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

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In the paper, simultaneous removal of Al(III) and Cu(II) from dilute aqueous solutions by ion and precipitate flotation methods is investigated. Influence of the pH of the initial solution, the surface active collector concentration and the gas flow rate on the final removal ratio and the course of ion and precipitate flotations is presented. The results show that simultaneous flotations of $Al(OH)_3$ and $Cu(OH)_2$ insoluble species occur allowing to achieve their almost complete removal in the pH range between 7 and 9. An increase of the surface active agent concentration causes a decrease of the final removal ratio as well as of the flotation rate constant. An increase of the gas flow rate results in an increase of ion and precipitate flotation rates.

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

Introduction

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

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

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

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

Insoluble metal hydroxide particles create an insoluble surface active product as a result of electrostatic interactions between the surface charge of the precipitate and the oppositely charged functional group of the collector in the precipitate flotation process. The formed aggregates are adsorbed at the gas–liquid interface of bubbles rising up through the bubble layer. The resultant charge of the aggregate is much lower than that due to the simple addition of each individual charge. Therefore, the amount of the collector required for the precipitate flotation is much smaller than that required for the ion flotation. Precipitate flotation of copper was studied, i.e., by Rubin & Johnson (1967). Kawalec-Pietrenko and Selecki (1984) studied the precipitate Cr(III) flotation. Ghazy and El-Morsy (2008) performed a comparative series of experiments in terms of aluminum and copper precipitate flotation.

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

Experimental

The following chemical substances were used: $Al_2(SO_4)_3 \cdot 16H_2O$ (Sigma–Aldrich, Steinheim, Germany), $CuSO_4 \cdot 5H_2O$ (POCH, Gliwice, Poland), H_2SO_4 (CHEMPUR, Piekary Śląskie, Poland), NaOH (STANLAB, Lublin, Poland), anionic collector, sodium dodecylsulfate (SDS; POCH, Gliwice, Poland), cationic collector, cetyl trimethylammonium bromide (CTAB; International Enzymes Limited, Windsor, UK).

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

Aqueous solutions of $Al_2(SO_4)_3 \cdot 16H_2O$ and $CuSO_4 \cdot 5H_2O$, respectively, were prepared using distilled water. The pH value was adjusted by means of sulfuric acid or sodium hydroxide solutions. Then, freshly prepared surfactant aqueous solution of an appropriate collector, anionic or cationic, depending on the distribution of Al(III) and Cu(II) species,, was added. The initial solution volume poured into the column was 1 dm^3. Then, air flow was started. Experiments were carried out at the temperature of (20 ± 1) °C. Two series of experiments with equimolar initial concentrations of Al(III) and Cu(II) equal to 1.5×10^{-4} mol dm^{-3} and 2×10^{-3} mol dm^{-3} were done. Each experiment was repeated three times.

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

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

Temporary removal ratio was described as follows:

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

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

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

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

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

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

$$-\frac{\mathrm{d}\,c}{\mathrm{d}\,t} = k\left(c_t - c_\infty\right) \qquad (3)$$

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

Integration of Eq. (3):

$$\int_{c_0}^{c_t} \frac{\mathrm{d}c}{c - c_\infty} = -\int_0^t k\mathrm{d}t \qquad (4)$$

resulted in Eq. (5):

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

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

Results and discussion

Effect of pH on the effectiveness and course of foam separation

Figs. 1 and 2 present the influence of the initial pH on the final removal ratio of the foam separation processes. Experimental curves obtained for Al(III) and Cu(II) show the flat final removal ratio maxima in the broad range of pH values. The results can be explained by taking electrochemical data presented in Figs. 3a and 3c into account. At pH values lower than 4.0, the dominant species are Al(III) and Cu(II). Therefore, the ion flotation process using an anionic collector is possible and low values of the final removal ratio are observed (Fig. 1), because of the substoichiometric concentration of SDS with respect to the concentration of both ions. The Al(III) final removal increases when the pH value increases from 4.0 up to about 6.0 (Fig. 1). This is due to the precipitate flotation which progressively replaces the ion flotation as the pH increases (Fig. 3a).

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

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

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

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

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

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

Results shown in Figs. 1 and 2 indicate not only an influence of the pH value on the final removal ratio of the flotation of Al(III) and Cu(II), but also the pH range for the possible exclusive separation of Al(III) or Cu(II) from their mixture. The flat maxima of the Al(III) and Cu(II) final removal ratio are related to different solubility of their hydroxides in the given pH regions (Blais et al., 2008). Al(III) can be separated from the mixture at the pH values between 4.5–5.5 (Fig. 1) or at pH of about 5 (Fig. 2) depending on the initial concentration. Cu(II) is exclusively floated in the pH range of 10.0–11.0 (Fig. 1) and at pH of about 11.5 (Fig. 2). Instead, separation using anionic SDS is possible for both Al(III) and Cu(II).

Influence of the pH value of the initial solution on the Al(III) and Cu(II) flotation rate constant is shown in Tables 2 and 3. Values of the rate constant were found as the slope of the straight line (Eq. (5)) in the semilogarithmic coordinate system $\ln \frac{c_t - c_\infty}{c_0 - c_\infty} = f(t)$ using the least squares method. The correlation coefficient values for the linear regression ranged from 0.95 to 0.99 in all investigated cases. This justifies the assumption that the course of both the ion and the precipitate flotation can be described using an equation analogous to the first-order chemical reaction rate equation. The first-order kinetic model characterizing the named processes has also been applied by other researchers (Shakir & Samy, 1979; Kawalec-Pietrenko & Selecki, 1984; Stoica et al., 2003; Medina et al., 2005).

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

The highest values of the Al and Cu flotation rate constants were observed in the pH regions of the highest fraction of insoluble $Al(OH)_3$ and $Cu(OH)_2$, i.e., their solubility is the lowest one (Blais et al., 2008). This corresponds to the pH regions of the maximum dependence of the final removal ratio on the pH value. An analysis of the results presented in

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

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

Effect of collector concentration on the effectiveness and course of foam separation

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

Ion flotation of Al(III) and Cu(II) is possible at pH = 3.0. At such conditions, Al(III) and Cu(II) ions are the dominant species. The maximum removal of both ions ($R > 0.95$) is achieved for SDS concentrations exceeding 0.75×10^{-3} mol dm^{-3} (Fig. 4), which is the stoichiometric concentration of the collector taking into account the sum of Al(III) and Cu(II) concentrations (Filippov, 2000). For SDS concentrations lower than 0.5×10^{-3} mol dm^{-3}, exclusively Al(III) is removed from the solution. Such phenomenon suggests the competition between Al(III) and Cu(II) ions to create a compound with the collector. This assumption was supported by an analysis of the ion flotation course (Fig. 5). During the first 20 min of the process, exclusively Al(III) is floated while the removal of Cu(II) is low. When the concentration of Al(III) decreases by about 75 % of the initial value, effective flotation of Cu(II) starts.

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

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

Results (Figs. 6 and 7) show that above a certain collector concentration, the values of the colligend final removal ratio do not further increase. Therefore, application of a too high concentration of a surface active substance not only does not improve the separation efficiency, but it is economically and environmentally inappropriate. Moreover, an increase of the surfactant concentration causes a decrease of the rate of foam separation in the investigated parameter range (Tables 2 and 3). Such phenomenon can be explained by the competition of two kinds of surface-active species to occupy the limited space at the gas bubble–liquid interface at the SDS concentration exceeding the value (i.e. $c_{\mathrm{SDS}} > 0.16 \times 10^{-3}$ mol dm^{-3}, Fig. 7) necessary for effective precipitate flotation, they are agglomerates containing micelles of Al(III) and Cu(II) hydroxides with adsorbed SDS molecules and free SDS ions. The larger the excess of the collector, the larger fraction of the bubble surface is occupied by its ions (Kawalec-Pietrenko & Selecki, 1984) and, consequently, the possibility of the mentioned agglomerates adhesion to the bubble surface is lower. Additionally, the adsorption of the second layer of SDS ions on the agglomerates by hydrophobic forces is possible. The SDS ions in the second layer are oriented with the polar ends towards the bulk solution. As the polar ends are hydrophilic, the precipitate containing Al(III) and Cu(II) becomes less floatable (Kawalec-Pietrenko & Selecki, 1984). This is why the values of Al(III) and Cu(II) flotation rate constant decrease with the increase of the collector concentration. Additionally, similar values of the k_{Al} and k_{Cu} constants for different SDS concentrations are in accordance with the previously formulated statement that at specified conditions (Tables 4 and 5), $Al(OH)_3$ and $Cu(OH)_2$ co-exist as a mixed precipitate, and can undergo the precipitate flotation process.

Effect of gas velocity on the course of foam separation

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

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

Conclusions

It was found that the pH value of the initial solution affects distinctly the effectiveness of the Al(III) and Cu(II) foam separation. The highest values of the final removal ratio were observed in the pH region of minimal solubility of $Al(OH)_3$ and $Cu(OH)_2$, which corresponds with the course of the process with respect to the mechanism of the precipitate flotation.

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

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

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

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

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

Symbols

c	temporary molar concentration of colligend	mol dm^{-3}
c_0	initial molar concentration of colligend	mol dm^{-3}
c_∞	final molar concentration of colligend	mol dm^{-3}
c_{CTAB}	molar concentration of cetyl trimethylammonium bromide (CTAB)	mol dm^{-3}
c_{t}	molar concentration of colligend after flotation time t	mol dm^{-3}
c_{SDS}	molar concentration of sodium dodecylsulfate (SDS)	mol dm^{-3}
IEP	isoelectric point	
k	flotation rate constant	s^{-1}
pH	negative decimal logarithm of hydrogen ions concentration	
R	dimensionless temporary removal ratio	
R_∞	dimensionless final removal ratio	
s	solid phase of $Al(OH)_3$ or $Cu(OH)_2$	

t	time of flotation	min
u_G	gas velocity	m s^{-1}

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

System	$Al(OH)_3$	$Cu(OH)_2$	Al(III) and Cu(II) flocks
pH of IEP	8.1–8.9 (Parks, 1965) 8.2 (experimental)	9.4 ± 0.4 (Parks, 1965) 9.8 (experimental)	9.7 (experimental)

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

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

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

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

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

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

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

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

Figure captions

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

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

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

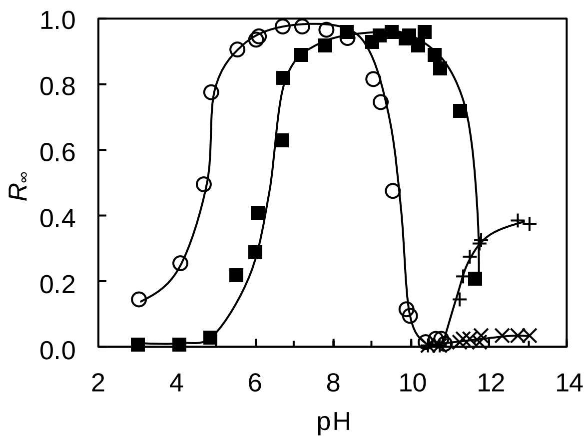
Fig. 4. Influence of SDS concentration on the Al (●) and Cu (□) final removal ratio: $c_{0\mathrm{Al}} = c_{0\mathrm{Cu}} = 1.5 \times 10^{-4}$ mol dm^{-3}, $u_{\mathrm{G}} = 1.51 \times 10^{-3}$ m s^{-1}, pH = 3.0.

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

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

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

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



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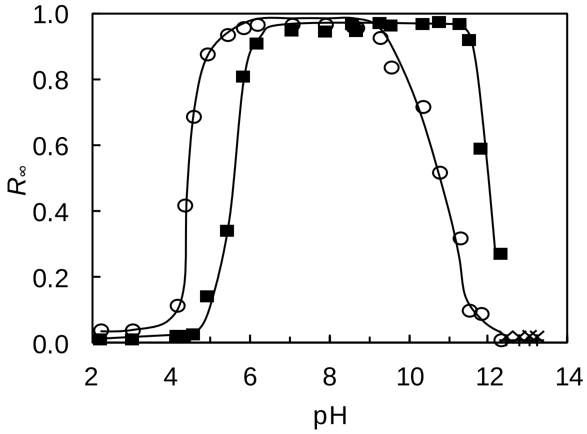

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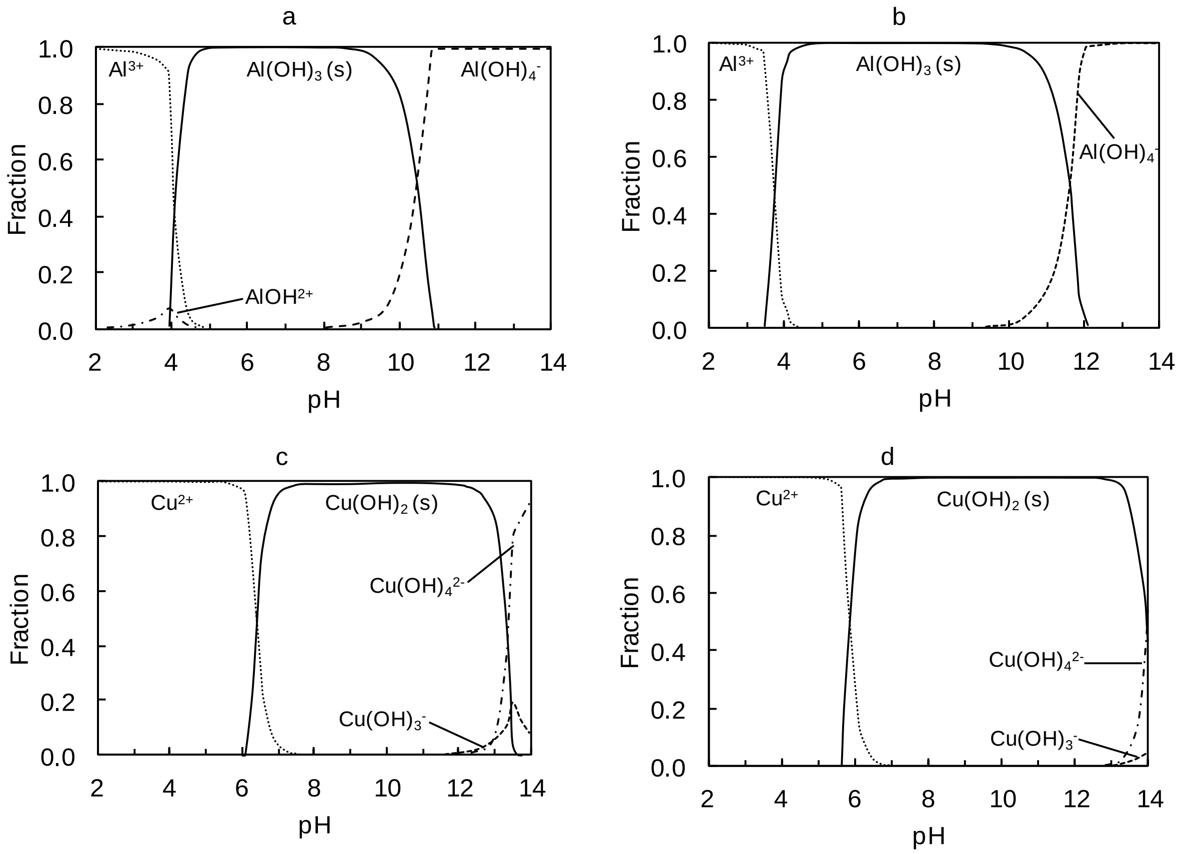

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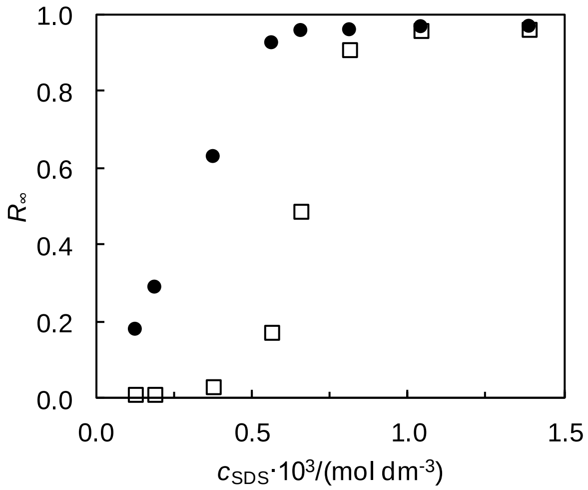

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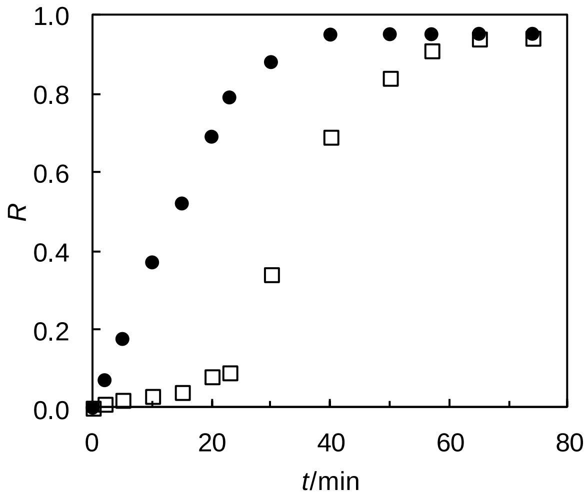


Fig. 5. Changes of the Al (●) and Cu (□) removal ratio with the flotation time: $c_{0\mathrm{Al}} = c_{0\mathrm{Cu}} = 1.5 \times 10^{-4}$ mol dm^{-3}, $u_\mathrm{G} = 1.51 \times 10^{-3}$ m s^{-1}, $c_\mathrm{SDS} = 0.940 \times 10^{-3}$ mol dm^{-3}, pH = 3.0.

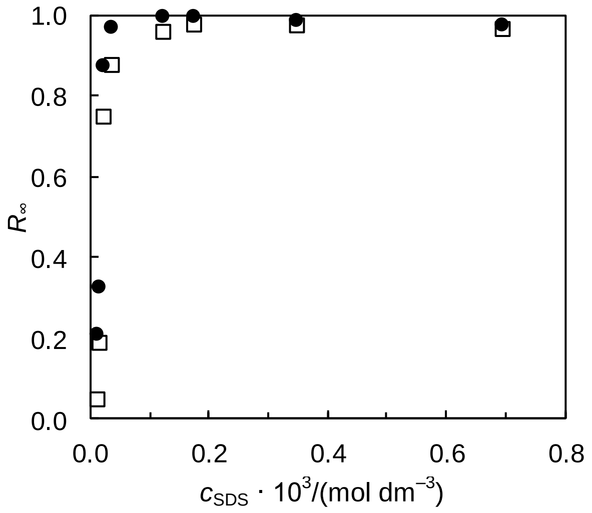


Fig. 6. Influence of SDS concentration on the Al (●) and Cu (□) final removal ratio: $c_{0\mathrm{Al}}$ = $c_{0\mathrm{Cu}} = 1.5 \times 10^{-4}$ mol dm^{-3}, $u_G = 1.51 \times 10^{-3}$ m s^{-1}, pH = 8.0.

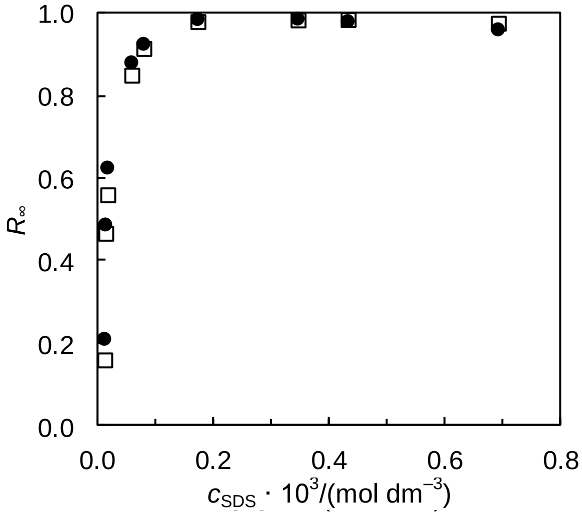
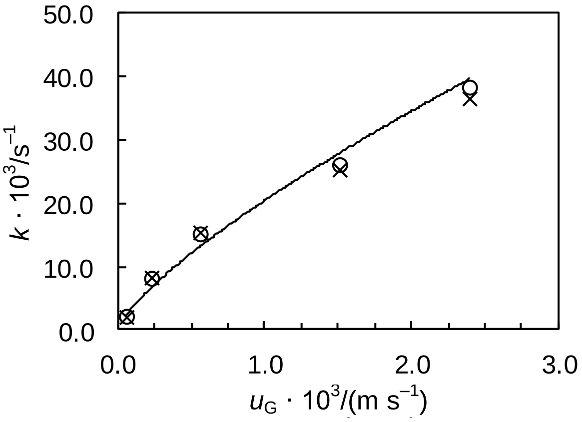


Fig. 7. Influence of SDS concentration on Al (●) and Cu (□) final removal ratio: $c_{0\mathrm{Al}} = c_{0\mathrm{Cu}} = 2 \times 10^{-3}$ mol dm^{-3}, $u_G = 1.51 \times 10^{-3}$ m s^{-1}, pH = 8.4.



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