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Physico-chemical Problems of Enrichment of Oxidized Zinc Minerals

Fizykochemiczne problemy wzbogacania utlenionych minerałów cynku

Физико-химические проблемы обогащения окисленных минералов цинка

As sulfide zinc ore (sphalerites, marmatites) deposits run out a necessity of exploitation of oxidized ores of the metal grows. From among the latter such zinc minerals as smithsonite (neutral zinc carbonate), hydrozincite (basic zinc carbonate), zincite (zinc oxide), willemite (zinc orthosilicate) deserve a special attention. Only a few deposits in the world contain oxidized zinc ores pure enough - and ample enough - to make possible the application of simple ore dressing. More often the minerals form micron sized impregnations in gangue accompanying sulfide zinc ores or, alternatively, oxidized lead and iron minerals. Thus, basic difficulty in upgrading the ores results from this very fine mineralization within the deposit, low grade of the ores, rather high dispersion as well as the physico-chemical properties of the useful minerals close to the properties of gangue minerals. Furthermore, to liberate zinc minerals from such ores the ore has to be finely ground and this results in formation of large amounts of gangue slimes with a considerable detriment to the flotation separation.

The problem of recovering of zinc from such ores is quite important as there are rather ample deposits of the ores in the country.

In general, there are two types of zinc ore deposits in Poland:

1. Sulfide ore deposits in Olkuszko-Częstochowski region. The valuable mineral is zinc blend which contains up to 20% of oxidized zinc minerals and dolomite is the gangue. Magnesium in dolomite may be partly substituted by zinc ions and then it is referred to as zinc dolomite. Presently, the oxidized minerals as well as zinc from zinc dolomite are not recovered. They go into the flotation reject which is an evident loss in terms of the metal as well as in terms of money.

2. Calamine ores with oxidized zinc minerals (smithsonite, hydrozincite and willemite) as the valuable ones and carbonates of calcium and magnesium, ferric and ferrous oxides and silicates as the gangue minerals. Zinc content in the ore comes up to 8%, with some admixtures of lead minerals. Because of mineralogical form of the valuable minerals it is not possible to upgrade them by flotation techniques at present state of their development. Thus, zinc from the ores is recovered by thermal distillation in rotary kilns. The limit of economical flissibility of the thermal technique is about 8% of zinc content in the ore.

In general, two methods of recovering of zinc from its oxidized ores are used in the world: firstly, flotation techniques using amine-type collectors mixture and pre-separation of fines in hydrocyclones; secondly, leaching techniques, mainly the alkaline ones, using mainly ammonium hydroxide and ammonium salts as well as amines.

Flotation methods as applied to oxidized zinc ores are especially well worked out in Soviet Union and Italy. In both cases the technique involves the use of a cationic collector (an aliphatic amine) and sodium sulfide. Abramov claims, that if these reagents are used in a form of emulsion the selectivity of flotation separation is much higher. In Italy, the oxidized zinc minerals are rendered floatable with an amine collector, then the flotation pulp is sulfidized and xanthate added. In this way collective sulfide-carbonate flotation

concentrates may be obtained or, alternatively, each type of the minerals may be obtained as a separate concentrate. Any of these techniques are limited to the ores which are easy to flotation upgrading.

Two main procedures are known to be used in flotation upgrading of oxidized zinc ores:

- 1) sulfidizing and then flotation with amine-type collectors;
- 2) sulfidizing, activation with copper and then flotation using xanthate-type collectors and, additionally;
- 3) a possibility of using a mixture of the two types of collectors: a xanthate + an amine which is supposed to give a collective concentrate of oxidized and sulfide zinc ores.

The idea of sulfidizing of smithsonite and then flotation with amines was stated and then verified by Klassen et al. [1] several years ago. Later, such investigations were done by Belov [2] and then by Rey [3], Gaidazhiev [4] as well as Cases, Trabelsi, Predali [5], Rinelli and Marabini [6]. All the studies quoted refer to sulfidization and then flotation with amine-type collectors with exception of Rey and Formanek [7] who discuss the possibility of flotation with xanthates. A weak point of the latter method is that the formed zinc sulfide layer is rather loosely bound to the mineral surface. Thus, the air bubble - mineral grain aggregates are not stable enough to render flotability of the mineral. Recently, Cases et al. [5] gave a wide review on physico-chemical studies on flotation of oxidized zinc minerals using amine-type collectors. The author elucidated mechanism of fixation of sulfide and zinc ions at smithsonite surface. They have also discussed two alternative mechanisms of fixation of an amine at the smithsonite surface: (a) by formation of the amine carbonate, and (b) formation of an amine - zinc surface complex. They have claimed the latter mechanism be more probable because of higher energy of formation of amine complexes. There is an disadvantage in using amine-type collectors in smithsonite flotation as the collectors are of rather low selectivity as well as render floatable carbonate minerals of gangue.

From the theoretical point of view, a flotation procedure involving sulfidizing and copper ions activation of oxidized

zinc minerals followed by flotation with xanthate-types collectors seems to be more rational. Moreover, the procedure would allow a collective flotation of sphalerite along with activated smithsonite, as it has been proved by M.C. Fuerstenau, that sulfidization of smithsonite is most effective at pH range from 8 to 9, and sphalerite flotation requires just a slightly alkaline solution.

Investigations on flotation of smithsonite which are carried out at our laboratory are pointed out into direction discussed above. This is justified by the fact that Polish sulfide zinc ores contain considerable percentage of oxidized minerals of the metal.

Synthetic neutral and basic zinc carbonates are being used in our experiments on sulfidizing and copper ions activation. Crystal structures of the precipitates are identical to these of smithsonite and hydrozincite. The synthetic precipitates were used because of great difficulty in selecting of pure crystals of hydrozincite and smithsonite from natural ore specimens.

Investigation on activation of the precipitates with copper ions proved that activation took place in fact and it was quite efficient. Isotherms of copper ions adsorption at smithsonite and hydrozincite from solutions of the same pH are shown in Figs. 1 and 2. Kinetics of copper ions adsorption at smithsonite is presented in Fig. 3. As it is seen from Figs. 1 and 2, copper ions adsorption was the same within a wide range of pH and initial concentration of copper ions. In case of smithsonite a new phase was formed at the surface and it was supposed to be a mixture of malachite and azurite. Rate of adsorption of copper ions - as it is seen in Fig. 3 - was quite rapid. Nearly whole of copper ions present initially in the solution had been adsorbed by the precipitate after a few minutes of contact. Investigations on the adsorption process showed that mechanism of the process involved exchange of zinc ions into copper ions which resulted in formation of the surface layer of copper carbonates. The surface layer of malachite or azurite allows the sulfidization process to take place very easily. As it is seen from Fig. 4, sulfidization of smithsonite activated with copper ions was very efficient within pH range of 7.5 - 8, which is in a good agreement with the results found in the literature.

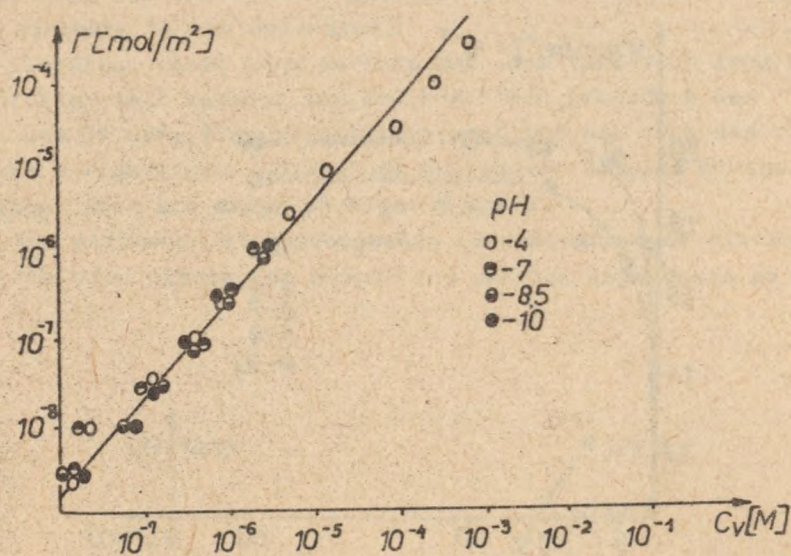


Fig. 1. Isotherms of copper ions adsorption at smithsonite

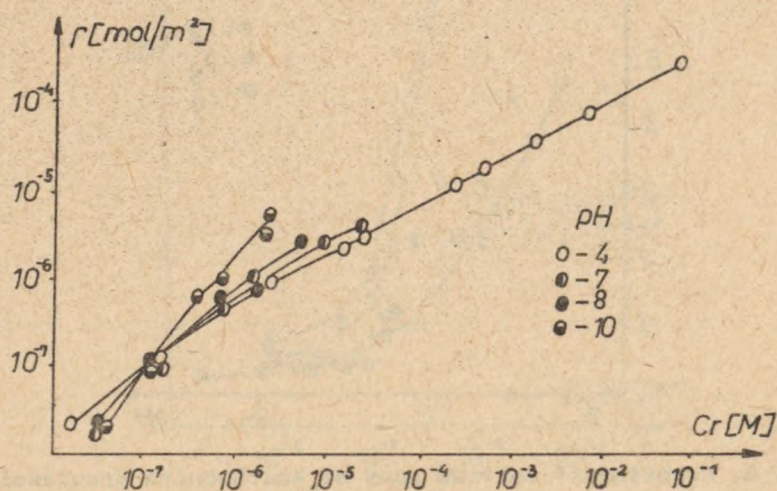


Fig. 2. Isotherms of copper ions adsorption at hydrozincite

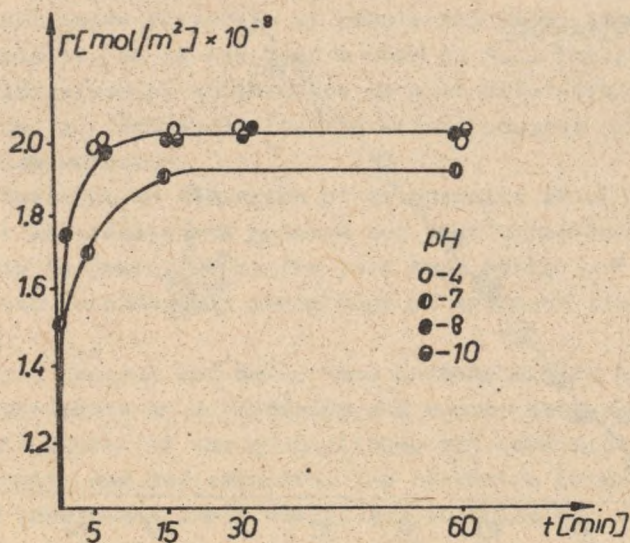


Fig. 3. Kinetics of adsorption of copper ions at smithsonite

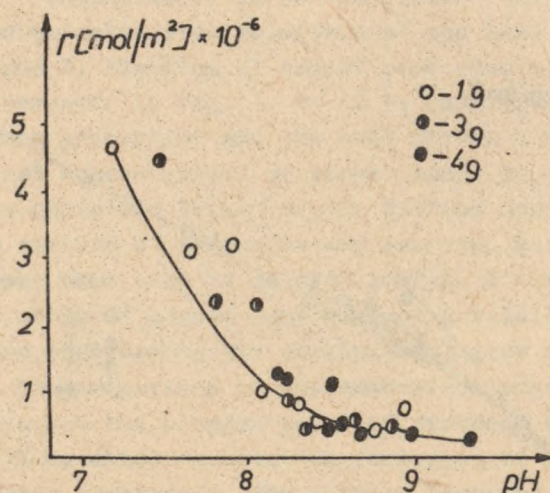


Fig. 4. Sorption of sulfide ions at smithsonite previously activated with Cu^{2+} ions

The mineral activated previously with copper ions and sulfide ions was tested in a laboratory flotation cell using ethyl xanthate as the collector.

Flotation tests were carried out in a tube-type laboratory flotation cell without any frother. This procedure was used because of very fine precipitate used and was supposed to avoid a significant mechanical carryover. Results of the flotation tests are shown in Figs. 5 and 6.

The influence of xanthogenate concentration of flotability of the precipitate, at copper and sulfide ions doses as well as

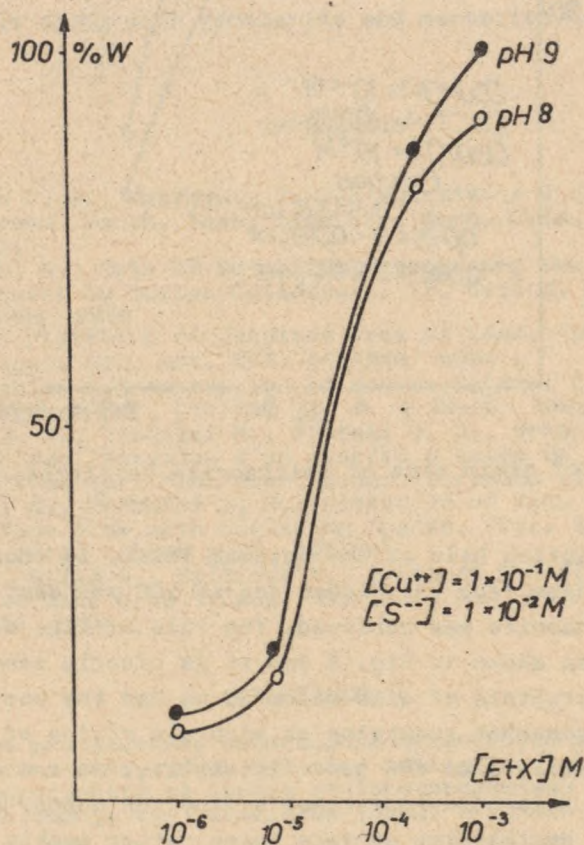


Fig. 5. Flotation of activated smithsonite vs. ethylxanthate concentration

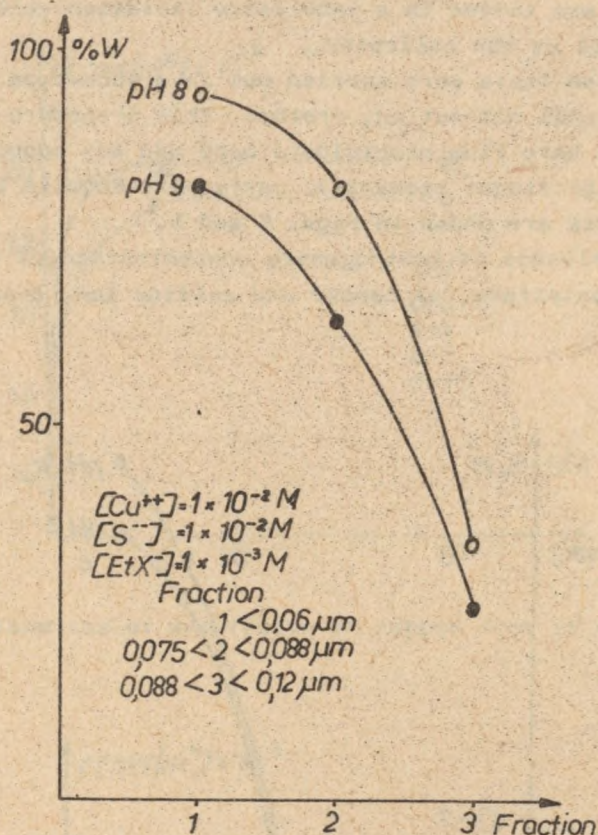


Fig. 6. Role of grain size of smithsonite in flotation recovery

pH of the solution held at the optimum level, is shown in Fig. 5. As it is seen from the Figure nearly 100 per cent flotability of smithsonite was achieved. The role of size of precipitate grains is shown in Fig. 6 and it is clearly seen that smithsonite crystals of size below 60 μm had the best flotability. It is somewhat surprising as minerals grains of size of 75-200 μm usually show the best flotability. We are of the opinion that this behaviour results from the copper sulfide layer at the smithsonite surface being rather weakly fixed to the surface. This resulted in detachment of the copper sulfide layer - together with the xanthate adsorbed - of the smith-

sonite surface on contact with an air bubble, because of high inertia of layer smithsonite crystals.

Investigation on collective flotation of smithsonite along with sphalerite, using the flotation collectors of the latter, is still carried on in this laboratory. The main topic of the investigations are as follows:

- 1) kinetics of activations with copper and sulfide ions;
- 2) determination of the set of flotation conditions ensuring the best flotation rate and efficiency for coarser smithsonite grains;
- 3) collective flotation of sphalerite and smithsonite.

Knowledge on basic physico-chemical aspects of flotation of oxidized zinc minerals makes the idea of collective flotation of minerals along with sphalerite and marmatite quite promising.

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STRESZCZENIE

Opisano problematykę wzbogacania utlenionych wysokozdyspergowanych minerałów cynku. Wykazano możliwość flotacji smitsonitu i hydrocynkitu za pomocą etyloksantogenianu potasu poprzez wstępną aktywację tych minerałów jonami miedziowymi i siarczowymi.

Резюме

В работе описана проблематика обогащения окисленных высокодиспергованных минералов цинка. Обнаружено возможность флотации смитсонита и гидроцинкита при использовании этилксантогената калия путем предварительной активации этих минералов медными и сульфидными ионами.