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AMINO ACID DEXTRINS AS SELECTIVE DEPRESSANTS IN FLOTATION OF CHALCOCITE AND GALENA

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A series of biodegradable, proecological depressants for selective flotation of galena and synthetic chalcocite was tested. These depressants, originating from dextrinization of potato starch with biogenic α-amino acids such as alanine, arginine, asparagic acid, cysteine, glutamic acid, glycine, histidine, isoleucine, leucine, lysine, methionine, proline, serine, threonine, tryptophane, tyrosine, phenylalanina and valine, appeared to be effective depressants. Among them dextrins from starch modified with asparagic acid, glutamic acid and threonine were superior as they provided good recovery of galena and significant depression of synthetic chalcocite at a concentration of 2-4 kg/Mg of minerals when sulfides were subjected to microflotation separately. Subsequently, threonine dextrin was tested as a copper mineral depressant for Polish industrial copper concentrates containing 18.28% Cu and 3.63 % Pb. The test was carried out in a laboratory flotation machine and it was found that threonine dextrin was highly selective but the results were opposite to the microflotation tests since it depressed lead mineral more efficiently than the copper minerals.

Key words: separation, flotation, upgrading, copper minerals

INTRODUCTION

Separation of lead minerals from Polish copper concentrates is a difficult task (Łuszczkiewicz et al., 1995) because it contains unusual pair of sulfides: chalcocite

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and galena at a ratio of 10:1. Separation of those sulfides involving purely physical methods conducted by means of hydrocyclones, concentrating tables, high field magnetic separators and other has been unsuccessful (Kubacz et al., 1984: 1985). Application of selected depressants such as thioglycolic acid (Luszczykiewicz and Drzymala, 1996) and ammonium acetate (Sanak-Rydlewksa et al., 1999) was more promising. In other countries polymers are frequently used depressants in selective flotation of complex ores. Among them polysaccharides evoked particular interest (Lin and Burdick, 1988; Pugh, 1989; Liu and Laskowski, 1999; Rath, 1999). Recently, preparations from dextrinization of potato starch under ammonia (Wiejak et al., 1991; Szychowska and Tomaski, 1997), hydrogen sulfide (Szychowska et al., 1998), and with gluten (Szychowska and Tomaski, 1996) were tested as depressants in flotation of individual galena and chalcopyrite samples and their mixtures. Only dextrins prepared from starch under ammonia proved to be suitable (Drzymala et al., 2000).

All compounds mentioned above constitute a group of reagents called first generation depressants. They provide, to a certain extent, separation of lead minerals from copper minerals. However, there is a need for a second generation depressants leading to copper concentrates and tailing in form of lead concentrates. For this sake, special novel dextrins were prepared. They resulted from the thermolysis of potato starch with α-amino acids (Kapusniak et al., 1999). These biodegradable and pros ecological preparations were used for model flotation studies involving chalcopyrite and galena.

MATERIALS

Dextrins resulted from thermolysis of potato starch with one of the following amino acids: alanine (ALA), arginine (ARG), cysteine (CYS), glycine (GLY), histidine (HIS), isoleucine (ILE), asparagic acid (ASPA), glutamic acid (GLUA), leucine (LEU), lysine (LYS), methionine (MET), phenylalanine (PHE), proline (PRO), serine (SER), threonine (THR), tryptophane (TRP), tyrosine (TYR), and valine (VAL). In the text they are denoted as ALA-dextrin, ARG-dextrins, and so on, respectively. Preparation of these dextrins was described by Kapusniak et al. (1999) and their properties were reported in a paper by the same authors (1999a). Prior to flotation 0.2 g of any dextrin was dissolved in 100 cm³ of water at 70-80ºC. Although dextrins did not solubilize completely non-filtered solutions were used. A 10⁻⁴ mol/dm³ solution of potassium butylxanthat (KBUTX) was used as collector. Synthetic chalcopyrite was provided by the Copper Metallurgical Enterprise in Legnica, Poland. Trzebionka Zinc-Lead Ore Mine, Poland, supplied us with galena. Prior to flotation samples of these minerals were identified by means of powder x-ray analysis in the Department of X-Ray Analyses in the Institute of Cryogenics and Structural Studies of the Polish Academy of Sciences in Wrocław, Poland.
METHODS

Minerals were crushed and pulverized in an agalite mortar followed by separation into fractions on the sieves. Only the 0.16-0.20 mm size fraction was used in the flotation tests. The period between crushing and beginning of flotation did not exceed 30 min. Microflotations were carried out in monobubble Hallimond apparatus equipped in calibrated receiver providing a continuous recording of the recovery as a function of time. Galena and chalcocite have different density therefore, standard weight of the samples of each mineral introduced into the apparatus was different. They were 1.10g for galena and 0.65 for chalcocite. Each mineral was subjected separately to flotation. The solid particles (0.2 cm³ i.e. either 1.1 g of PbS or 0.65 g of Cu₂S) were suspended in 120 cm³ of aqueous solution of depressant, then agitated for 5 minutes. The pH of the solution was usually between 6.4 and 7.2 unless otherwise stated. Amount of butyl xanthate subsequently added to the solution provided its final concentration of 0.0001 kmol/m³. After 5 min. agitation, the suspension was transferred to the Hallimond tube and floated for 15 minutes with the air flow of 0.625 cm³/s. Microflotation carried out at 20±2°C lasted 15 min. Recovery of minerals was calculated in form of volume of floated particles related to the original volume of particles. Kinetic output – time curve was determined for every test. From the recovery - time diagram recoveries after 15 min were taken and relationships in respect to the concentration of depressant were derived. Flotation tests were also carried out in a Mechanobr laboratory flotation machine, equipped with a 500 cm³ cell. A sample of 150 g of industrial concentrate was used in the experiment. Flotation was carried out in distilled water in the presence of 50g/Mg potassium ethyl xanthate, 50g/Mg α-terpineol and 1500g/Mg threonine dextrin. The solids were introduced to water followed by dextrins, collector and finally the frother. The pH of flotation was 7.99. During flotation of the sample three concentrates, after 1, 2 and 4 minutes of flotation, were collected and the solid remaining in the cell were labeled as tailing.

RESULTS AND DISCUSSION

Fig. 1a-s shows results of microflotation in a small Hallimond tube of chalcocite and, separately, galena in the presence of the investigated dextrins. It can be seen from that Figure that results of depression of sulfides varied from one dextrin to another. To show the results on one graph and compare the results an index, denoted here as index I, was designed. Index I is measure of a difference between the dose of a dextrin necessary for 95 % recovery of galena and 5% of chalcocite related to the dose of dextrin required for 5% of chalcocite and has a form:
Fig. 1a-f. Results of flotation of galena and separately synthetic chalcocite in the presence of butyl xanthate and various amino acid dextrins: a) ALA (alanine), b) ARG (arginine), c) CYS (cysteine), d) PHE (phenylalanine), e) GLY (glycine), f) HIS (histidine)
Fig. 1g-l. Results of flotation of galena and separately synthetic chalcocite in the presence of butyl xanthate and various amino acid dextrins: g) ILE (izoleucine), h) ASPA (asparagic acid), i) GLUA (glutamic acid), j) LEU (leucine), k) LYS (lysine), l) MET (methionine)
Fig. 1m-s. Results of flotation of galena and separately synthetic chalcocite in the presence of butyl xanthate and various amino acid dextrins: m) PRO (proline), n) SER (serine), o) THR (threonine), p) TRP (tryptophane), r) TYR (tyrosine), s) VAL (valine)
\[ I = \frac{C_{\text{Pb} 95\%} - C_{\text{Cu} 255\%}}{C_{\text{Cu} 255\%}} \]  

where \( C_{\text{Cu} 255\%} \) is the dose of the dextrin (kg/Mg of solids) required for 5% recovery of \( \text{Cu}_2\text{S} \), and \( C_{\text{Pb} 95\%} \) is the dose of the dextrin (kg/Mg of solids) required for 95% recovery of galena.

![Diagram](image)

**Fig. 2.** Selectivity index \( I \) (Eq.1) vs \( C_{\text{Cu} 255\%} \) for the investigated amino-acid dextrins. Five most promising dextrins are labeled with numbers from 1 to 5.

A higher value of index \( I \) at a lower value of \( C_{\text{Cu} 255\%} \) (Fig.2) points to a more efficient separation. Index \( I \) is helpful in selection of the most promising dextrins. It appears that the first five most promising selective dextrins are GLU-dextrin, ASP-dextrin, THR-dextrin, GLY-dextrin, and MET-dextrin. To check this finding a flotation test was performed in a laboratory flotation machine with a sample of an industrial copper concentrate from Lubin. The concentrate contained galena together with chalcocite apart from other sulfide minerals. THR-dextrin was used as the
depressant in the flotation test. The results involving industrial sample are shown in Table 1 and Fig. 3.

Table 1. Flotation of industrial copper concentrates in the presence of 1500 g of THR-dextrin per one megagram of solids. Other chemicals: KEtX 50 g/Mg, α-terpineol 50 g/Mg, pH 7.99. Flotation in a laboratory flotation machine

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield,%</th>
<th>Cu</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>content, λ%</td>
<td>recovery, ε%</td>
<td>content, λ%</td>
</tr>
<tr>
<td>Concentrate 1</td>
<td>21.34</td>
<td>43.40</td>
<td>50.65</td>
</tr>
<tr>
<td>Concentrate 2</td>
<td>9.52</td>
<td>33.75</td>
<td>17.58</td>
</tr>
<tr>
<td>Concentrate 3</td>
<td>8.97</td>
<td>22.75</td>
<td>11.17</td>
</tr>
<tr>
<td>Tailing</td>
<td>60.17</td>
<td>6.25</td>
<td>20.60</td>
</tr>
<tr>
<td>Feed</td>
<td>100</td>
<td>18.28</td>
<td>100</td>
</tr>
</tbody>
</table>

Fig. 3. Results of flotation from Table 1 in a graphical form. Good separation of lead and copper minerals is well visible from the figure.

Surprisingly, the flotation results for the industrial concentrate are inverted in relation to the results obtained from experiments with model samples, that is starch modified with threonine was a more powerful depressant towards synthetic chalcopyrite than for galena while for the industrial concentrate flotation of lead minerals was much more depressed than the copper minerals. The reason of the observed discrepancy is not clear and this calls for additional testing. A similar reversion of the selectivity of separation was observed by Liu and Laskowski (1999) in the galena-chalcopyrite system floated at pH 6 and pH 12. They explained the observed reversion
by the difference in the isoelectric point (iep) of oxidation products of sulfides that is Cu(OH)₂ (pH\text{iep} 7.6-9.0) and Pb(OH)₂ (pH\text{iep}=10-11). This and other possible reasons have to be checked by additional flotation tests.

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Przebadano szereg biodegradowalnych i proekologicznych depresorów pod kątem ich zastosowania do selektywnego flotacyjnego rozdziału galeny odchalkozynu. Depresory te otrzymano w wyniku dekstrynizacji skrobi ziemniaczanej α-aminokwasami (alanina, arginina, kwas asparaginowy, cysteina, kwas glutaminowy, glycina, histidyna, isoleucyna, leucyna, lizyna, metionina, prolina, seryna, threonina, tryptofan, tyrozyna, fenyloalanina i walina). Uzyskane depresory zastosowano do ksantogenianowej flotacji naturalnej galeny i osobno syntetycznego chalkozynu w celce Hallimonda przy pH około 6.5. Dla większości depresorów zaobserwowano silną depresję flotacji syntetycznego chalkozynu, podczas gdy zanik flotacji galeny obserwowano dopiero przy dużych stężeniu depresora. Największą różnicę stężeń niezbędną do depresji badanych siarczków uzyskano dla dekstryn modyfikowanych kwasem asparaginowym, kwasem glutaminowym oraz treoniną. Do dalszych badań, przeprowadzonych w laboratoryjnej maszynie flotacyjnej Mechanobr o pojemności celi flotacyjnej wynoszącej 0.5dm³, użyto dekstryny modyfikowanej treoniną. Depresor ten, zastosowany do flotacji końcowego koncentratu miedziowego z LGOMu, który zawierał 18.28% Cu i 3.63 % Pb. Uzyskano dobry rozdział mineralów miedzi od ołowiu, gdyż w produkcie pianowym uzyskano koncentrat miedzi, a w produkcie komorowym koncentrat ołowiu. Zatem, nieoczekiwane, minerały miedzi flotowały lepiej niż ołowiu, co oznacza, że depresji ulegały minerały ołowiu. Nie jest znana przyczyna niezgodności badań modelowych z badaniami z udziałem materiału technologicznego, ale prace dla jej wyjaśnienia są w toku.