

# Application of sulphuric(VI) acid leaching for magnesium removal from zinc concentrate

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In this paper the results of investigation of magnesium removal from raw zinc concentrate have been presented. The raw materials derive from ZG Trzebionka and ZGH Bolesław. The differences in zinc and magnesium contents are characteristic of these materials. The experiments were carried out in the periodical reactor at 25°C using the H<sub>2</sub>SO<sub>4</sub> solution of 20, 50, and 70% (v/v) concentration. The weight ratio of the solid phase to the liquid phase was 1:10 and 1:2. On the basis of the experimental results it can be stated that the application of sulphuric(VI) acid leaching permits to increase the zinc yield in Zn-Pb ore processing. This method permits to obtain zinc concentrate containing more than 60% Zn and MgO below 0.3% and CaO about 1.4%.

**Keywords:** zinc concentrate, magnesium removal, chemical treatment, sulphuric(VI) acid leaching.

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## INTRODUCTION

Zinc ore deposits occurred in Poland, in the Silesia-Cracow region contains from 3.2 to 4.5% Zn. The main mineral components of this ore are as follows: sphalerite (ZnS), galena (PbS), oxide minerals (ZnCO<sub>3</sub>, ZnO), dolomite (CaCO<sub>3</sub>·MgCO<sub>3</sub>) and clay minerals<sup>1</sup>. Polimorphic nature of the ore is the main problem of their enrichment and processing<sup>2-7</sup>.

Metallic zinc can be produced from raw materials by two methods, in pyrometallurgical or hydrometallurgical processes. Pyrometallurgical method is losing in importance progressively and is not applied in EU for simple zinc concentrate. About 80% of total world production of zinc is realised in hydrometallurgical way<sup>4</sup>.

The technology of metallic zinc production based on hydrometallurgical process is as follows: sulphide concentrates are calcinated in roasting furnace to zinc oxide and sulphur dioxide. ZnO from furnace is collected and cooled, and then leached with H<sub>2</sub>SO<sub>4</sub>. During the process of dissolution some of components of gangue material are also leached and transferred into the solution. The components can have negative influence on quality of the cathodic zinc and technological and economical indexes of electrolysis process. Roaster gases containing mainly SO<sub>2</sub> are dedusted and afterwards converted to sulphuric(VI) acid<sup>4</sup>.

In Poland selective and collective concentrates of zinc and lead are produced. Their characteristics, quality parameters are dependent not only on Zn and Pb concentrations, but also the content of the accompanying components (Ag, Au compounds) and the presence of contaminations. The particularly disadvantageous element for the hydrometallurgical zinc production process is magnesium (from dolomite) because it has adverse effects on the technical and economical parameters of the zinc production process and the quality of cathodic zinc. That is why it would be expedient to reduce the magnesium content in the concentrate before electrowinning of zinc. For the correct process of zinc electrowinning, the reduction of magnesium content in the concentrate below 0.5% is eli-

gible<sup>2, 5-7</sup>. The similarity of Zn and Mg chemical characteristics enhances the problem grade.

In industry two methods can be used to eliminate the magnesium:

- systematic collection of a portion of the solution from the electrolysis system,
- leaching of magnesium with sulphuric(VI) acid from sulphide zinc concentrates before they are directed to roasting and electrolysis<sup>5</sup>.

The main drawback of the first method is the need to remove large volumes of the electrolyte from the cycle which contributes, among other things to the losses of the metals contained in the solution and to the environmental pollution.

The process of acid leaching is based on ZnS and PbS resistance to low concentrate H<sub>2</sub>SO<sub>4</sub> solution treatment in contradistinction to dolomite. The higher alkalinity of magnesium then causes a ready reaction of dissolution of dolomite in acids. Magnesium sulphate(VI) is transferred into the solution, whereas calcium sulphate(VI) as a gypsum is removed by flotation.

The aim of this procedure was to determine the conditions of magnesium removal from the raw concentrates by leaching with aqueous sulphuric acid solutions. The authors try to substantiate the existing relationships as well as the optimum conditions for the procedure suggested.

## EXPERIMENTAL

### Materials characteristics

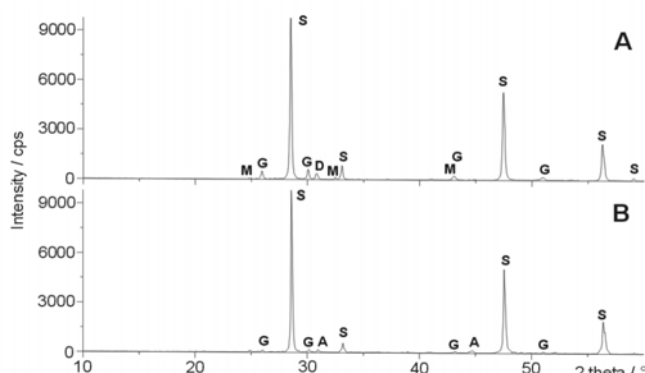
In the experiments zinc concentrates derived from ZG Trzebionka and ZGH Bolesław were used. The chemical characteristics of the typical samples of these materials dried at 105°C were given below in Table 1.

The mineralogical composition of the concentrates was identified by the X-ray diffraction method. In Fig. 1 phase analysis results of the samples were presented.

The main component of the materials is zinc sulphide, sphalerite. The concentrates contain 53.79% and 55.12% of Zn, which corresponds to 80 and 82% of ZnS, respec-

**Table 1.** Chemical characteristics of Zn-concentrates

Sample	Chemical composition, %					
	Zn	Mg	Ca	Fe	Pb	Cd
ZG Trzebieńka	53.79	1.06	2.06	1.26	3.63	0.41
ZGH Bolesław	55.12	0.40	0.93	3.74	2.26	0.29

**Figure 1.** X-ray diffraction patterns of zinc concentrates derived from: A – ZG Trzebieńka, B – ZGH Bolesław (A – ancerite, D – dolomite, G – galena, M – magnesite, S – sphalerite)

tively. It is accompanied by ancerite ( $\text{Ca}(\text{Mg}_{0.67}\text{Fe}_{0.33})(\text{CO}_3)_2$ ) in the concentrate from Bolesław and by dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) in the concentrate from Trzebieńka. The differences of the Mg contents were characteristic of the materials. The considerable elements were found in the concentrate derived from ZG Trzebieńka. The presence of galena – PbS, was also stated in the materials. From the chemical analysis results it follows that these concentrates contain other compounds, but their identification is difficult or impossible due to a low concentration and/or amorphous nature.

### Magnesium leaching

For magnesium leaching the  $\text{H}_2\text{SO}_4$  solutions of the concentration of 20, 50 and 70% (v/v) were applied. The process was realised for the solid phase to the liquid phase mass ratios as 1:10 and 1:2.

In a typical laboratory experiment, 20 g of the concentrate was stirred for 2 hours at the temperature of 25°C with an acid solution. The process characteristics was based on the analysis results of the leachate sampled every 30 minutes. The suspension sample ( $V \sim 5\text{cm}^3$ ) centrifuged to remove the solid particles and the obtained solution was analysed by ICP AES method using Perkin-Elmer „PLASMA40” spectrometer to Mg, Zn, Fe(II), Pb, Ca and Cd concentrations estimation. The results are shown in Table 2.

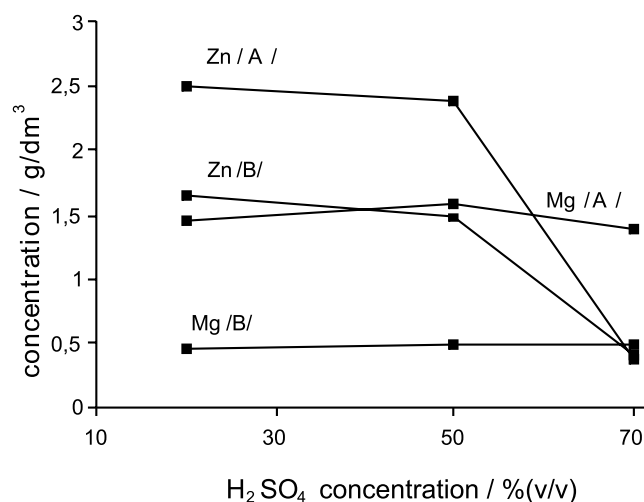
The following conclusions can be drawn from the investigation results,  $\text{H}_2\text{SO}_4$  reacts with the components of zinc concentrates leaches dolomite and the oxidized zinc and lead compounds. To solution  $\text{Fe}^{2+}$  and  $\text{Cd}^{2+}$  ions are transferred. The leaching process depends on the  $\text{H}_2\text{SO}_4$  concentrations and the process time.

The maximum yield of Mg extraction was observed for the 50% solution of  $\text{H}_2\text{SO}_4$ , but the application of the condition is not satisfactory because of heavy zinc losses. A change of the acid concentration to 70% does not interfere considerably with magnesium leaching, but it means limiting Zn extraction. The dependence is shown in Fig. 2.

The ratio of Zn to Mg concentrations in the leachates for the extraction process with 20% and 50%  $\text{H}_2\text{SO}_4$  varied from 1.07 to 1.85 for the concentrate from Trzebieńka and from 3.08 to 4.01 for the concentrate from Bolesław instead of using 70%  $\text{H}_2\text{SO}_4$  results in it decreasing even to 0.27 and to 0.71, respectively.

**Table 2.** The result of Zn-concentrate leaching (chemical analyses of the leachate) with 20, 50, and 70% of  $\text{H}_2\text{SO}_4$  solution for the solid phase to the liquid phase mass ratio 1:10

Sample	Time, h	Concentration, g/dm <sup>3</sup>						$C_{\text{Zn}}/C_{\text{Mg}}$
		Zn	Mg	Ca	Fe	Pb	Cd	
ZG Trzebieńka	20% $\text{H}_2\text{SO}_4$							
	0.5	1.63	1.40	0.25	0.42	0.014	0.009	1.16
	1.0	2.16	1.45	0.23	0.48	0.015	0.013	1.49
	1.5	2.50	1.45	0.24	0.48	0.010	0.015	1.73
	2.0	2.67	1.44	0.22	0.51	0.012	0.017	1.85
	50% $\text{H}_2\text{SO}_4$							
	0.5	1.71	1.59	0.04	0.54	0.006	0.007	1.07
	1.0	2.14	1.65	0.03	0.59	0.008	0.009	1.30
	1.5	2.38	1.59	0.03	0.56	0.012	0.011	1.50
	2.0	2.35	1.58	0.03	0.46	0.004	0.014	1.48
	70% $\text{H}_2\text{SO}_4$							
	0.5	0.45	1.59	1.51	0.27	0.035	0.015	0.28
1.0	0.39	1.43	1.03	0.16	0.028	0.017	0.27	
1.5	0.38	1.39	0.90	0.10	0.028	0.019	0.27	
2.0	0.39	1.31	0.71	0.07	0.028	0.023	0.30	
ZGH Bolesław	20% $\text{H}_2\text{SO}_4$							
	0.5	1.65	0.41	0.25	0.22	0.019	0.011	4.01
	1.0	1.62	0.43	0.23	0.23	0.004	0.010	3.81
	1.5	1.64	0.45	0.23	0.25	0.011	0.011	3.68
	2.0	1.72	0.45	0.22	0.26	0.010	0.011	3.84
	50% $\text{H}_2\text{SO}_4$							
	0.5	1.68	0.44	0.04	0.28	0.010	0.006	3.82
	1.0	1.57	0.45	0.03	0.28	0.011	0.006	3.51
	1.5	1.47	0.48	0.03	0.28	0.007	0.006	3.08
	2.0	1.42	0.46	0.03	0.26	0.006	0.006	3.09
	70% $\text{H}_2\text{SO}_4$							
	0.5	0.34	0.48	0.84	0.16	0.032	0.008	0.71
1.0	0.41	0.48	0.78	0.14	0.034	0.010	0.85	
1.5	0.41	0.48	0.78	0.10	0.019	0.013	0.84	
2.0	0.40	0.43	0.68	0.05	0.018	0.016	0.92	



**Figure 2.** The dependence of zinc and magnesium concentration in the leachate on the sulphuric(VI) acid concentration and the type of zinc concentrate (A – ZG Trzebionka, B – ZGH Bolesław)

For both of the Zn-concentrates the amounts of the leached Pb, Ca and Cd decrease with a change of  $H_2SO_4$  concentration from 20 to 50% and increase when the acid concentration is 70%. Low  $Ca^{2+}$  concentration in the leachate is caused by gypsum crystallization. It should be removed from the system, for example using an additional flotation process. High calcium and lead content in the solution obtained in the extraction process with 70% acid are connected with Ca and Pb sulphates(VI) dissolution in the concentrated sulphuric(VI) acid as a consequence of the  $HSO_4^-$  ion formation.

The application of the concentrated sulphuric(VI) acid (70%) is complicated by its aggressive nature and filtration problems resulting from the clammy consistency of the separated suspension.

The magnesium extraction process was run for 2 hours, and was controlled at intervals every 30 minutes. For the Zn-concentrates derived from ZGH Bolesław increasing of  $Mg^{2+}$  concentration in the leachate with time was observed for the processes with the 20% and 50%  $H_2SO_4$  solutions. For the 70%  $H_2SO_4$ ,  $Mg^{2+}$  concentration in the solution is not varied much. The effects of the treatment of the zinc concentrate from ZG Trzebionka are different from these, presented above. The concentration of magnesium in the leachates is higher and the application of 20% or 50%  $H_2SO_4$  does not effect the  $Mg^{2+}$  content in the solution with extraction prolongation. In these cases the changes were insignificant. In the process with 70%  $H_2SO_4$  the  $Mg^{2+}$  concentration in the leachate decreased with the leaching time. The differences are big, the concentrations varied from 1.59 to 1.31  $g/dm^3$ .

The amount of the leached Zn increases in the process extraction with 20%  $H_2SO_4$  for the concentrate from ZGH Bolesław and in the processes with 20% and 50%  $H_2SO_4$  for the concentrate from ZG Trzebionka. In the other cases the zinc concentration in the leachate decreased with the process prolongation.

The ratios of the leached Zn and Mg also varied with the process time. The relationships are shown in Fig. 3.

The advantageous extraction conditions for the concentrate from ZG Trzebionka are high concentration of  $H_2SO_4$  and a short time of the leaching process, for the concentrate from ZGH Bolesław the high concentration of acid, also, but the optimal reaction time is 1.5 h.

The change of the mass ratio of the solid phase to the liquid phase ( $p_s:p_l$ ) from 1:10 to 1:2 has an advantageous effect on Mg removal process from the Zn-concentrate. The result is particularly perceptible for the concentrate of high magnesium content. The results of Mg extraction from the studied materials for the solid phase to the liquid phase mass ratio of 1:2 are shown in Table 3.

Under these conditions the amounts of Zn leached from the samples of the concentrate derived from ZG Trzebionka and from ZGH Bolesław are comparable and lower than for  $p_s:p_l = 1:10$ , whereas the  $Mg^{2+}$  concentration in the obtained solutions is higher. In these experiments the values of  $c_{Zn}$  to  $c_{Mg}$  ratio are favourable.

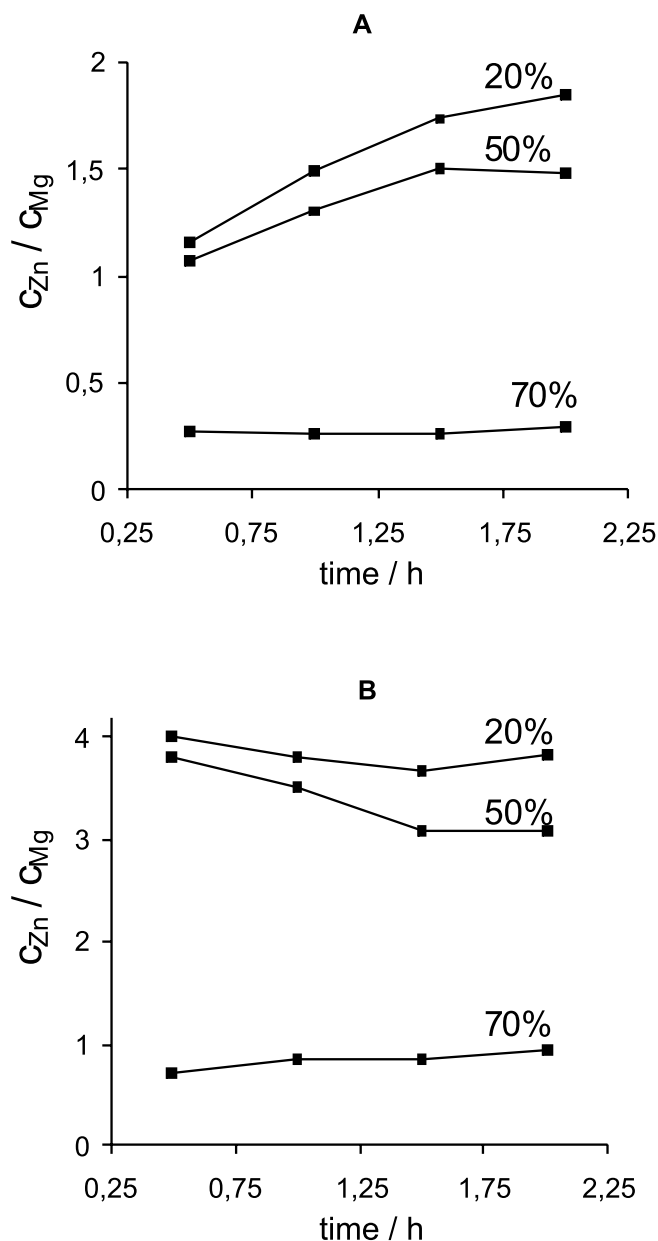
While investigating Mg removal from the Zn-concentrates, other constituents of the material passing into the leachate should receive attention. It concerns among other elements iron and cadmium. The content of Fe in the leachates is relatively high. Iron extraction from the concentrates is easier for the lower concentrations of  $H_2SO_4$  (20 and 50%). The use of 70%  $H_2SO_4$  and the change of the solid to the liquid phase ratio from 1:10 to 1:2 influences the decreasing of iron leaching. Cadmium concentration in the leachates decreases with acid concentration increasing from 20 to 50% and increases when  $H_2SO_4$  grows to 70%. In all the experiment series  $Cd^{2+}$  extraction yield increases with the reaction time. Moreover,  $Cd^{2+}$  concentration in the leachate achieved in the process with  $p_s:p_l = 1:10$  is generally higher than the concentration obtained with  $p_s:p_l = 1:2$ . Determining the leachate composition is of great importance with the view to its rendering harmless and/or utilization.

## RECAPITULATION AND CONCLUSION

In conclusion it can be stated that the amount of the removed magnesium from Zn-concentrate depends on the sulphuric(VI) acid concentration, the leaching time and the ratio of the solid to the liquid phase. Zinc and other components of the ore are also solubilized. The optimal

**Table 3.** The result of Zn-concentrate leaching (chemical analyses of the leachate) with the  $H_2SO_4$  solution for the solid phase to the liquid phase mass ratio 1:2

Sample	Time, h	Concentration, $g/dm^3$						$c_{Zn}/c_{Mg}$
		Zn	Mg	Ca	Fe	Pb	Cd	
ZG Trzebionka	70% $H_2SO_4$							
	0.5	0.27	2.70	0.51	0.11	0.046	0.006	0.10
	1.0	0.30	1.62	0.27	0.06	0.024	0.013	0.19
ZGH Bolesław	2.0	0.32	1.70	0.17	0.05	0.022	0.030	0.19
	70% $H_2SO_4$							
	0.5	0.26	1.74	0.76	0.19	0.030	0.014	0.15
	1.0	0.32	1.63	0.41	0.09	0.013	0.015	0.20
	1.5	0.37	1.33	0.25	0.04	0.018	0.016	0.28
2.0	0.46	1.19	0.16	0.03	0.006	0.019	0.39	



**Figure 3.** The dependence of  $c_{Zn}/c_{Mg}$  in the leachate on the sulphuric(VI) acid concentration and the leaching time for zinc concentrates derived from: A – ZG Trzebionka, B – ZGH Bolesław

conditions of the chemical treatment studied concentrates varied in the zinc and magnesium contents are different, for the concentrate from ZG Trzebionka they are as follows: the high concentration of H<sub>2</sub>SO<sub>4</sub> and the short time of the leaching process, for the concentrate from ZGH Bolesław – the high concentration of the acid and the reaction time 1.5 h. The change of the mass ratio of the solid phase to the liquid phase from 1:10 to 1:2 is favourable for Mg removal from the zinc blend concentrate.

#### ACLOWLEDGMENT

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