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## **A flotational-chemical method of reducing lead content in copper concentrate**

### **Key words**

Copper concentrate, chemical treatment, flotation, lead content

### **Abstract**

This paper presents the results of laboratory studies performed on copper concentrate sample containing about 30 percent Cu and about 1.55 percent Pb. The objective of the study was to demonstrate that by combining chemical treatment and flotation one can obtain a concentrate with reduced lead content.

As a result of pre-treatment of the sample with a 10% (by weight) ammonium acetate solution and subsequent flotation in the presence of a collector added at a ratio of 10 g/Mg, the material can be separated into two products:

- one obtained at a yield of 37%, containing about 44% copper and about 0.9% lead
- and one containing about 19% Cu and up to 1.6% Pb.

Thus obtained products can be directed to different copper-recovery metallurgical processes.

### **Introduction**

Polish copper ores are typical of sulphide ores and yet are fairly difficult to beneficiate. This is due to the exceptionally fine mineralization of their useful components and the presence of organic substances that facilitate the passage of gangue to the concentrate. Studies of flotation technology of these ores confirmed that bituminous clays containing small injections of copper sulphides form rather long cycles of semi-products in the technological process, thus shortening the effective time of flotation. These clays can pass to either concentrates, thus lowering their

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quality, or to wastes thus reducing the yield of the metal (Wójtowicz et al. 1971; Łuszczkiewicz et al. 1995; Sadowska 1993).

Those ores, in addition to many other elements, contain lead — mainly in sulphide form, as galena. Galena is the best floating sulphide. This is a mineral of low hardness and thus it passes to very fine grain classes during grinding before flotation, which does not facilitate its removal during flotation. In flotation of Polish copper ores, galena co-floats with copper sulphides. Studies conducted by IMN researchers (Madej et al. 1977; Bortel et al. 1987) indicate that lead content in copper concentrates can reach values from 1% to as high as about 2.5%.

Much research has been done on the problem of reducing the content of impurities in copper concentrate, focusing on obtaining lead as a separate product or separating it in as a semi-product that is subsequently returned to the copper processing cycle. So far, attempts to separate lead directly from copper ores have not been successful which is attributed to:

- fine graining of galena — from 200 to 300  $\mu\text{m}$ , with an average size of about 35  $\mu\text{m}$ ,
- in addition to lead occurring as galena, some portion of lead occurs as non-galena lead and is mainly contained in bornites and other ore minerals (Harańczyk et al. 1973; Banaś et al. 1976; Konstantynowicz-Zielińska 1993),
- in some portions of deposits lead is highly oxidized (Harańczyk et al. 1973),
- high differences in lead occurrence in individual lithologic varieties of the ore (Banaś, et al. 1976).

Also, attempts were made to separate the concentrate into two products of different copper and lead content, using hydrocyclones and a concentrating table (Madej et al. 1973; Bortel et al. 1987; Studium uwarunkowań... 1995). The separation led to some differences in Cu and Pb content in the concentrates obtained but organic carbon accumulates predominantly in the product with lower metal content. Poor copper concentrates are generally directed to copper matte smelting where bitumens are unwanted. That is why such method of processing has no economic justification.

It is currently proposed to reduce the content of lead in the flotation feed by limiting the ripping of the ore deposit roof. This is because there is an opinion that in deposits where most of the lead is associated with carbonate rocks, the highest lead mineralization occurs in the roof of the deposit (Banaś et al. 1976).

Recognizing that galena contained in the concentrate is finely grained, studies were conducted on leaching lead with ammonium acetate (Chaplygina et al. 1990; Sanak-Rydlowska et al. 1999). Results of these studies indicate that it is possible to reduce lead content in copper aggregate to about 1%. Further research is required.

## **1. Subject and method of the study**

The subject of the study was a sample of final concentrate originating from the ZWR Rudna (the Rudna Ore Beneficiation Plant). The sample contained on the average 29.7% copper and 1.55% lead. The grading of the sample and the distribution of copper and lead in individual grain classes are summarised in Table 1. Analysis of results shows that the tested material contained mainly fine grains, below 45  $\mu\text{m}$  — this grain class accounted for about 62%. The content of lead

TABLE I

Grain-size distribution of the copper concentrate studied and distribution of copper and lead content in grain-size classes

TABELA I

Skład granulometryczny badanego koncentratu miedziowego i rozkład zawartości miedzi i ołowiu w klasach ziarnowych

No.	Grain class [mm]	Yield [%]	Content [%]	
			Cu	Pb
1	+ 0.1	6.42	28.75	0.68
2	0.1—0.071	13.57	35.95	0.90
3	0.071—0.063	5.45	30.05	0.95
4	0.063—0.050	11.51	34.38	1.27
5	0.050—0.045	1.79	33.95	1.32
6	-0.045	61.26	27.80	1.86
7	FEED	100.00	29.95	1.53

increases with decreasing grain size — from about 0.68% in the +0.1 mm class to about 1.86% in the class -0.045 mm.

The scope of the study included:

- a preliminary chemical treatment with an ammonium acetate solution,
- a second flotation of the product obtained after chemical treatment with ammonium acetate.

The experiments were so performed that samples of crude concentrate were treated chemically with 100 cm<sup>3</sup> of ammonium acetate solution with concentrations of 10% or 40% by weight, at room temperature. The samples were treated for 60 minutes and then floated.

Two series of experiments were conducted:

- in the first series, pre-treated samples were transferred, without prior decantation, to the flotation cell, filled up with water to 1 dm<sup>3</sup> and floated,
- in the second series, samples were floated after draining.

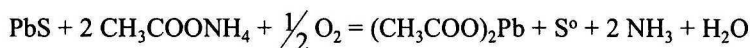
The flotation was done in a laboratory-size mechanical flotation machine with a cell of 1 dm<sup>3</sup>. A mixture of ethyl and isobutyl xanthates was added (10 g per 1 Mg of the feed) or a frothing agent (20 g per 1 Mg of the feed). The frother was a mixture of alcohols (with an unspecified composition) — the reagent used at the Rudna Ore Beneficiation Plant. The results and conditions of the experiments are given in Tables 2—4.

## 2. Discussion of the results

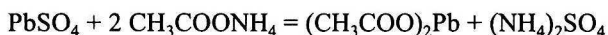
The purpose of the study was to develop a method to reduce lead content in copper concentrates produced by flotation. The quantity of lead introduced to the copper recovery

process is the highest at the Rudna Mine due to the highest content of this element in the feed and in the final concentrate, as well as due to the highest amount of ore that is processed in this mine (Opracowanie... 1995).

It is known that lead can be leached in the presence of ammonium. It is assumed that lead is leached from galena in the reaction:



Ammonium acetate dissolves lead sulphate in the reaction:



Consequently, the use of ammonium acetate would make it possible to remove also this portion of lead that occurs as a product of surface oxidation of galena. Research showed (Opracowanie... 1995) that as a result of leaching with 10 or 40% ammonium acetate solutions at room temperature, about 12—17% of lead and 5 to 7% of copper passes to the solution. A further reduction in lead content was noted after thermal treatment but it was accompanied by the passage of copper into the solution (Opracowanie... 1995; Sanak-Rydlewska et al. 1999). Consequently, an attempt was made to study the possibility of further reduction in lead content using a chemical-flotational method. The results are shown in Tables 2—4.

Table 4 (flotation I) shows flotation results for crude concentrate, without chemical treatment and without any flotation reagents. The results confirmed that lead minerals float together with copper minerals. The froth product obtained after three minutes' flotation contained 33.5% Cu and 1.67% Pb (at about 29.24% Cu and 1.5% Pb in the feed) and a copper yield of about 86% and lead yield of about 83.7%.

Tables 2 through 4 summarise flotation results for samples pre-treated with 10 or 40% ammonium acetate solutions at room temperature.

Tables 2 and 3 present results of two series of experiments:

- 1 — the sample was floated along with the solution obtained through leaching,
- 2 — the sample was floated after draining.

The samples were floated with the addition of frother only — about 20 g per Mg of the feed. The analysis of flotation results seems to indicate that xanthate desorption from the mineral surface occurs during flotation, irrespective of the amount of the leaching agent and the method of treatment before flotation. The obtained froth products were characterised by low copper content (about 16.2 to 18.5%). It should be emphasised that the method of treating the sample (whether drained or not) significantly affected the froth product yield. Drained samples floated with a yield 19 to 20% higher as compared to undrained samples. The difference between lead content in the products should be considered unsatisfactory in all the cases.

Table 4 summarizes results of flotation after chemical pre-treatment (without draining) with the addition of ethyl alcohol and isobutyl xanthate mixture at a feed ratio of 10 g/Mg. The obtained results indicate that the addition of frother increased the yield of the froth product (as compared with flotation I, Tables 2 and 3) and flotation selectivity. Froth products (Table 4,

TABLE 2

Flotation results after leaching with a 10% ammonium acetate solution

TABELA 2

Wyniki flotacji próbki po ługowaniu 10% roztworem octanu amonu

Flotation Number	Flotation conditions		Product	Yield $\gamma$ [%]	Content [%]		Recovery [%]	
	description	flotation time [minutes]			Cu	Pb	Cu	Pb
I	undrained sample	5	Froth prod.	19.07	18.26	1.40	11.70	80.64
	Only frother added, about 20 g/Mg	—	Tailings	80.93	32.45	1.375	88.30	19.36
		—	Feed	100.00	29.74	1.38	100.00	100.00
II	drained sample Only frother added, about 20 g/Mg	1	Froth prod. I	15.34	16.44	1.27	8.48	15.97
		4	Froth prod. II	17.25	18.49	1.39	10.72	19.66
		—	Tailings	67.41	35.65	1.17	80.80	64.37
		—	Feed	100.00	29.74	1.22	100.00	100.00
		5	Total of froth products	32.59	17.53	1.33	19.20	35.63

TABLE 3

Flotation results after leaching with a 40% ammonium acetate solution

TABELA 3

Wyniki flotacji próbki po ługowaniu 40% roztworem octanu amonu

Flotation Number	Flotation conditions		Product	Yield $\gamma$ [%]	Content [%]		Recovery [%]	
	description	flotation time [minutes]			Cu	Pb	Cu	Pb
I	undrained sample	5	Froth prod.	11.91	16.27	1.40	6.52	11.50
	Only frother added, about 20 g/Mg	—	Tailings	88.09	31.56	1.475	93.48	88.50
		—	Feed	100.00	29.74	1.45	100.00	100.00
II	drained sample Only frother added, about 20 g/Mg	1	Froth prod. I	17.86	16.18	1.11	9.72	16.69
		4	Froth prod. II	15.14	18.23	1.36	9.28	17.33
		—	Tailings	67.41	35.96	1.17	81.00	65.98
		—	Feed	100.00	29.74	1.19	100.00	100.00
		5	Total of froth products	33.00	17.12	1.22	19.00	34.02

TABLE 4

Flotation results for crude concentrate samples and samples chemically pre-treated with a 10 or 40% ammonium acetate solution (without draining)

TABELA 4

Wyniki flotacji koncentratu surowego oraz próbek koncentratu po obróbce chemicznej octanem amonu o stężeniu 10 lub 40% (bez odsączania)

Flotation Number	Flotation conditions		Product	Yield $\gamma$ [%]	Content [%]		Recovery [%]	
	description	flotation time [minutes]			Cu	Pb	Cu	Pb
I	Untreated sample. pH flot.= 7.5—7.8 . flot. with no reagents added	3	Froth prod.	75.07	33.51	1.67	86.03	83.67
		—	Tailings	24.93	16.39	0.98	13.97	16.33
		—	Feed	100.00	29.24	1.50	100.00	100.00
II	After treatment with a 10% ammonium acetate solution, pH = 6.7, collector about 10 g/Mg	3	Froth prod.	62.51	18.90	1.58	41.85	74.80
		—	Tailings	37.49	43.79	0.89	58.15	25.20
		—	Feed	100.00	28.23	1.32	100.00	100.00
III	After treatment with a 40% ammonium acetate solution, pH = 6.04, collector — about 10 g/Mg	5	Froth prod.	54.37	11.67	1.42	23.10	61.76
		—	Tailings	45.63	46.29	1.05	76.90	38.34
		—	Feed	100.00	27.47	1.25	100.00	100.00

flotation I and II) show reduced copper content and an increased lead content. For instance, the sample treated before flotation with a 10% ammonium acetate solution yielded:

— froth product with copper content higher by about 19% and lead content higher by about 1.6% relative to the crude concentrate, at a yield of about 62.5% (Table 4). (The crude sample contained about 29.2% Cu and about 1.5% Pb),

— tailings (the residue in the flotation cell) at a yield of about 37.5%, containing 44% Cu and about 0.9% Pb.

It can be thus concluded that the combination of leaching with ammonium acetate and flotation can be used to obtain two types of copper concentrate which, considering the difference in content of the two analyzed metals, would be subsequently directed to two different copper recovery processes.

### 3. Summary of the results

The subject of the study was a flotation copper concentrate originating from the Rudna Ore Beneficiation plant, containing on the average 30% Cu and about 1.5% Pb. The chemical-

-flotational method developed to reduce lead content consists of preliminary treatment of copper concentrate with ammonium acetate and flotation of the product obtained by chemical treatment. For this method a reactor must be installed for leaching the final concentrate with ammonium acetate. The product obtained through the treatment should be directed to "purifying" flotation to be separated into two concentrates. These processes produce two concentrates differing in both copper and lead content; e.g. as a result of treatment with a 10% ammonium acetate solution and subsequent flotation the following products were obtained:

- froth product, at a yield of 62.5%, containing about 19% Cu and up to 1.6% Pb,
- tailings (residue after flotation), at a yield of 37.5%, containing about 44% copper and about 0.9% lead.

These products, considering the differences in the content of the analyzed metals, could be subsequently directed to two separate copper recovery processes.

The chemical treatment of copper concentrate with ammonium acetate also produces post-leaching solutions that can contain copper (about 2 g/cm<sup>3</sup>) and lead (about 0.2—0.3 g/dm<sup>3</sup>) (Opracowanie... 1995; Bieszczad et al. 1999). Those are acetate solutions with pH of 5.5 to 6.0 from which Cu and Pb should be recovered whereas the remaining solution, after its composition is corrected with ammonia, can be returned to repeated chemical treatment of the concentrate.

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#### BADANIA NAD FLOTACYJNO-CHEMICZNĄ METODĄ OBNIŻENIA ZAWARTOŚCI OŁOWIU W KONCENTRACIE MIEDZIOWYM

##### Słowa kluczowe

Koncentrat miedzi, obróbka chemiczna, flotacja, zawartość ołowiu

##### Streszczenie

Artykuł przedstawia wyniki badań laboratoryjnych wykonane dla próbki koncentratu miedzi zawierającego około 30% Cu i około 1,55% Pb. Celem badań było wykazanie, że połączone metody obróbki chemicznej i flotacji mogą dać w wyniku produkt o obniżonej zawartości ołowiu w koncentracie.

Wstępna obróbka chemiczna badanej próbki za pomocą octanu amonu o stężeniu 10% wag., a następnie flotacja w obecności zbieracza o stężeniu 10 g/Mg pozwala rozdzielić materiał na dwa produkty:

- jeden o wychodzie około 37% i zawartości miedzi około 44%, a ołowiu około 0,9%;
- drugi zawierający około 19% miedzi i około 1,6% ołowiu.

Każdy z tak otrzymanych produktów może być kierowany do otrzymywania miedzi różnymi metodami metalurgicznymi.