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PRECIPITATE FLOTATION OF COPPER (II), NICKEL (II), AND OTHER METAL CATIONS FROM COPPER INDUSTRY WASTEWATERS

Results of the comparative study on precipitate flotation process of the copper industry wastewaters, applying both glass column technique and a flotation machine, as well as those of sedimentation process have proven that precipitate flotation process is highly effective in removal of metals in the form of hydroxides, carbonates, and sulphides, resulting both in higher metal recoveries and slugde volume reduction ratios, except for removal of sulphides from acidic solutions. To improve the wastewater treatment efficiency and cut down the process duration time and the treatment costs, the application of lime and anionic surfactants is recommended in the precipitate flotation. Surfactant and metal recovery techniques from the concentrated sludges have been also described.

1. INTRODUCTION

This is a common practice that copper industry acidic wastewaters are neutralized with lime milk. It eliminates their acidity but results in the irreclaimable lose of metals. Thus, the investigations on physicochemical processes of metal recovery from copper industry wastewaters are of significant importance. The scale of the problem implies a simple and intensive unit operations and application of a simple equipment.

The principle of precipitate flotation, first described by Baarson and Ray [1], consists in the introduction of dispersed gas bubbles into bulk solution containing a suspension of precipitate of ionic species and chosen surfactant. Due to interaction between surfactant and precipitate particles, the latter are attached to gas bubble surface and, consequently, concentrated in the resulting foam layer. The electric charge of surfactant ion determines its activity with respect to the precipitate particles possessing the opposite surface charge [7]. The nature of surfactant—precipitate particle interaction explains the fact that the precipitate flotation process may be effective at a much lower molar surfactant concentrations than the initial total molar concentration of species to be floated. The molar ratio of surfactant to precipitated species reaches 0.01 and less [4]. A substan-

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tial differences in process kinetics were found between the ion flotation and precipitate flotation. The rate of the latter process is usually much higher [5].

For the precipitate flotation process the optimum initial metal ions concentration in feed solution ranges from 0.01 to 5.0 kg/m^3, the process rate being direct proportional to the concentration. The hydroxides, carbonates, and lime milk are usually used as precipitants for metal ionic species. The precipitation process may be controlled by the acidity of the feed solution, especially for metals which form hydroxides at definite pH values. Main advantages of the precipitate flotation are the high process rate, selectivity, and low surfactant consumption. The latter can be substantially reduced by processing of resultant concentrate for the surfactant recovery and reuse [3].

Settling — an alternative unit operation for separation of solid phase from the aqueous suspension — may be inconvenient, especially when large volume of feed stream is to be processed. This is mainly because of large capacity of clarifiers, usually long retention time and necessity of processing and drying the resultant precipitate. The overflow rate is determined by the installation capacity. Although addition of coagulants accelerates the settling, their irreclaimable consumption makes the process expensive for processing large volumes of diluted aqueous suspension. These inconveniences become much more important when fine aqueous suspensions like metal hydroxides, carbonates or sulphides are to be treated.

Thus, it may be assumed that precipitate flotation may allow the recovery of copper, nickel, and other metals from acidic copper wastewaters. The above assumption is to be proved in the present work.

2. EXPERIMENTAL PROCEDURE

The following model feed solution was applied in the lab. experiments: Cu^{2+} — 159 g/m^3, Ni^{2+} — 21.6 g/m^3, Ca^{2+} — 101 g/m^3, Mg^{2+} — 28 g/m^3, Fe^{3+} — 7.0 g/m^3, Zn^{2+} — 2.1 g/m^3, and H_2SO_4 — 73.5 g/m^3. This composition was evaluated based on real copper smelter's wastewaters. The following commercial anionic surfactants were used in the flotation process: monoalkyl sodium sulphonate of C_{15} average carbon chain (Mersolan E-30), potassium oleate (Lawon MC), and technical grade dodecylbenzene sodium sulphonate (Deterlon A). Lauroseptol, a technical quaternary ammonium salt, was used as a cationic surfactant.

The glass laboratory flotation column of the capacity of 0.26 dm^3 (fig. 1) was filled with 0.170 dm^3 of feed solution, then the adequate amount of precipitant was introduced. Finally, water was added up to final volume equal to 0.200 dm^3. The nitrogen bubbles were introduced through the porous glass diffuser. The gas flow rate was kept constant and equal to 18 cm^3/min. The time of each flotation run was constant and equal to 5 min.

Recovery of metals was calculated, taking account of the metal content in residual and feed solutions analized by Atomic Absorption Spectrometry (Perkin Elmer Model

403). Volume reduction ratio was calculated as volumetric ratio of feed solution to wet flotating concentrate.

Some experiments were also done using a laboratory flotation machine (Mekhanobr type) of cell volume 1.0 dm^3 with mechanical stirrer. Laboratory sedimentation tests were conducted in standard Imhoff's funnels for the period 24 hours.

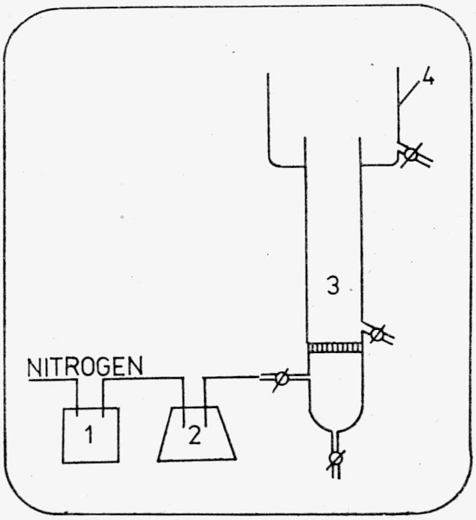

Fig. 1. Glass laboratory flotation column

1 — gas flow and pressure regulator, *2* — humidifier, *3* — flotation column, *4* — foam receiver

Rys. 1. Szklana kolumna flotacyjna

1 — człon regulujący przepływ gazu i ciśnienie, *2* — nawilżacz, *3* — kolumna flotacyjna, *4* — odbiornik piany

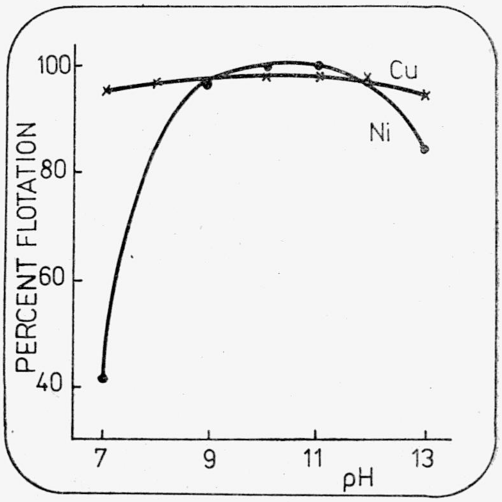

Fig. 2. Recovery of copper and nickel hydroxides at various pH values. Surfactant — Lawon MC — 2×10^{-4} M

Rys. 2. Odzysk wodorotlenku miedzi i niklu przy różnych wartościach pH. Surfaktant — Lawon MC — 2×10^{-4} M

3. FLOTATION OF HYDROXIDE PRECIPITATES

Metal hydroxides were precipitated from feed solution in the flotation column by sodium hydroxide and the resulting suspension was floated with the anionic surfactant (Lawon MC) at various pH values (fig. 2). As it follows from the data in fig. 2, almost total recovery of copper is achieved at pH values not lower than 7.0, whereas over 95% of nickel is floated at pH between 9.0 and 12. From the data, which are not presented in fig. 2, it follows that at pH above 9, 98% of iron, 95% of zinc, and only 6% of calcium and 28% of magnesium are removed. Recovery of copper and nickel hydroxides decreases when pH exceeds 12.0, at pH equal to 13.0 it reaches 94% and 82%, respectively. The volume reduction ratio was the highest (33) at the lowest pH of 7.0.

The limiting pH values for 90% metal hydroxide precipitation can be calculated from reference [6]. These pH limits are 6.45, 8.87, and 8.99 for $Cu(OH)_2$, $Ni(OH)_2$, and $Zn(OH)_2$, respectively. Precipitation of $Ca(OH)_2$ and $Mg(OH)_2$ begins at pH 12.78 and 10.69, respectively.

An other anionic surfactant, Mersolan E-30, was also found to be highly effective for flotation of copper and nickel hydroxides. At pH 9.0 and surfactant concentration of 2×10^{-4} M, 99.7% of copper and 97.9% of nickel were floated at volume reduction ratio of 33.

A much cheaper neutralizing reagent, calcium oxide, was used in the next few runs with this surfactant. The minimum surfactant concentration necessary for 90% flotation was determined as 4×10^{-4} M. More than 99% of copper, nickel, iron, and zinc are floated at pH 10 and surfactant concentration of 5×10^{-4} M.

In the laboratory tests using flotation machine it was found that after 5 min. of flotation, at pH 9.0 and 3×10^{-4} M of Mersolan E-30, more than 95% of copper and 94% of nickel precipitated by sodium hydroxide may be recovered. The flotation recoveries reached 97% for both copper and nickel using calcium oxide as precipitant. Volume reduction ratios were 50 and 25 for sodium hydroxide and calcium oxide as precipitants, respectively.

4. FLOTATION OF CARBONATE PRECIPITATES

Sodium carbonate was used as precipitant of the metals in the subsequent flotation experiments to study the influence of precipitant concentration on metal recovery (fig. 3).

It was found that at the anionic surfactant (Lawon MC) concentration of 2×10^{-4} M, metal recovery increases with the increasing sodium carbonate concentration and it reaches its maximum at 2.5-fold stoichiometric excess of sodium carbonate versus total metal ions and sulphuric acid concentrations in the feed solution. The maximum recoveries of metals in the flotation process were 96%, 91%, 87%, and 97% for copper, nickel, iron, and zinc, respectively. The volume reduction ratio was equal to 50.

A high flotation recoveries (over 99% of copper and nickel) were also achieved using an other anionic surfactant (Mersolan E-30) at the same experimental conditions.

Somewhat worse results of precipitate flotation were achieved using flotation machine. The process was effective only with Lawon MC since 93% of copper and 83% of nickel were recovered at the volume reduction ratio equal to 33.

5. FLOTATION OF SULPHIDE PRECIPITATES

A preliminary study on flotation of copper sulphide precipitated from the model solution containing 159 g Cu^{2+}/m^3 showed that the flotation process is effective in weakly acidic or weakly alkaline conditions using cationic surfactant (Lauroseptol). Moreover, the limiting conditions for flotation of copper sulphide are the following: dosage of 50%

to 75% of stoichiometric excess of sodium sulphide as precipitant over the total copper amount in the feed solution. The interdependence of copper and nickel flotation recovery and pH of aqueous suspension containing 159 g Cu/m^3 and 21.6 g Ni/m^3 is shown in fig. 4.

These data indicate that acidity of feed suspension plays an essential role in flotation of sulphide precipitates and at pH 3.2 recoveries of copper and nickel sulphides reach 88% and 16%, respectively. Nickel sulphide is removed in 90% at pH 4.7. It may by concluded that flotation of sulphide precipitates from a weakly acidic suspension (pH ~3) results in almost complete recovery of copper, whereas the other metal ions essentially remain in the flotation column: i.e. at pH 3.0, 99% of copper, 12% of nickel, and 27% of zinc were recovered using Lauroseptol at the concentration of 3.5×10^{-4} M. The volume reduction ratio reached 50.

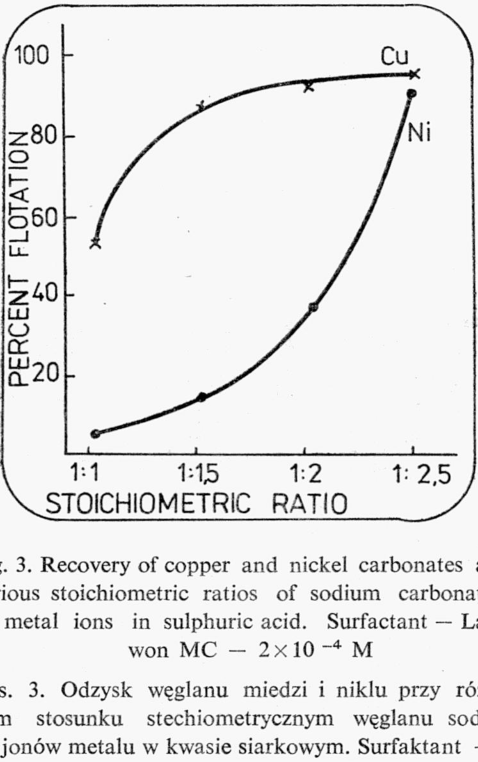

Fig. 3. Recovery of copper and nickel carbonates at various stoichiometric ratios of sodium carbonate to metal ions in sulphuric acid. Surfactant — Lawon MC — 2×10^{-4} M

Rys. 3. Odzysk węglanu miedzi i niklu przy różnym stosunku stechiometrycznym węglanu sodu do jonów metalu w kwasie siarkowym. Surfaktant — — Lawon MC — 2×10^{-4} M

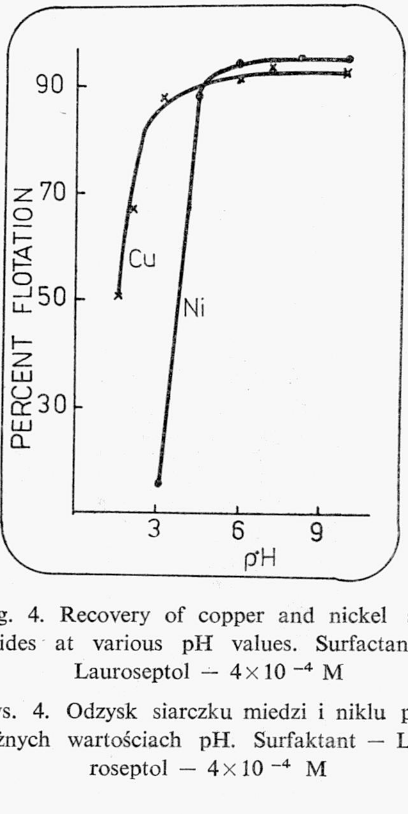

Fig. 4. Recovery of copper and nickel sulphides at various pH values. Surfactant — Lauroseptol — 4×10^{-4} M

Rys. 4. Odzysk siarczku miedzi i niklu przy różnych wartościach pH. Surfaktant — Lauroseptol — 4×10^{-4} M

When the flotation machine was applied at the same experimental conditions (except for the flotation time being equal to 10 min.) 96% of copper, 25% of nickel, and 25% of zinc were recovered with the volume reduction ratio of 33. Further flotation of hydro-

Table

Results of metals recovery from copper smelter's wastewaters by precipitate flotation* and settling (initial solution: Cu – 159 g/m³, Ni – 21.6 g/m³, Ca – 101 g/m³, Mg – 28 g/m³, Fe – 7.0 g/m³, Zn – 2.1 g/m³, H_2SO_4 – 73.5 g/m³)

Wyniki odzysku metali ze ścieków huty miedzi metodą flotacji* i osadzania (roztwor wyjściowy: Cu – 159 g/m³, Ni – 21.6 g/m³, Ca – 101 g/m³, Mg – 28 g/m³, Fe – 7.0 g/m³, Zn – 2.1 g/m³, H_2SO_4 – 73.5 g/m³)

Item	Sulphides pH = 3.2		Sulphides pH = 10.0		Carbonates ratio 1:2.5		Oxides** pH = 10.0	
	Flotation	Settling	Flotation	Settling	Flotation	Settling	Flotation	Settling
Surfactant type	Lauroseptol	–	Lauroseptol	–	Lawon MC	–	Mersolan E-30	–
Surfactant concentration (g/m³)	76	–	90	–	64	–	91	–
Volume reduction ratio	27	15*** 41****	30	8.5*** 27****	33	2.4*** 13****	25	3.2*** 10.5****
Metal content in residual solution (g/m³)								
Cu^{2+}	4.7	17	4.4	1.2	12	1.7	3.5	2.6
Ni^{2+}	17.0	18	2.7	0.51	3.6	0.15	0.46	0.30
Fe^{3+}	24.0	14	3.9	0.05	2.6	0.20	0.81	0.43
Zn^{2+}	–	–	0.6	0.05	–	0.04	0.09	0.05
Consumption of precipitant in kg per m³ of wastewater	Na_2S – 0.181		Na_2S – 0.181 Na_2CO_3 – 1.2		Na_2CO_3 – 2.0		CaO – 0.3	

* – applying lab. flotation machine.
** – applying $Ca(OH)_2$.
*** – after 0.5 hrs settling.
**** – after 24 hrs settling.

xide precipitates from resultant residual solution can be suggested as the second treatment step in order to remove all the metals. Subsequent experiments in the flotation machine show that the precipitated hydroxides were recovered by flotation at pH 8.6 using the anionic surfactant Lawon MC in concentration of 1×10^{-4} M with the flotation recovery of 82%, 92%, 83%, and 93% for copper, iron, nickel, and zinc, respectively.

When the mixture of sodium carbonate and sodium sulphide was used as precipitants at pH 10 and the precipitate was recovered by flotation using cationic surfactant Lauroseptol at concentration of 4.5×10^{-4} M, the flotation recovery of copper and nickel were 97%, and 87%, respectively.

6. CONCLUSIONS

The results of the comparative study on precipitate flotation in a glass column and in a lab. flotation machine as well as those of settling process are presented in a paper (table).

On the basis of the results achieved the following conclusions can be formulated:

sedimentation of carbonate and sulphide precipitates allows better metal recovery with respect to the flotation process, except for hydroxide precipitates where metal recovery is equal for both sedimentation and precipitate flotation,

precipitate flotation of hydroxide, carbonate, and sulphide precipitates gives higher sludge volume reduction ratios over the settling process, hydroxide precipitates where metal recovery is equal for both sedimentation and precipitate flotation,

satisfactory precipitate flotation process takes about 10 minutes, whereas the similar metal recovery by settling is achieved after 24 hours.

Results on precipitate flotation from slightly acidic wastewater show that the process is highly effective for recovery of metals. It is specially important that flotation machine can be used together with domestic, technical grade, surfactants. Calcium oxide is recommended as the precipitant because of good flotation results and its lowest price among the precipitants studied.

Further surfactant recovery and reuse would reasonably promote precipitate flotation process for processing copper smelter wastewaters. Coacervation [2, 3] seems to be a good example of process for surfactant recovery from concentrate. The concentrate, after dissolving in sulphuric acid at pH 1.5, may be separated into aqueous metal sulphate solution and solid precipitate of the anionic surfactants (Lawon MC or Mersolan E-30) in acidic form. Separation of above phases and subsequent precipitation of metal ions from aqueous sulphate solution allows to obtain a rich and valuable metal concentrate. A preliminary test on recovery of Mersolan E-30 from precipitate flotation concentrate by coacervation process showed that the surfactant recovered at the efficiency of 85% was fully effective in the subsequent precipitate flotation process.

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FLOTACJA MIEDZI (II), NIKLU (II) I INNYCH KATIONÓW METALI W ŚCIEKACH POCHODZĄCYCH Z PRZEMYSŁU MIEDZIOWEGO

W wyniku badań porównawczych nad flotacją osadów metali ze ścieków przemysłu miedziowego, stosując technikę kolumnową, urządzenia flotacyjne i proces sedymentacji, stwierdzono wysoką efektywność flotacji w usuwaniu wodorotlenków, węglanów i siarczków metali. Miarą tej wysokiej efektywności jest większy odzysk metali i zmniejszenie objętości finalnego produktu. W celu uzyskania lepszej efektywności, skrócenia czasu oraz zmniejszenia kosztów oczyszczania ścieków zalecane jest stosowanie wapna jako odczynnika wytrącającego metale i surfaktanów anionowych. Opisano również technikę odzysku surfaktanta i metali z koncentratu flotacyjnego.

FLOTATION VON Cu (II), Ni (II) UND ANDERER METALLIONEN AUS DEN ABWÄSSERN DER KUPFERINDUSTRIE

Anhand von vergleichenden Untersuchungen der Flotation mit den Abwässern der Kupferindustrie in der Kolonnentechnik, im Flotationsverfahren und Sedimentation, wurde eine hohe Effektivität der Flotation zur Eliminierung von Hydroxiden, Karbonaten und von Metallsulfiden festgestellt. Das Resultat ist eine weit höhere Metallrückgewinnung und Verminderung des Schlammvolumens mit Ausnahme der Sulfideliminierung aus sauren Lösungen. Um diese hohe Effektivität, eine Zeitminderung und Senkung der Betriebskosten zu erreichen, ist die Zugabe von Kalk und von anionaktiven Detergentien im Flotationsverfahren wünschenswert. Beschrieben wird die Technik der Rückgewinnung der Detergentien und Metalle aus dem eingedickten Schlamm.

ФЛОТАЦИЯ МЕДИ (II), НИКЕЛЯ (II) И ДРУГИХ КАТИОНОВ МЕТАЛЛОВ ИЗ СТОЧНЫХ ВОД МЕДНООБРАБАТЫВАЮЩЕЙ ПРОМЫШЛЕННОСТИ

В результате сравнительных исследований по флотации осадков металлов из сточных вод меднообрабатывающей промышленности при применении колонной техники, флотационных установок и процесса седиментации была отмечена высокая эффективность флотации при удалении гидроокисей, карбонатов и сульфидов металла. Мерой этой высокой эффективности является извлечение металлов и уменьшение объёма финалного осадка. Для достижения высшей эффективности, сокращения времени, а также уменьшения расходов очистки сточных вод желательно применять известь для осаждения металлов и анионные поверхностно-активные вещества для флотации. Описана также техника регенерации поверхностно-активного вещества и металлов из флотационного концентрата.