

## Al(III) and Cu(II) simultaneous foam separation: Physicochemical problems

Bożenna Kawalec-Pietrenko\*, Piotr Rybarczyk

*Department of Chemical and Process Engineering, Chemical Faculty, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland*

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12 In the paper, simultaneous removal of Al(III) and Cu(II) from dilute aqueous solutions  
13 by ion and precipitate flotation methods is investigated. Influence of the pH of the initial  
14 solution, the surface active collector concentration and the gas flow rate on the final removal  
15 ratio and the course of ion and precipitate flotations is presented. The results show that  
16 simultaneous flotations of Al(OH)<sub>3</sub> and Cu(OH)<sub>2</sub> insoluble species occur allowing to achieve  
17 their almost complete removal in the pH range between 7 and 9. An increase of the surface  
18 active agent concentration causes a decrease of the final removal ratio as well as of the  
19 flotation rate constant. An increase of the gas flow rate results in an increase of ion and  
20 precipitate flotation rates.

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22 **Keywords:** aluminum, copper, ion flotation, precipitate flotation, removal ratio, rate constant

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### Introduction

26

27 Pollution of aquatic systems by metal ions, resulting from the increasing productivity  
28 of many industrial branches, seems to be a very serious problem from the ecological point of  
29 view (Fu & Wang, 2011). Aluminum and copper ions are present in wastewaters as the result  
30 of the production of brass and brass elements used in various production processes. High  
31 concentration of soluble copper species may cause weakness and liver damages, while

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\*Corresponding author, e-mail: [kawalec@chem.pg.gda.pl](mailto:kawalec@chem.pg.gda.pl)

32 pulmonary fibrosis and Alzheimer's disease occur in case of excessive aluminum intake  
33 (Ghazy & El-Morsy, 2008; Blais et al., 2008). Therefore, due to both health-related and  
34 economical reasons, effective elimination of metal ions from wastewater streams is necessary  
35 (Kurniawan et al., 2006).

36 Among different methods proposed for the treatment of industrial effluents polluted by  
37 metal ions, foam separation methods may be of importance (Zouboulis & Matis, 1987). These  
38 methods are based on the adsorption of surface active species from the solution at the gas–  
39 liquid interface. The most important feature of the above mentioned methods is their high  
40 effectiveness in the treatment of dilute solutions. Moreover ion and precipitate flotation  
41 methods seem to be attractive for the metal ions separation from large wastewater volumes of  
42 low concentration of ions (Filippov, 2000) because of the relatively low investment as well as  
43 exploitation costs.

44 Ion flotation involves the removal of surface active compounds generated between the  
45 metal ion (colligend) and the surface active ion of the surface active substance (collector). The  
46 product is adsorbed at the air bubble–liquid interface. Air bubbles rise up through the bubble  
47 layer into the foam created above the top liquid surface in a bubble column. The ion  
48 concentration in the foam condensate is distinctly higher than that in the aerated solution. Ion  
49 flotation of several metals is well described in literature. Kawalec-Pietrenko and Selecki  
50 (1984) studied the ion Cr(III) flotation, Jurkiewicz (1984) studied ion flotation of cadmium  
51 cations, Uribe-Salas et al. (2005) studied flotation of lead cations. Ion flotation of copper was  
52 investigated by Zhang et al. (2009). Zouboulis (1995) and Reyes et al. (2012) investigated  
53 silver ion flotation. Walkowiak (1991) observed a good agreement between the values of the  
54 ionic potential of metal cations and the selectivity sequence for the affinity of cations to  
55 anionic surfactants. Ehrampoush et al. (2011) studied cadmium ion flotation from effluent  
56 containing mixtures of Cd–Ca, Cd–Cu, Cd–Pb, and Cd–Zn and related the selectivity order  
57 between the metal ions and the anionic collector to the magnitude of the crystalline ion radius  
58 of the same charge. According to Charewicz et al. (1999), the ion flotation can be applied for  
59 selective separation of components from their mixture. However, the main disadvantage of the  
60 ion flotation method is the high collector consumption because of the requirement of its  
61 stoichiometric concentration in relation to the colligend concentration (Filippov, 2000).

62 Insoluble metal hydroxide particles create an insoluble surface active product as a  
63 result of electrostatic interactions between the surface charge of the precipitate and the  
64 oppositely charged functional group of the collector in the precipitate flotation process. The

65 formed aggregates are adsorbed at the gas–liquid interface of bubbles rising up through the  
66 bubble layer. The resultant charge of the aggregate is much lower than that due to the simple  
67 addition of each individual charge. Therefore, the amount of the collector required for the  
68 precipitate flotation is much smaller than that required for the ion flotation. Precipitate  
69 flotation of copper was studied, i.e., by Rubin & Johnson (1967). Kawalec-Pietrenko and  
70 Selecki (1984) studied the precipitate Cr(III) flotation. Ghazy and El-Morsy (2008) performed  
71 a comparative series of experiments in terms of aluminum and copper precipitate flotation.

72 Although foam separation of single metal ions has been intensively investigated for  
73 about forty years, only a few papers concern the ion and precipitate flotation of two or more  
74 ions simultaneously floated from the solution (Jurkiewicz, 2005). Therefore, the objective of  
75 the current work was to investigate the influence of the main process parameters, i.e. pH value  
76 of the initial solution, collector concentration, and gas flow rate on the effectiveness and the  
77 course of the simultaneously occurring Al(III) and Cu(II) flotations. According to the authors’  
78 knowledge, no paper dealing with the foam separation of the system containing a mixture of  
79 the above mentioned metal ions has been published.

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## Experimental

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84 The following chemical substances were used:  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  (Sigma–Aldrich,  
85 Steinheim, Germany),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (POCH, Gliwice, Poland),  $\text{H}_2\text{SO}_4$  (CHEMPUR, Piekary  
86 Śląskie, Poland), NaOH (STANLAB, Lublin, Poland), anionic collector, sodium  
87 dodecylsulfate (SDS; POCH, Gliwice, Poland), cationic collector, cetyl trimethylammonium  
88 bromide (CTAB; International Enzymes Limited, Windsor, UK).

89 Flotation experiments were carried out in a semibatch bubble column of 510 mm in  
90 height and 50 mm in internal diameter. Compressed air was supplied through a G-4 porous frit  
91 mounted at the bottom of the column. Air pressure and the compressed air flow rate were  
92 measured under the frit to recalculate the compressed air flow rate for actual atmospheric  
93 conditions. The foam was condensed in a foam container with a rotating horizontal Teflon  
94 plate and the volume of the foam condensate was measured. Samples of the actual liquid were  
95 taken from the axis of the column at the height of 250 mm above the air distributor. Flotation  
96 time was set to be equal to 60 min due to the constant concentration of Al(III) or Cu(II) in the  
97 liquid after the mentioned time.

98 Aqueous solutions of  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , respectively, were  
 99 prepared using distilled water. The pH value was adjusted by means of sulfuric acid or sodium  
 100 hydroxide solutions. Then, freshly prepared surfactant aqueous solution of an appropriate  
 101 collector, anionic or cationic, depending on the distribution of Al(III) and Cu(II) species,, was  
 102 added. The initial solution volume poured into the column was  $1 \text{ dm}^3$ . Then, air flow was  
 103 started. Experiments were carried out at the temperature of  $(20 \pm 1) \text{ }^\circ\text{C}$ . Two series of  
 104 experiments with equimolar initial concentrations of Al(III) and Cu(II) equal to  $1.5 \times 10^{-4} \text{ mol}$   
 105  $\text{dm}^{-3}$  and  $2 \times 10^{-3} \text{ mol dm}^{-3}$  were done. Each experiment was repeated three times.

106 Zeta potential measurements were performed using a Malvern ZetaSizer Nano ZS  
 107 (Malvern Instruments, UK). Samples containing metal hydroxides were prepared in a similar  
 108 way as those for the flotation experiments.

109 Concentrations of aluminum and copper in the temporary samples were determined  
 110 spectrophotometrically, using a HACH LANGE DR 5000 apparatus (HACH LANGE,  
 111 Düsseldorf, Germany). The Al(III) concentration was determined by the xylenol orange  
 112 method (Mochizuki & Kuroda, 1982). Cu(II) was determined using the cuprizone method  
 113 (Marczenko & Balcerzak, 1998).

114 Temporary removal ratio was described as follows:

115

$$116 \quad R = \frac{c_0 - c}{c_0} \quad (1)$$

117

118 where  $c_0$  and  $c$  are the Al(III) or Cu(II) concentrations in the initial solution and the temporary  
 119 ones in the solution during the flotation.

120 Effectiveness of the ion and precipitate flotations was discussed using the final  
 121 removal ratio after the above mentioned flotation time:

122

$$123 \quad R_\infty = \frac{c_0 - c_\infty}{c_0} \quad (2)$$

124

125 where  $c_\infty$  is the Al(III) or Cu(II) concentration in the solution when flotation is finished, i.e.  
 126 when the concentration did not change any more.

127 It was assumed that the courses of the Al(III) and Cu(II) ion and precipitate flotation  
 128 can be described by the following equation, which is analogous to the first-order reaction rate  
 129 equation:

130

$$131 \quad -\frac{dc}{dt} = k(c_t - c_\infty) \quad (3)$$

132

133 where  $k$  is the Al(III) or Cu(II) flotation rate constant and  $t$  is time.

134 Integration of Eq. (3):

135

$$136 \quad \int_{c_0}^{c_t} \frac{dc}{c - c_\infty} = -\int_0^t k dt \quad (4)$$

137

138 resulted in Eq. (5):

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$$140 \quad \ln \frac{c_t - c_\infty}{c_0 - c_\infty} = -kt \quad (5)$$

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142 Eq. (5) was used to determine the flotation rate constant using the least squares  
 143 method.

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## 146 Results and discussion

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### 149 *Effect of pH on the effectiveness and course of foam separation*

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151 Figs. 1 and 2 present the influence of the initial pH on the final removal ratio of the  
 152 foam separation processes. Experimental curves obtained for Al(III) and Cu(II) show the flat  
 153 final removal ratio maxima in the broad range of pH values. The results can be explained by  
 154 taking electrochemical data presented in Figs. 3a and 3c into account. At pH values lower than  
 155 4.0, the dominant species are Al(III) and Cu(II). Therefore, the ion flotation process using an  
 156 anionic collector is possible and low values of the final removal ratio are observed (Fig. 1),

157 because of the substoichiometric concentration of SDS with respect to the concentration of  
158 both ions. The Al(III) final removal increases when the pH value increases from 4.0 up to  
159 about 6.0 (Fig. 1). This is due to the precipitate flotation which progressively replaces the ion  
160 flotation as the pH increases (Fig. 3a).

161 It can be observed (Fig. 3c) that the  $\text{Cu(OH)}_2$  precipitate exists at pH values higher  
162 than 6.0. However, an increase of the Cu(II) final flotation recovery begins at the pH value  
163 higher than 5.5 (Fig. 1), which can be attributed to the adsorption of Cu(II) ions at the surface  
164 of the  $\text{Al(OH)}_3$  colloidal precipitate present in the solution at given conditions (Crawford et  
165 al., 1993). Maximum values of the final flotation recovery for both investigated metals were  
166 observed in the pH range between 7.0 and 8.5. It is the range of the precipitate flotation of  
167 micelles containing  $\text{Al(OH)}_3$  and  $\text{Cu(OH)}_2$  (Fig. 1).

168 The Al(III) removal decreases (Fig. 1) with the pH value increase above 8.5 due to the  
169 formation of more  $\text{Al(OH)}_4^-$  species (Fig. 3a). On the other hand, broad flat maxima of the  
170 Cu(II) final removal ratio are observed for the pH range between 7.5 and 11. This is in  
171 accordance with the pH region of insoluble  $\text{Cu(OH)}_2$  existence (Fig. 3c). At pH values above  
172 11.0, a decrease of the Cu(II) removal using anionic SDS was observed (Fig. 1), which can be  
173 explained by the change of the surface charge of micelles, containing mainly insoluble  
174  $\text{Cu(OH)}_2$  at the given conditions, from positive to negative (Grieves & Bhattacharyya, 1967).  
175 Only anionic species of Al and Cu, beside copper hydroxide, exist in the solution at pH values  
176 above 11.5. Thus, adsorption of  $\text{Al(OH)}_4^-$ ,  $\text{Cu(OH)}_3^-$ , and  $\text{Cu(OH)}_2^-$  forms is responsible for  
177 the negative surface charge of the named micelles. The above mentioned ionic species of Al  
178 and Cu hydrolysis, beside  $\text{H}^+$  and  $\text{OH}^-$ , are the potential determining ions and they play a  
179 crucial role during the adsorption of collector ions on metal hydroxides (Leja, 1982; Degen &  
180 Kosec, 2000). Thus, at pH values exceeding 11.5, ions of SDS are repulsed from the  
181 precipitate and the formation of hydrophobic agglomerates between the colligend and the  
182 anionic collector is impossible. It is in agreement with the pH values of the isoelectric point  
183 (IEP) of precipitates containing Al(III) and Cu(II) (Table 1).

184 It is well known that the electrical properties are very important from the point of view  
185 of the interfacial phenomena. In case of simultaneous Al(III) and Cu(II) precipitate flotation,  
186 the surface charge of flocks containing hydroxides of the mentioned metals can be evaluated  
187 by the observation of the zeta potential value variations with respect to the pH value. IEPs of  
188 freshly prepared precipitates of Al(III) and Cu(II) were noted at pH values of about 8.2 and



189 9.8, respectively. The obtained results agree well with the literature data regarding the IEPs of  
190 aluminum and copper hydroxides (Parks, 1965). IEP of a precipitate containing both Al(III)  
191 and Cu(II) was found to occur at pH of about 9.7. Huang et al. (1984) found the IEP of a flock  
192 containing  $\text{Co}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$  at the pH value of about 11.2. IEPs of  $\text{Co}(\text{OH})_2$  and  
193  $\text{Fe}(\text{OH})_3$  appear at the pH values of about 7 and 11.4, respectively (Parks, 1965). These results  
194 show a similar trend in the IEPs variation as our experimental results considering the  
195 influence of the agglomerate composition. However, it has to be noted that the pH value of the  
196 isoelectric point is influenced by the particular way of the precipitate formation (Leja, 1982).

197 An increase of the Cu(II) flotation recovery with cationic CTAB was observed (Fig. 1)  
198 at pH above 11.2. This phenomenon supports the above statement that the insoluble  $\text{Cu}(\text{OH})_2$   
199 attains a negative surface charge at the given alkaline conditions. Relatively low values of the  
200 Cu(II) final removal ratio ( $R < 0.5$ ) may be related with the dissolution of copper hydroxide at  
201 pH values higher than 12.0 (Fig. 3c). Extremely low values of the Al(III) removal, i.e.  $R <$   
202  $0.05$ , are caused by only dissolved forms of Al(III) being present in the solution, and therefore  
203 only ion flotation process can proceed. In such a case, at least the stoichiometric concentration  
204 of CTAB is necessary to achieve an almost total removal of aluminum.

205 Results presented in Fig. 2 concern the flotation when the Al and Cu concentration in  
206 the solution is one order of magnitude higher than that presented in Fig. 1. A large plateau of  
207 the maximum final removal ratio can be observed for both metals using the anionic SDS as a  
208 function of the pH value. The highest values of the Al(III) removal ratio were observed at pH  
209 between 5.0 and 9.5 and between 6.0 and 11.8 in case of Cu(II). These are the pH regions of  
210 the occurrence of insoluble  $\text{Al}(\text{OH})_3$  and  $\text{Cu}(\text{OH})_2$  (Fig. 3b and 3d). However, flotation  
211 removal using cationic CTAB is not observed at highly alkaline conditions. Anionic species  
212 predominate at pH above 11.5 in case of Al(III), and at pH above 13.6 in case of Cu(II) (Figs.  
213 3b and 3d). The negative charge of micelles containing mainly insoluble  $\text{Cu}(\text{OH})_2$  may not be  
214 sufficient at  $\text{pH} > 13$ . Additionally, because of the high hydration of the mentioned micelles at  
215 high pH values, the interactions with cationic CTAB may be hindered (Charewicz et al.,  
216 1999). Furthermore, low effectiveness of flotation with cationic CTAB at high pH values (i.e.,  
217  $\text{pH} > 12$ ) can probably be attributed to the chemical instability of the cationic collector at such  
218 conditions due to the changes of the collector dissociation or the possibility of the formation  
219 of floatable amines.

220 Results shown in Figs. 1 and 2 indicate not only an influence of the pH value on the  
221 final removal ratio of the flotation of Al(III) and Cu(II), but also the pH range for the possible

222 exclusive separation of Al(III) or Cu(II) from their mixture. The flat maxima of the Al(III) and  
223 Cu(II) final removal ratio are related to different solubility of their hydroxides in the given pH  
224 regions (Blais et al., 2008). Al(III) can be separated from the mixture at the pH values  
225 between 4.5–5.5 (Fig. 1) or at pH of about 5 (Fig. 2) depending on the initial concentration.  
226 Cu(II) is exclusively floated in the pH range of 10.0–11.0 (Fig. 1) and at pH of about 11.5  
227 (Fig. 2). Instead, separation using anionic SDS is possible for both Al(III) and Cu(II).

228 Influence of the pH value of the initial solution on the Al(III) and Cu(II) flotation rate  
229 constant is shown in Tables 2 and 3. Values of the rate constant were found as the slope of the  
230 straight line (Eq. (5)) in the semilogarithmic coordinate system  $\ln \frac{c_t - c_\infty}{c_0 - c_\infty} = f(t)$  using the

231 least squares method. The correlation coefficient values for the linear regression ranged from  
232 0.95 to 0.99 in all investigated cases. This justifies the assumption that the course of both the  
233 ion and the precipitate flotation can be described using an equation analogous to the first-order  
234 chemical reaction rate equation. The first-order kinetic model characterizing the named  
235 processes has also been applied by other researchers (Shakir & Samy, 1979; Kawalec-  
236 Pietrenko & Selecki, 1984; Stoica et al., 2003; Medina et al., 2005).

237 The influence of pH on the course of foam separation can be explained by examining  
238 the changes of the flotation rate constant for aluminum (Table 2). Al(III) is the predominant  
239 form at the pH value of 4.3. Thus, the process follows the mechanism of ion flotation and the  
240 value of the Al(III) rate constant is relatively low. The mechanism of the flotation process  
241 changes from ion to precipitate flotation when the pH value increases within the range of 4.0–  
242 5.0. Therefore, the flotation rate constant,  $k_{Al}$ , value increases. Similar explanation can be  
243 given for the increase of the Cu(II) flotation rate constant when pH changes from 4.8 to 8.0.  
244 Species adsorbing at the gas–liquid interface due to electrostatic interactions between the  
245 charged precipitate and ions of the surfactant are floated in the precipitation flotation process.  
246 Such species consisting of copper and aluminum hydroxide micelles include much more  
247 copper and aluminum atoms than it results from the stoichiometry of surface-active  
248 compounds formed in the ion flotation. Thus, Al(III) and Cu(II) flotation rate constants attain  
249 much higher values for the precipitate flotation than for ion flotation.

250 The highest values of the Al and Cu flotation rate constants were observed in the pH  
251 regions of the highest fraction of insoluble Al(OH)<sub>3</sub> and Cu(OH)<sub>2</sub>, i.e., their solubility is the  
252 lowest one (Blais et al., 2008). This corresponds to the pH regions of the maximum  
253 dependence of the final removal ratio on the pH value. An analysis of the results presented in



254 Table 2 indicates that at pH values between 6.0 and 8.4,  $k$  values for Cu(II) flotation as well as  
255 those for Al(III) flotation are similar. This may be due to the flotation of aggregates containing  
256 micelles of both Al(III) and Cu(II) hydroxides and molecules of anionic SDS. The  
257 phenomenon is supported by the fact that the formation of hydroxides is usually accompanied  
258 by coprecipitation or adsorption of metal hydroxides, which leads to the formation of a mixed  
259 precipitate (Blais et al., 2008).

260 Values of both Al(III) and Cu(II) flotation rate constant decrease (Table 2) at the pH  
261 values higher than 8.0, which can be attributed mainly to the increase of the  $\text{Al(OH)}_3$   
262 solubility and the formation of soluble anionic species of Al(III). Further increase of the pH  
263 value results in a decrease of the positive surface charge of the precipitate. Finally, transition  
264 proceeds to a negatively charged precipitate containing mainly insoluble Cu(II), which means  
265 that smaller number of SDS molecules is needed for the neutralization of the precipitate  
266 charge. Free SDS molecules compete with the colligend–collector product to occupy the gas–  
267 liquid interface decreasing thus the rate of the process. Similar discussion explains the results  
268 presented in Table 3.

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### 271 *Effect of collector concentration on the effectiveness and course of foam separation*

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273 Influence of the collector concentration on the ion and precipitate flotation was studied  
274 for Al(III) and Cu(II) at highly acidic conditions, i.e. pH = 3, and in moderate alkaline  
275 conditions, i.e. pH = 8–8.5. Such approach results from the possible applications of the  
276 investigated processes in the industry. Acidic aqueous solutions are generated, e.g., during  
277 washing of soils contaminated with metal ions (Wömmel & Calmano, 1992). On the other  
278 hand, finishing operations on metal alloys result typically in the formation of alkaline  
279 wastewaters (Bartkiewicz, 2007).

280 Ion flotation of Al(III) and Cu(II) is possible at pH = 3.0. At such conditions, Al(III)  
281 and Cu(II) ions are the dominant species. The maximum removal of both ions ( $R > 0.95$ ) is  
282 achieved for SDS concentrations exceeding  $0.75 \times 10^{-3} \text{ mol dm}^{-3}$  (Fig. 4), which is the  
283 stoichiometric concentration of the collector taking into account the sum of Al(III) and Cu(II)  
284 concentrations (Filippov, 2000). For SDS concentrations lower than  $0.5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  
285 exclusively Al(III) is removed from the solution. Such phenomenon suggests the competition  
286 between Al(III) and Cu(II) ions to create a compound with the collector. This assumption was

287 supported by an analysis of the ion flotation course (Fig. 5). During the first 20 min of the  
288 process, exclusively Al(III) is floated while the removal of Cu(II) is low. When the  
289 concentration of Al(III) decreases by about 75 % of the initial value, effective flotation of  
290 Cu(II) starts.

291 It is known that the affinity of metal cations towards anionic surfactants is higher for  
292 the cations characterized by a higher value of the Cartledge ionic potential (Walkowiak, 1991;  
293 Charewicz et al., 1999). The ionic potential is defined as a ratio of the cation net charge to its  
294 radius (elementary charge per Å) and the respective values of ionic potential for Al(III) and  
295 Cu(II) are 5.77 and 2.74 (Ibezim-Ezeani et al., 2012; Jensen, 2012). This is why Al(III) ion  
296 flotation prevails over Cu(II) flotation when substoichiometric concentrations of SDS are  
297 used.

298 Figs. 6 and 7 show the dependencies of the Al(III) and Cu(II) final removal ratios on  
299 the collector concentration at the precipitate flotation conditions. It can be seen that the SDS  
300 concentration required for high removal of both metals ( $R > 0.95$ ), is much lower than it  
301 results from the stoichiometry of the colligend–collector compounds formation in the ion  
302 flotation process. It is because ions of the collector neutralize the oppositely charged ions  
303 adsorbed at the micelle surface, i.e. insoluble metal hydroxides, in the precipitate flotation.  
304 The resultant micelle charge is distinctly lower than it results from a simple addition of  
305 individual charges. Therefore, the amount of the collector required for the precipitate flotation  
306 is much lower than that in the ion flotation.

307 Results (Figs. 6 and 7) show that above a certain collector concentration, the values of  
308 the colligend final removal ratio do not further increase. Therefore, application of a too high  
309 concentration of a surface active substance not only does not improve the separation  
310 efficiency, but it is economically and environmentally inappropriate. Moreover, an increase of  
311 the surfactant concentration causes a decrease of the rate of foam separation in the  
312 investigated parameter range (Tables 2 and 3). Such phenomenon can be explained by the  
313 competition of two kinds of surface-active species to occupy the limited space at the gas  
314 bubble–liquid interface at the SDS concentration exceeding the value (i.e.  $c_{\text{SDS}} > 0.16 \times 10^{-3}$   
315 mol dm<sup>-3</sup>, Fig. 7) necessary for effective precipitate flotation, they are agglomerates  
316 containing micelles of Al(III) and Cu(II) hydroxides with adsorbed SDS molecules and free  
317 SDS ions. The larger the excess of the collector, the larger fraction of the bubble surface is  
318 occupied by its ions (Kawalec-Pietrenko & Selecki, 1984) and, consequently, the possibility  
319 of the mentioned agglomerates adhesion to the bubble surface is lower. Additionally, the

320 adsorption of the second layer of SDS ions on the agglomerates by hydrophobic forces is  
321 possible. The SDS ions in the second layer are oriented with the polar ends towards the bulk  
322 solution. As the polar ends are hydrophilic, the precipitate containing Al(III) and Cu(II)  
323 becomes less floatable (Kawalec-Pietrenko & Selecki, 1984). This is why the values of Al(III)  
324 and Cu(II) flotation rate constant decrease with the increase of the collector concentration.  
325 Additionally, similar values of the  $k_{Al}$  and  $k_{Cu}$  constants for different SDS concentrations are  
326 in accordance with the previously formulated statement that at specified conditions (Tables 4  
327 and 5), Al(OH)<sub>3</sub> and Cu(OH)<sub>2</sub> co-exist as a mixed precipitate, and can undergo the precipitate  
328 flotation process.

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### 331 *Effect of gas velocity on the course of foam separation*

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333 It is known that at fixed process conditions, the flotation rate constant depends  
334 strongly on the gas–liquid interface formation (Rubin et al., 1966; Kawalec-Pietrenko &  
335 Selecki, 1984; Reyes et al., 2012), i.e. on the gas flow rate (Uribe-Salas et al., 2005). An  
336 increase of the gas flow rate results in an increase of the gas–liquid interfacial area.

337 As it is shown in Fig. 8, an increase of the gas velocity results in an increase of the  
338 flotation rate. Calculation results (Eq. 5) show that the flotation rate constant,  $k$ , is  
339 proportional to the gas velocity with the exponent value of about 0.76, both for Al(III) and  
340 Cu(II). The appropriate value of the exponent for the ion flotation ( $c_{0Al} = c_{0Cu} = 1.5 \times 10^{-4}$  mol  
341  $dm^{-3}$ ,  $c_{SDS} = 0.94 \times 10^{-3}$  mol  $dm^{-3}$ , pH = 3.0) is the same. This is in accordance with other  
342 published results regarding the kinetics of ion and precipitate flotation (Kawalec-Pietrenko &  
343 Selecki, 1984).

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## 346 **Conclusions**

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348 It was found that the pH value of the initial solution affects distinctly the effectiveness  
349 of the Al(III) and Cu(II) foam separation. The highest values of the final removal ratio were  
350 observed in the pH region of minimal solubility of Al(OH)<sub>3</sub> and Cu(OH)<sub>2</sub>, which corresponds  
351 with the course of the process with respect to the mechanism of the precipitate flotation.

352 For specified values of pH, selective flotation of Al(III) or Cu(II) from their mixture is  
353 possible.

354 Results of the kinetic studies show that the flotation rate constants for Al(III) and  
355 Cu(II) reach the highest value in the pH regions, where the precipitate flotation prevails.  
356 Additionally, values of the rate constant for both metals are similar, indicating that a mixed  
357 precipitate containing micelles of insoluble Al(III) and Cu(II) species undergoes the process of  
358 flotation.

359 During the ion flotation at acidic conditions, competition between Al(III) and Cu(II) to  
360 form compounds with the anionic collector was observed. Due to the higher value of the ionic  
361 potential for Al(III) compared to that for Cu(II), aluminum species are preferentially adsorbed  
362 at the gas–liquid interface.

363 The presented results indicate that the precipitate flotation, at the same gas velocity  
364 and the colligend and collector concentrations, is a much more effective as well as faster  
365 process than the ion flotation.

366 An increase of the collector concentration results in a decrease of the precipitate  
367 flotation rate constant and an increase of the gas flow rate results in an increase of the rates of  
368 the ion and precipitate flotation processes.

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### Symbols

372

373	$c$	temporary molar concentration of colligend	$\text{mol dm}^{-3}$
374	$c_0$	initial molar concentration of colligend	$\text{mol dm}^{-3}$
375	$c_\infty$	final molar concentration of colligend	$\text{mol dm}^{-3}$
376	$c_{\text{CTAB}}$	molar concentration of cetyl trimethylammonium bromide (CTAB)	$\text{mol dm}^{-3}$
377	$c_t$	molar concentration of colligend after flotation time $t$	$\text{mol dm}^{-3}$
378	$c_{\text{SDS}}$	molar concentration of sodium dodecylsulfate (SDS)	$\text{mol dm}^{-3}$
379	IEP	isoelectric point	
380	$k$	flotation rate constant	$\text{s}^{-1}$
381	pH	negative decimal logarithm of hydrogen ions concentration	
382	$R$	dimensionless temporary removal ratio	
383	$R_\infty$	dimensionless final removal ratio	
384	$s$	solid phase of $\text{Al(OH)}_3$ or $\text{Cu(OH)}_2$	

385	$t$	time of flotation	min
386	$u_G$	gas velocity	$\text{m s}^{-1}$

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390

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482





484 **Table 1.** Isoelectric points for aluminum hydroxide, copper hydroxide, and flocks containing  
 485 mixed Al(III) and Cu(II)

486

System	Al(OH) <sub>3</sub>	Cu(OH) <sub>2</sub>	Al(III) and Cu(II) flocks
pH of IEP	8.1–8.9 (Parks, 1965)	9.4 ± 0.4 (Parks, 1965)	9.7 (experimental)
	8.2 (experimental)	9.8 (experimental)	

487

488

489 **Table 2.** Influence of pH on the flotation rate constant:  $c_{0\text{Al}} = c_{0\text{Cu}} = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $c_{\text{SDS}}$   
 490  $= 1.25 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $u_{\text{G}} = 1.51 \times 10^{-3} \text{ m s}^{-1}$

491

pH	4.3	4.8	6.1	7.1	8.0	8.4	9.3	10.3
$k_{\text{Al}} \cdot 10^3/\text{s}^{-1}$	2.70	7.02	12.02	17.48	26.05	22.90	10.27	0.43
$k_{\text{Cu}} \cdot 10^3/\text{s}^{-1}$	0.24	1.28	0.70	16.10	25.27	23.05	18.28	13.53

492

493

494 **Table 3.** Influence of pH on the flotation rate constant:  $c_{0\text{Al}} = c_{0\text{Cu}} = 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $c_{\text{SDS}} =$   
 495  $1.56 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $u_G = 1.51 \times 10^{-3} \text{ m s}^{-1}$

496

pH	4.8	6.2	7.0	7.9	8.4	9.1	10.3	11.3
$k_{\text{Al}} \cdot 10^3/\text{s}^{-1}$	6.36	12.72	14.23	15.07	18.98	14.95	16.67	2.37
$k_{\text{Cu}} \cdot 10^3/\text{s}^{-1}$	5.02	11.88	13.87	15.27	21.68	15.65	13.43	8.45

497

498

499 **Table 4.** Influence of SDS concentration on the precipitate flotation rate constants:  $c_{0\text{Al}} = c_{0\text{Cu}}$   
 500  $= 1.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $u_G = 1.51 \times 10^{-3} \text{ m s}^{-1}$ ,  $\text{pH} = 8.0$

501

$C_{\text{SDS}} \cdot 10^3 / (\text{mol dm}^{-3})$	0.06	0.13	0.19	0.31	0.63
$k_{\text{Al}} \cdot 10^3 / \text{s}^{-1}$	33.55	26.05	26.70	15.60	13.23
$k_{\text{Cu}} \cdot 10^3 / \text{s}^{-1}$	31.53	25.27	18.08	14.87	13.88

502

503

504 **Table 5.** Influence of SDS concentration on the precipitate flotation rate constants:  $c_{0\text{Al}} = c_{0\text{Cu}}$   
 505  $= 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $u_G = 1.51 \times 10^{-3} \text{ m s}^{-1}$ ,  $\text{pH} = 8.4$

506

$C_{\text{SDS}} \cdot 10^3 / (\text{mol dm}^{-3})$	0.16	0.41	0.63	0.94	1.25
$k_{\text{Al}} \cdot 10^3 / \text{s}^{-1}$	18.97	10.47	8.22	6.70	5.82
$k_{\text{Cu}} \cdot 10^3 / \text{s}^{-1}$	17.18	10.58	8.72	6.72	6.25

507

508

## Figure captions

509

510

511 **Fig. 1.** Influence of the initial pH on the Al ( $\circ$ ,  $\times$ ) and Cu ( $\blacksquare$ ,  $+$ ) final removal ratio using SDS  
 512 ( $\circ$ ,  $\blacksquare$ ) and CTAB ( $\times$ ,  $+$ ).  $c_{0\text{Al}} = c_{0\text{Cu}} = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $c_{\text{SDS}} = 1.25 \times 10^{-4} \text{ mol dm}^{-3}$ ,  
 513  $c_{\text{CTAB}} = 1.10 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $u_{\text{G}} = 1.51 \times 10^{-3} \text{ m s}^{-1}$ .

514

515 **Fig. 2.** Influence of the initial pH on the Al ( $\circ$ ,  $\times$ ) and Cu ( $\blacksquare$ ,  $+$ ) final removal ratio using SDS  
 516 ( $\circ$ ,  $\blacksquare$ ) and CTAB ( $\times$ ,  $+$ ).  $c_{0\text{Al}} = c_{0\text{Cu}} = 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $c_{\text{SDS}} = 1.56 \times 10^{-4} \text{ mol dm}^{-3}$ ,  
 517  $c_{\text{CTAB}} = 1.65 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $u_{\text{G}} = 1.51 \times 10^{-3} \text{ m s}^{-1}$ .

518

519 **Fig. 3.** Dependencies of the Al(III) (a, b) and Cu(II) (c, d) forms on the pH value of the  
 520 aqueous solution (Puigdomenech, 2010). The relations are valid for simultaneous  
 521 presence of Al and Cu in an aqueous solution. Other than the shown forms of Al(III)  
 522 and Cu(II) are not presented because of their negligible concentration:  $c_{0\text{Al}} = c_{0\text{Cu}} = 1.5$   
 523  $\times 10^{-4} \text{ mol dm}^{-3}$  (a, c) and  $c_{0\text{Al}} = c_{0\text{Cu}} = 2 \times 10^{-3} \text{ mol dm}^{-3}$  (b, d).

524

525 **Fig. 4.** Influence of SDS concentration on the Al ( $\bullet$ ) and Cu ( $\square$ ) final removal ratio:  $c_{0\text{Al}} =$   
 526  $c_{0\text{Cu}} = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $u_{\text{G}} = 1.51 \times 10^{-3} \text{ m s}^{-1}$ ,  $\text{pH} = 3.0$ .

527

528 **Fig. 5.** Changes of the Al ( $\bullet$ ) and Cu ( $\square$ ) removal ratio with the flotation time:  $c_{0\text{Al}} = c_{0\text{Cu}} =$   
 529  $1.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $u_{\text{G}} = 1.51 \times 10^{-3} \text{ m s}^{-1}$ ,  $c_{\text{SDS}} = 0.940 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{pH} = 3.0$ .

530

531 **Fig. 6.** Influence of SDS concentration on the Al ( $\bullet$ ) and Cu ( $\square$ ) final removal ratio:  $c_{0\text{Al}} =$   
 532  $c_{0\text{Cu}} = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $u_{\text{G}} = 1.51 \times 10^{-3} \text{ m s}^{-1}$ ,  $\text{pH} = 8.0$ .

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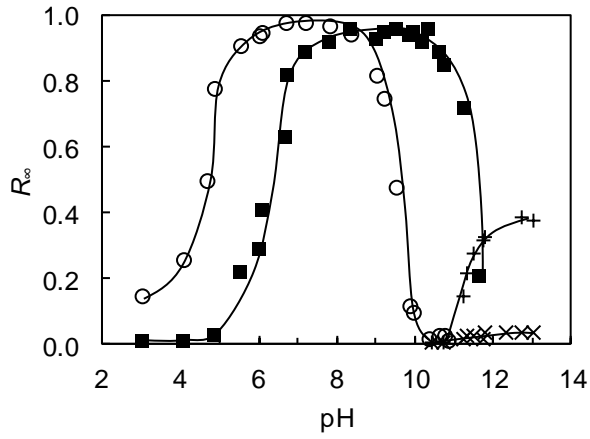
534 **Fig. 7.** Influence of SDS concentration on Al ( $\bullet$ ) and Cu ( $\square$ ) final removal ratio:  $c_{0\text{Al}} = c_{0\text{Cu}} =$   
 535  $2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $u_{\text{G}} = 1.51 \times 10^{-3} \text{ m s}^{-1}$ ,  $\text{pH} = 8.4$ .

536

537 **Fig. 8.** Influence of the air flow rate on the Al ( $\circ$ ) and Cu ( $\times$ ) flotation rate constant during the  
 538 foam separation:  $c_{0\text{Al}} = c_{0\text{Cu}} = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $c_{\text{SDS}} = 0.94 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{pH} =$   
 539  $8.0$ .

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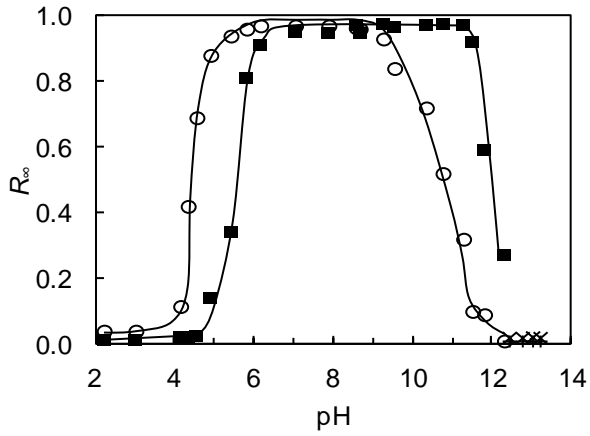
543 **Fig. 1.** Influence of the initial pH on the Al (○, ×) and Cu (■, +) final removal ratio using SDS

544 (○, ■) and CTAB (×, +).  $c_{0Al} = c_{0Cu} = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $c_{SDS} = 1.25 \times 10^{-4} \text{ mol dm}^{-3}$ ,

545  $c_{CTAB} = 1.10 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $u_G = 1.51 \times 10^{-3} \text{ m s}^{-1}$ .

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548

549 **Fig. 2.** Influence of the initial pH on the Al (○, ×) and Cu (■, +) final removal ratio using SDS

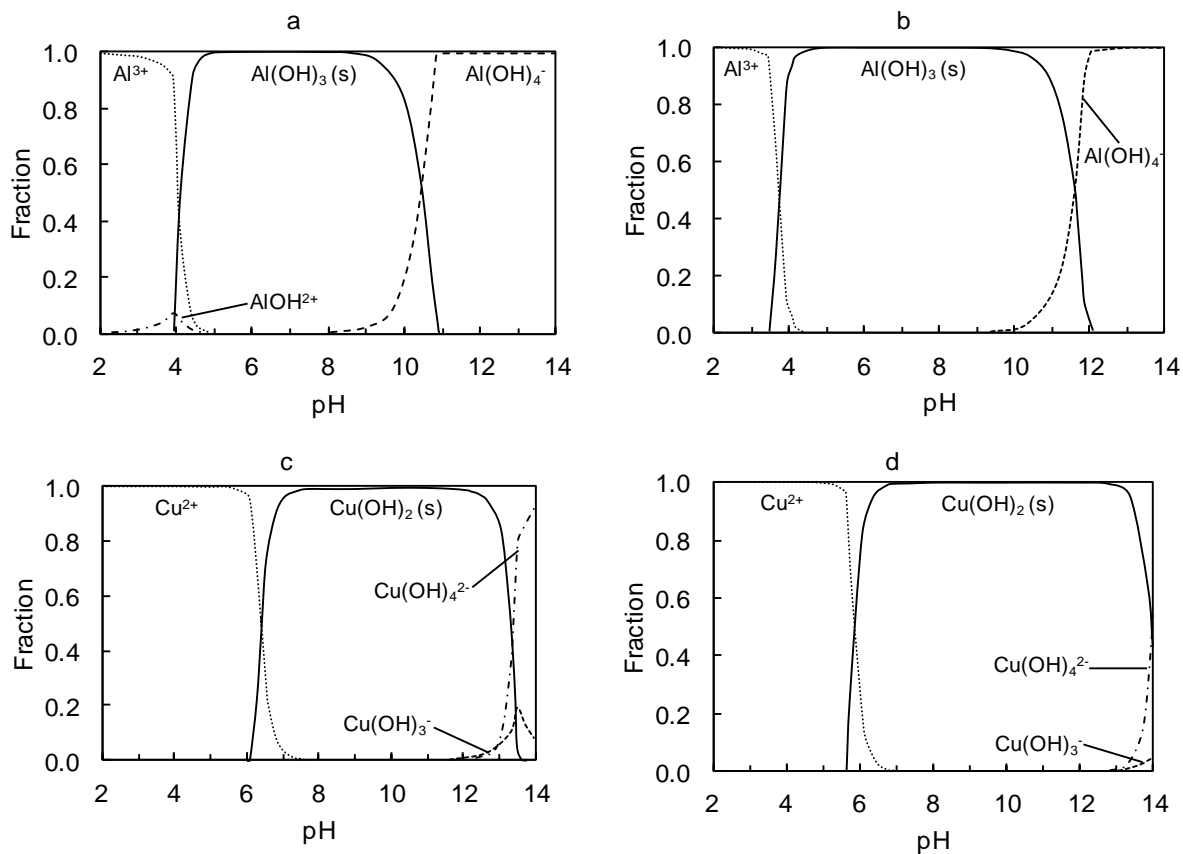
550 (○, ■) and CTAB (×, +).  $c_{0\text{Al}} = c_{0\text{Cu}} = 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $c_{\text{SDS}} = 1.56 \times 10^{-4} \text{ mol dm}^{-3}$ ,

551  $c_{\text{CTAB}} = 1.65 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $u_{\text{G}} = 1.51 \times 10^{-3} \text{ m s}^{-1}$ .

552

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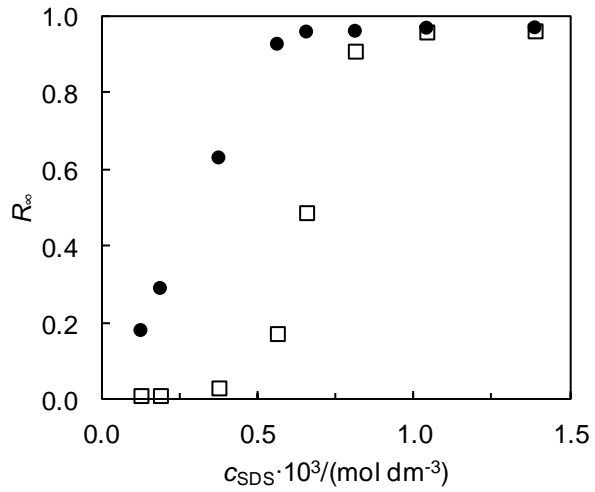


554

555 **Fig. 3.** Dependencies of the Al(III) (a, b) and Cu(II) (c, d) forms on the pH value of the  
 556 aqueous solution (Puigdomenech, 2010). The relations are valid for simultaneous  
 557 presence of Al and Cu in an aqueous solution. Other than the shown forms of Al(III)  
 558 and Cu(II) are not presented because of their negligible concentration:  $c_{0\text{Al}} = c_{0\text{Cu}} = 1.5$   
 559  $\times 10^{-4} \text{ mol dm}^{-3}$  (a, c) and  $c_{0\text{Al}} = c_{0\text{Cu}} = 2 \times 10^{-3} \text{ mol dm}^{-3}$  (b, d).

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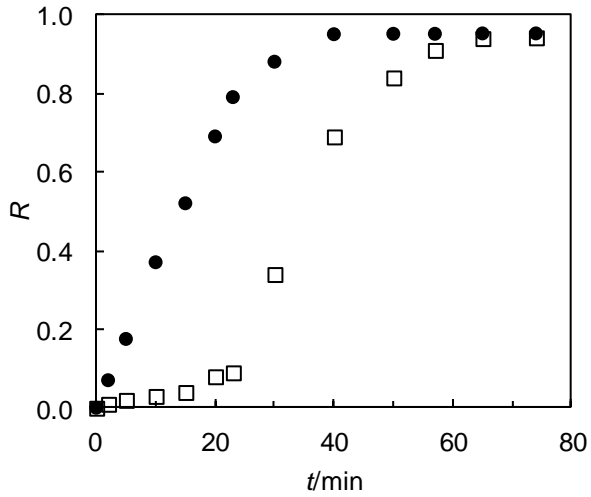


562

563 **Fig. 4.** Influence of SDS concentration on the Al (●) and Cu (□) final removal ratio:  $c_{0\text{Al}} =$   
 564  $c_{0\text{Cu}} = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $u_G = 1.51 \times 10^{-3} \text{ m s}^{-1}$ ,  $\text{pH} = 3.0$ .

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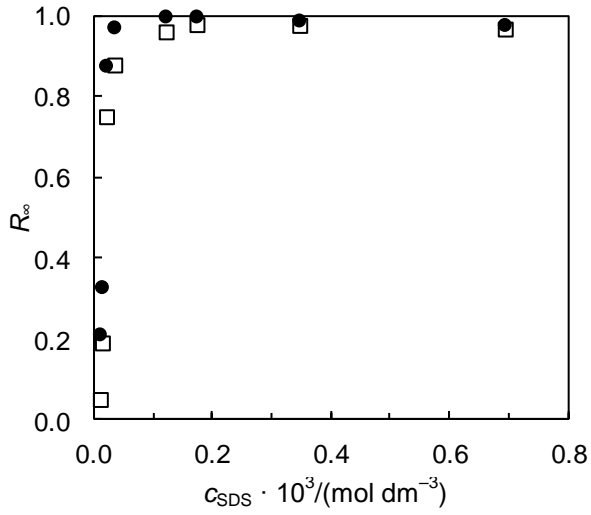


567

568 **Fig. 5.** Changes of the Al (●) and Cu (□) removal ratio with the flotation time:  $c_{0\text{Al}} = c_{0\text{Cu}} =$   
 569  $1.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $u_G = 1.51 \times 10^{-3} \text{ m s}^{-1}$ ,  $c_{\text{SDS}} = 0.940 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{pH} = 3.0$ .

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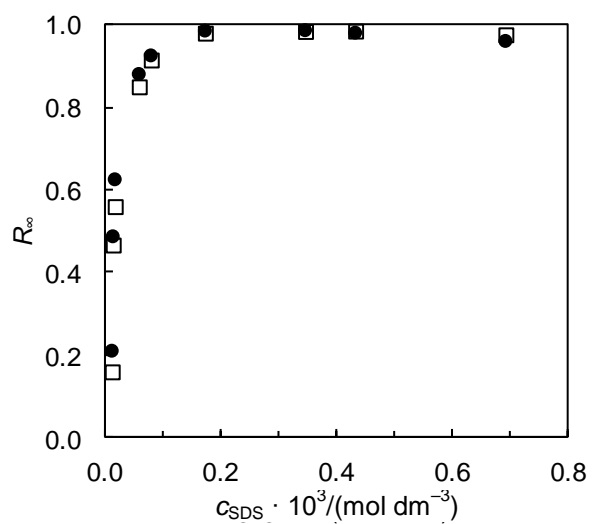


572

573 **Fig. 6.** Influence of SDS concentration on the Al (●) and Cu (□) final removal ratio:  $c_{0\text{Al}} =$   
 574  $c_{0\text{Cu}} = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $u_G = 1.51 \times 10^{-3} \text{ m s}^{-1}$ ,  $\text{pH} = 8.0$ .

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576

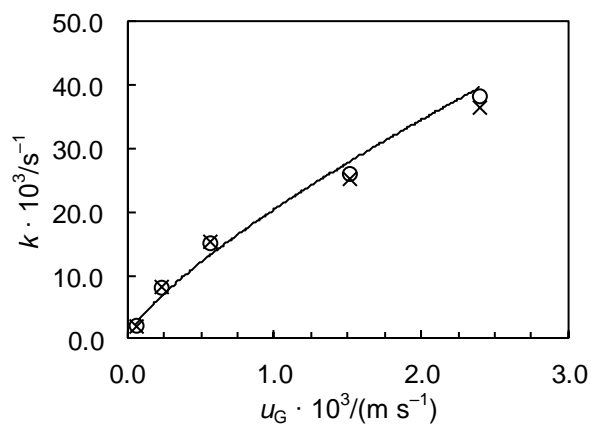


577

578 **Fig. 7.** Influence of SDS concentration on Al (●) and Cu (□) final removal ratio:  $c_{0\text{Al}} = c_{0\text{Cu}} =$   
 579  $2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $u_G = 1.51 \times 10^{-3} \text{ m s}^{-1}$ , pH = 8.4.

580

581



582

583 **Fig. 8.** Influence of the air flow rate on the Al ( $\circ$ ) and Cu ( $\times$ ) flotation rate constant during the  
584 foam separation:  $c_{0\text{Al}} = c_{0\text{Cu}} = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $c_{\text{SDS}} = 0.94 \times 10^{-3} \text{ mol dm}^{-3}$ , pH =  
585 8.0.

586