stirring speeds 100 and 130 rpm (amplitude 6) respectively, every time using 25g of flotation tailings and 100 cm^3 of 2M H_2SO_4. The time of leaching was 1.5 h and the temperature 293 K for all trials. The results of metal concentration in the filtrate after leaching are shown in Table 3.

Table 3. Metal concentration in filtrate after leaching at 293 K with 2M H_2SO_4 for 1.5 hours applying different vibration frequency

Exp.#	The stirring frequency cycle/min (cpm)	Metal concentration in the filtrates				
		Mg [g/dm^3]	Zn [g/dm^3]	Cd [mg/dm^3]	Pb [mg/dm^3]	Fe [g/dm^3]
1	100	9.20	0.66	4.82	8.12	1.20
2	130	10.68	0.71	4.54	5.35	1.77

The results of metal concentration after leaching, shown in Table 3, point to a considerable influence of stirring intensity on the magnesium recovery from flotation tailings.

INFLUENCE OF TEMPERATURE

The influence of temperature on magnesium recovery from flotation tailings during Zn-Pb tailings leaching was also investigated. In each experiment, there was 25 g of flotation tailing and 100 cm^3 of 2M H_2SO_4. The time of leaching was 1.5 h and the temperatures were 303 K, 313 K, 323 K, and 333 K.

The results of metal concentration in the solutions after leaching are shown in Table 4 and Fig 4.

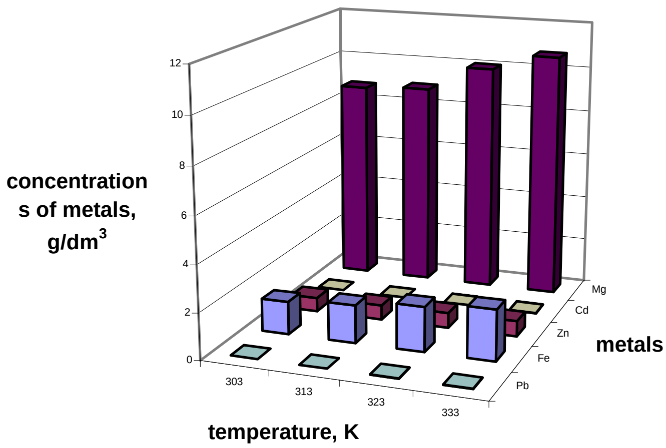

Fig. 4. Influence of temperature on the concentrations of metals in solutions during leaching of the Zn-Pb flotation tailings

The obtained results confirmed that there was an increase in solubility of magnesium compounds in aqueous solution in the examined range of temperatures (Rubisov, 2000; www.phase).

Table 4. Dependence of metals concentration in the filtrates in relation to different temperatures

Exp. #	Temperature of leaching process, K	Metal concentrations in the filtrates				
		Mg [g/dm^3]	Zn [g/dm^3]	Cd [mg/dm^3]	Pb [mg/dm^3]	Fe [g/dm^3]
1	303	8.77	0.61	4.55	9.57	1.42
2	313	8.90	0.63	4.42	10.11	1.63
3	323	10.01	0.66	4.27	13.08	1.94
4	333	10.72	0.67	4.02	13.20	2.19

Figure 5 shows the Arrhenius plot for the reaction rate data *k*, estimated and calculated from the magnesium leaching experiments shown in Table 4. The activation energy of 6.013 kJ/mol has been calculated from the slope indicating diffusively controlled reaction. Mass transfer may be the rate controlling step.

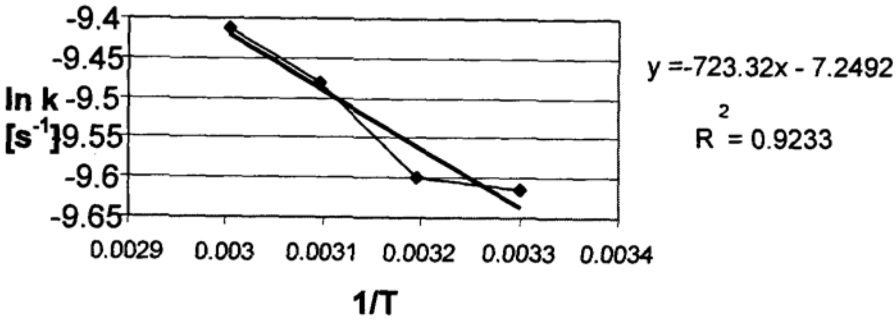

Fig. 5. Arrhenius diagram for determining activation energy

CHARACTERISTICS OF MAGNESIUM SULPHATE FROM THE ACID DIGESTION OF Zn-Pb FLOTATION TAILINGS

Flotation tailings can be used as raw material for production of magnesium compounds (Jrosiński et al., 2005) and a test was conducted for this purpose. The objective of the test was to determine the properties the magnesium sulphate from the Zn-Pb flotation tailings of the Boleslaw Mine and Metallurgical Plant. A 250g sample of the flotation tailings was treated with 1 M H_2SO_4 solution and the pulp was stirred at 293 K for 3 hours and filtered under vacuum. The obtained raw filtrate was subjected to purification from iron compounds with H_2O_2 and, as a consequence, iron(III) compounds precipitated. Next, the solutions were subjected to crystallization with fast water evaporation and drying with a drying evaporator. It was found, on the bases of the thermogravimetric analysis that the obtained product was $MgSO_4 \cdot 7 H_2O$.

PHASE COMPOSITION OF FLOTATION TAILINGS

The phase composition of the tailings before and after leaching was determined by means of X-ray analysis. The main component of the tailings is ferruginous dolomite, which is accompanied with calcite, quartz, sulphides such as pyrite and marcasite as well as sphalerite. Other minerals constitute admixtures and traces: cerussite, bassanite, smithsonite and feldspar.

As a result of tailings leaching with 1M acid H_2SO_4, mineral components were quantitatively reorganized. It was found that there is bassanite, pyrite with marcasite, sphalerite and quartz as dominating phases, whereas feldspars and cerussite appeared in the form of admixtures. Considerable changes were observed in the tailings leached with 1 M acid, where prevailing component was anhydrite and the remaining phases appeared from between ten and twenty to several per cent by volume. They were pyrite, marcasite, sphalerite, quartz, bassanite, dolomite kizerite, feldspars and calcite.

CONCLUSIONS

On the basis of the research conducted, the following conclusions were drawn:

- increasing H_2SO_4 concentration in leaching solutions causes a decrease in the extraction efficiency of magnesium leaching from flotation tailings (from 87.71 % for 1 M H_2SO_4, to 82.46% for 4M H_2SO_4),
- with the increase in digestion time, the increase in the rate of metal leaching from tailings has occurred. Leaching in 2M H_2SO_4 for 3 hours creates the most favourable magnesium concentrations in the solution equal to 11.70 g/dm^3,
- metal concentration in the solution after leaching increases with the increase in the tailings mass in proportion to the amount of the leaching solution. The highest magnesium concentration (20.93 g/dm^3) has been observed at the ratio of solid phase to liquid phase 1:2,
- a significant influence of stirring intensity on the demagnetization of tailings has been shown,
- the obtained results concerning the influence of temperature on the digestion of flotation tailings confirm the known relations concerning the increase in the solubility of magnesium compounds with the increase in temperature within the examined range,
- quantitative reorganization of mineral components takes place during leaching and bassanite, pyrite with marcasite, sphalerite and quartz as dominating phases have been found,
- the obtained results will be used for further research on flotation tailings from the Boleslaw Mine in the scope of biohydrometallurgical methods – bioleaching.

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W pracy przedstawiono wstępne rezultaty badań kwasowego roztwarzania odpadów poflotacyjnych, pochodzących ze wzbogacania rud Zn-Pb z Zakładów Górniczo-Hutniczych Bolesław S.A., które miały na celu wstępną chemiczną utylizację odpadów na drodze neutralizacji alkalicznych składników skały płonnej oraz odzysk związków magnezu z filtratów. Stała pozostałość po ługowaniu stanowić będzie surowiec w dalszych procesach bioługowania odpadów poflotacyjnych z udziałem mikroorganizmów o charakterze kwasolubnym.

W artykule przedstawiono wyniki badań nad wpływem czynników fizykochemicznych (stężenie H_2SO_4, czas, temperatura, stosunek f. stałej do f. ciekłej) na stopień wyługowania magnezu, cynku, kadmu, żelaza, ołowiu w procesie kwasowego roztwarzania odpadów poflotacyjnych, oraz charakterystykę stałej pozostałości po ługowaniu i związków magnezu uzyskanych w procesie zatężania i krystalizacji filtratu.