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Separation of Copper and Zinc by Solvent Extraction During Reprocessing of Flotation Tailings

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Results from the solvent extraction of copper and zinc from pregnant solutions after bioleaching of re-floated tailings from the Kipushi concentrator in DR of Congo are presented. LIX984N has been used as extractant for copper, while D2EHPA as such for zinc, following prior removal of the ferric iron via precipitation. The McCabe-Thiele diagrams constructed for Cu and Zn extraction have theoretically suggested the need for two stages for copper and one for zinc. Stripping these metals to the aqueous phase by sulphuric acid has yielded rich electrolytes with 48.5 g/L copper and 85.5 g/L zinc. Thus, copper and zinc could be further recovered from the stripped solutions by electrolysis.

Keywords flotation tailings; heavy metals; solvent extraction

INTRODUCTION

During its nearly 40-year operation, the Kipushi concentrator in the Katanga province, Democratic Republic of Congo has accumulated about 37 million tons of sulphide tailings. It is estimated that nearly 127,000 tons of copper and 88,0000 tons of zinc, an amount quite appreciable to be neglected, are contained in this already ground material (1). The reprocessing of this material apart from reduction in environmental pollution will have implication on the conservation of natural resources by the way of metal values recovery. The hydrometallurgical techniques known by proven operational simplicity and robustness are frequently the most preferred option for re-treatment of such tailings. For the selective recovery of the dissolved metals, solvent extraction could offer both capital and operating cost advantage. Solvent extraction is a technique that separates and concentrates metallic ions in aqueous solution by utilization of extractant diluted in organic solvent. After vigorous mixing of the aqueous solution containing the metals of interest with the organic solvent, the latter is separated by decantation. Further, the extractant-metal complex is stripped with fresh acidic solution to produce highly concentrated metal liquor suitable for the final step of electrowinning or precipitation.

The extraction and the stripping are two reactions in equilibrium which are principally controlled by the pH of the medium according to the following relationship:

$$M^{++}_{(aq)} + 2RH_{(org)} \underset{\text{Stripping}}{\overset{\text{Extraction}}{\rightleftharpoons}} R_2M_{(org)} + 2H^{+}_{(aq)}$$

where:

$M^{++}_{(aq)}$ – metallic ion in aqueous solution,
$2RH_{(org)}$ – extractant dissolved inside the organic phase,
$R_2M_{(org)}$ – charged metal organic complex inside the organic phase,
$2H^{+}_{(aq)}$ – acidity of the raffinate.

Moreover, the equilibrium is such that all the metal will be extracted or stripped in a single contact, so that multistage extraction and stripping circuits are required to reach the desired recovery. Multistage operation is most economically carried out when the phases flow counter-current to each other.

Solvent extraction is nowadays adapted by a large number of hydrometallurgical plants worldwide with the aim for solution purification or for upgrading various metals like Cu, Co, Ni, Zn, U, Ta, Nb etc. (2–4). It is estimated that approximately 25% of the world copper production is generated directly at mine sites through heap leaching of oxide ores followed by solvent extraction and electrowinning to high quality cathode (5). Carboxylic acids could be used for the solvent extraction of copper, but the pH range for extraction is much higher than the normal pH of the leach solutions, so that alkali consumption is high and the raffinate after extraction could not be recycled to leaching operations. Therefore companies like Cognis (previous Henkel Corporation) and Cytec have

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developed reagents from the LIX and ACORGA series respectively, which are based on primary oximes chemistries (6). Their principal advantages are the fast extraction kinetics and high extractant strength, offering the extraction of copper from highly acidic pregnant leach solutions with sufficient selectivity towards iron (III). Often, the extraction of zinc necessitates preliminary elimination of iron (III) ions from the pregnant leach solutions prior to their contact with extractants like di(2-ethylhexyl)phosphoric acid (D2EHPA) (7,8). In order to improve the selectivity of the D2EHPA, tri-butyl phosphate is used as a modifier (9).

In our recent studies (10,11) we have reported about the use of mesophilic and themophilic bacteria in bio-leaching of copper and zinc from the tailings of Kipushi concentrator in DR of Congo, following their up-grade by flotation. The obtained results have demonstrated that it is possible to bioleach the flotation concentrate and to obtain a pregnant leach solution warranting downstream metal recovery. The present work has aimed to test the solvent extraction as a method for processing of this solution. Focus has been placed on the selectivity of copper and zinc extraction over iron (III) in sulphate media and on the ease of metals stripping from the loaded extractants. In order to establish the optimal extraction for copper and zinc, the following process parameters have been investigated: extractant type, pH of aqueous feed, phase ratio, and number and sequence of the extraction/stripping cycles.

MATERIALS AND METHODS

The mineralogical study of the tailings before their subjection to re-flotation and bioleaching has revealed that the principal copper mineral is chalcopyrite, while zinc is met as sphalerite with abundant presence of pyrite and gangue being of dolomite character. The prolonged period of material stocking inside the pond has rendered the mineralogical composition relatively complex, which has required an intensive test-work for the optimization of both flotation and bioleach process parameters. Before being subjected to re-flotation the tailings have been first re-grinded in a ball mill for 5 minutes and screened at 75 microns. The 75 microns undersize fraction has been subjected to bulk flotation comprising one rougher and two cleaning operations. The micrograph from a polished section of the thus obtained polymetalic concentrate is shown in Fig. 1. It could be noted that the re-grinding has merely refreshed grains surfaces, but has not achieved complete liberation of the copper sulphides from the pyrite. The re-flotation however has enriched significantly non-ferrous metals and especially zinc in the concentrate. The zinc content has increased from 2.6 to 19% and that of copper - from 0.6 to 3.3%, with average recoveries of 79% for the zinc and 70% for the copper. Further details about flotation and bioleaching procedures are described elsewhere (Kitobo 2009, Kitobo et al., 2007). The concentration of the principal metals of interest in the pregnant leach solution after bioleaching of the flotation concentrate is given in Table 1.

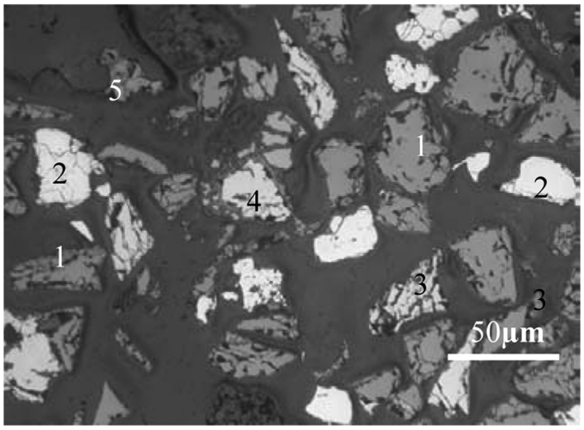

FIG. 1. Typical view of ore particles found in the bulk flotation concentrate (fraction +20 μm). Sphalerite (1), pyrite (2), chalcopyrite (3), bornite (4), covellite (5). *Refl. Light (×50)*.

Sulphuric acid and sodium hydroxide of analytical grade (Merck AG, Darmstadt) have been used to maintain the desired equilibrium pH during extraction. Organic reagents LIX984N (Cognis) and D2EHPA (di(2-ethylhexyl) phosphoric acid) (Fluka) have been employed as received without further purification. Commercial grade kerosene has been chosen as a diluent for the LIX984N and ESCAID 100 as such for the D2EHPA. The LIX984N has been used in 15% concentration while the D2EHPA as 30% solution. The choice of these concentrations has been based upon the results from preliminary equilibrium studies with the pregnant leach solution.

After bioleaching, the pulp has been subjected to solid liquid separation using a filter paper (5 μm pore openings) and the clarified leach liquor submitted to solvent extraction. In the solvent extraction studies about the effect of pH of feed solution, equal volume (200 mL) each of the aqueous solution and the extractant have been mixed. In the experiments about the effect of O/A ratio, suitable proportions of the organic and the aqueous phases have been brought in contact keeping the volume of the final mixture at 200 ml. The agitation procedure has been realized inside a 1-liter glass reactor using an agitator (Janke & Kunkel IKa-Werk RW20) at 800 rpm equipped

TABLE 1
Principal characteristics of the aqueous feed solution (PLS)

	pH	Cu (g/L)	Zn (g/L)	Fe (g/L)	Pb (mg/L)	Mn (mg/L)
PLS	1.90	3.20	7.20	2.82	2	120

with a glass stirrer. A pH meter (WTW 3151) has been used to measure the pH directly inside the agitation vessel.

Immediately after equilibration, the two phases have been separated using a decanting funnel. The concentration of the metals in the aqueous phase (raffinate) has been determined by atomic absorption spectrometry (Perkin Elmer 1100B), while for the organic phase this has been calculated from the difference between the initial concentration in the aqueous feed and the concentration of the respective metal in the raffinate.

The stripping of the metals from the loaded organics has been accomplished by the use of acidic solutions containing 150 g/L H_2SO_4 and 33 g/L copper and 60 g/L zinc. These concentrations have been intentionally chosen for resembling the ones met in spent electrolytes after electrowinning. For ensuring good equilibrium between the phases, 4-minute contact time has been maintained for both the extraction and the stripping stages. The extraction has been realized at the temperature of $33 \pm 2°C$, while the stripping has been performed at $40 \pm 2°C$. During the precipitation of iron, the pH has been controlled by the addition of 10 N NaOH. The McCabe-Thiele diagrams have been constructed in view of the prediction on extraction and stripping performance following a described methodology (12).

RESULTS AND DISCUSSIONS

Influence of Feed Solution pH upon the Extraction of Metals

The first experimental series have been aimed to study the effect of equilibrium pH upon the extraction of copper, zinc, and iron with the two solvent extraction reagents under consideration. The ratio between the organic and the aqueous phase has been kept as one and the pH has been varied between 0.5 and 3.5. The results obtained when LIX984N was used (Fig. 2), indicate a rise in copper extraction degree with concomitant increase in equilibrium pH. High efficiency of copper extraction could be obtained (nearly 95%) within the pH interval 1.5 to 3.5, where zinc is virtually not extracted. The extraction of iron by this system is quite low (4% at pH 2). At pH values higher than 2.5, ferric iron begins to precipitate, therefore its extraction has been followed up to this pH region. The data about copper extraction beyond the pH of 2.5 have been nevertheless generated after filtration of the precipitated iron and analysis of the filtrate. The order of metals separation for the LIX984N indicates that copper could be selectively extracted at pH range 1.5–2 which corresponds well with the pH of the aqueous feed solution after the bioleaching.

When D2EHPA was used as extractant (Fig. 3), a high separation degree of zinc has been observed at equilibrium pH above 2.5 (almost 99%). For this solvent extraction system, an equilibrium pH above 3 is required for the copper extraction to commence. The results indicate a substantial extraction of iron implying high affinity of the D2EHPA for this element. In the light of this limitation, iron should be eliminated first if zinc has to be selectively recovered.

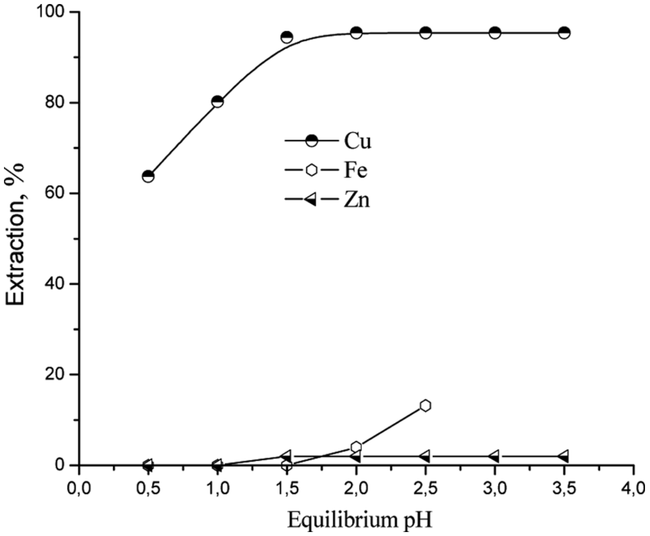

FIG. 2. Influence of equilibrium pH upon metals extraction with LIX984N (15% v/v; PLS g/L: Cu - 3.2, Fe - 2.8, Zn - 7.2; contact time –4 minutes).

Extraction of Copper by LIX984N – Effect of Organic/Aqueous Ratio

The conditions for realizing efficient and selective extraction of copper have been examined further on. The effect of O/A ratio has been studied with 15% LIX984N (v/v) in kerosene in single contact with the same feed solution after bioleaching having characteristics shown in

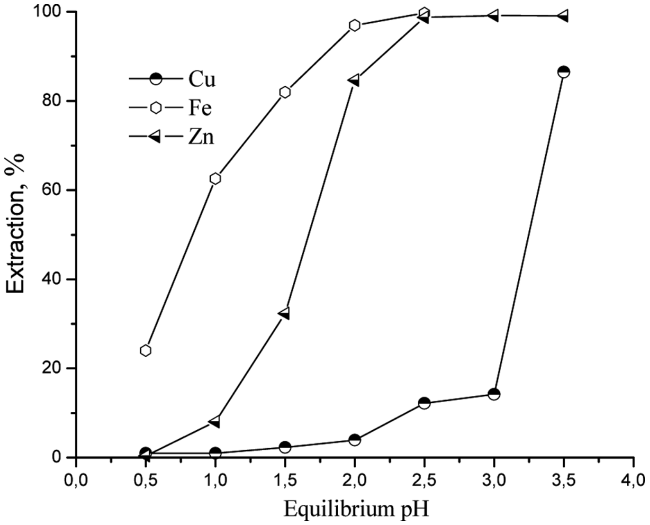

FIG. 3. Influence of equilibrium pH upon metals extraction with D2EHPA (30% v/v; PLS g/L: Cu - 3.2, Fe - 2.8, Zn - 7.2; contact time –4 minutes).

TABLE 2
Concentration of metals in the raffinate (AP) and of Cu in the organic phase (OP) during extraction of copper with LIX984N at different O/A ratio

O/A	AP in equilibrium			OP in equilibrium
ratio	Cu (mg/L)	Fe (g/L)	Zn (g/L)	Cu (g/L)
5/1	16	2.78	7.10	0.64
2/1	18	2.78	7.10	1.59
1/1	65	2.78	7.10	3.14
1/2	435	2.78	7.10	5.5
1/3	1100	2.78	7.10	6.3

Table 1. The perusal of the results presented in Table 2 suggests a decrease in copper concentration in the raffinate with increase of O/A ratio. The presented data indicate that the selectivity of LIX984N for copper over zinc and iron is high, the co-extraction of zinc being below 2% and that of iron almost negligible. It should be noted as well, that copper and zinc co-extraction is not affected by variation of the O/A ratio.

For drawing the McCabe-Thiele diagram (Fig. 4), it was necessary to first construct the copper extraction isotherm using the data shown in Table 2 (O/A ratio and equilibrium metal concentration in OP). Further on, the operating line has been traced and from the resulting diagram a requirement for two extraction stages in a counter-current manner could be predicted, for ensuring copper concentration of 65 mg/L in the final raffinate and of 5.2 g/L in the organic phase at equilibrium pH of 1.8 and at O/A ratio of one. The copper extraction efficiency above 99% could be reached under such configuration of the extraction cycles. It should be noted, that during the counter-current simulation, the aqueous phase in the second stage has not been contacted with fresh organic, but rather with a one containing initially 2.1 g/L Cu. This has been the actual copper content after stripping of the organic phase and in such a way it has been possible to approach work conditions closer to those expected at industrial scale.

Extraction of Zinc by D2EHPA – Effect of Organic/Aqueous Ratio

Before the study for zinc extraction to be carried out, an elimination of the ferric iron from the raffinate after copper extraction has been realised by adjusting the pH to 3. This step has been necessary due to the following considerations:

(1) risk of iron precipitation during zinc extraction at pH higher than 2.5 and
(2) preserving the extractant's capacity for the zinc, since ferric ions are easily extracted by the D2EHPA even at equilibrium pH close to 1 where zinc extraction does not take place.

In Table 3 the characteristics of the raffinate coming from copper extraction before and after elimination of ferric iron are presented. The perusal of these results indicates that the precipitation of iron is accompanied by less than 5% co-precipitation of zinc.

It is to be expected that during zinc extraction, the pH will evolve naturally towards the acidic region due to

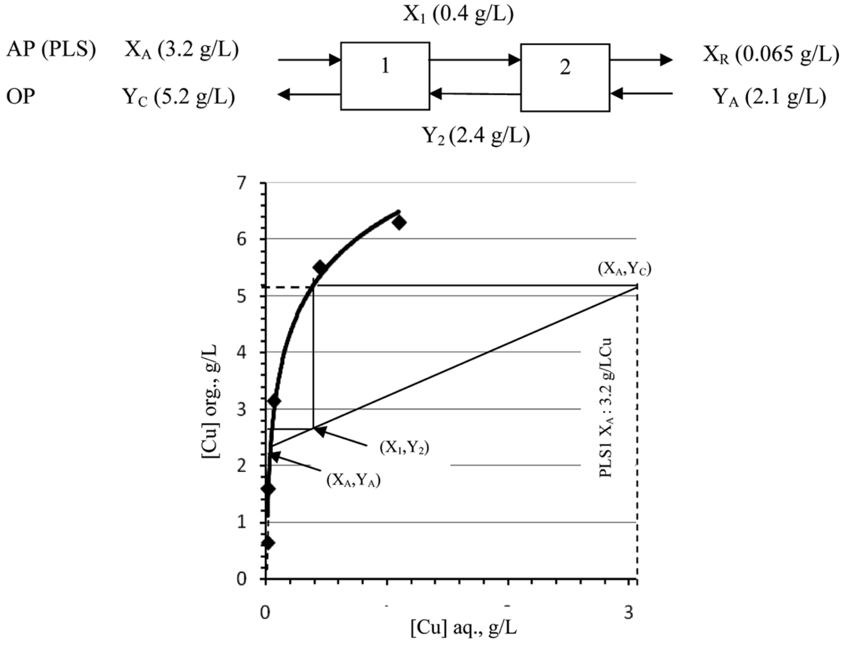

FIG. 4. McCabe-Thiele diagram for determination number of stages for copper extraction at equilibrium pH 1.8 with LIX984N 15% (v/v) kerosene.

TABLE 3
Characteristics of the raffinate from copper extraction before and after precipitation of iron

	pH	Cu (mg/L)	Fe (mg/L)	Zn (g/L)	Mn (mg/L)	Pb (mg/L)
Raffinate before	1.7	65	2780	7.1	119	–
Raffinate after	3.5	41	650	6.75	110	–

protons release. To counterbalance the latter effect and owing to the fact that zinc is most efficiently extracted at pH above 2.5, it was thought that the final pH of the system should be adjusted to that value. Therefore in the next series of tests aimed at the construction of the equilibrium isotherm, the pH has been continuously corrected and maintained constantly at 2.5. The results from this set of experiments are presented in Table 4. It could be noted, that at O/A ratio equal to or above one, the residual zinc concentration is below 13 mg/L indicating quite acceptable extraction efficiency. However, it is obvious that D2EHPA suffers from lower selectivity over iron in comparison to the LIX984N. Iron being not totally precipitated is co-extracted to some extent with the zinc. Hence it is advisable that further fine-tuning of the iron removal step should be envisaged in order to reduce zinc residual concentration.

In order to estimate theoretically the number of necessary extraction stages, the data from Table 4 has been used in a case similar to the copper case manner to plot the zinc loading isotherm. From the McCabe-Thiele diagram illustrated in Fig. 5 and the operating line at O/A ratio of one, it could be concluded that loaded organic with zinc concentration of 8.5 g/L could be obtained in a single stage, thus reaching extraction efficiency above 99%. Iron co-extraction at the chosen phase ratio of one is 503 mg/L (650 – 147). Under particular industrial circumstances this level value can be reduced further by choosing a lower O:A phase ratio. The number of extraction cycles however will remain the same. It should be noted that no risk of D2EHPA contamination with iron is foreseen, since iron is not accumulated in this extractant. The co-extracted iron reports in the aqueous phase after D2EHPA stripping. Its presence should be nevertheless considered in view of optimising the current density and efficiency during zinc electrolysis.

TABLE 4
Concentration of metals in the raffinate (AP) and of Zn in the organic phase (OP) during extraction of zinc with 30% D2EHPA (v/v) at different O/A ratio and pH 2.5

	AP in equilibrium			OP in equilibrium
O/A ratio	Cu (mg/L)	Zn (mg/L)	Fe (mg/L)	Zn (g/L)
Feed	41	6750	650	
5/1	0.0	3.5	5	1.35
3/1	0.0	4.5	7.5	2.25
2/1	0.0	7.5	50	3.37
1/1	0.0	12.5	147	6.74
1/3	0.0	129	470	19.86
1/4	0.0	1025	538	22.9

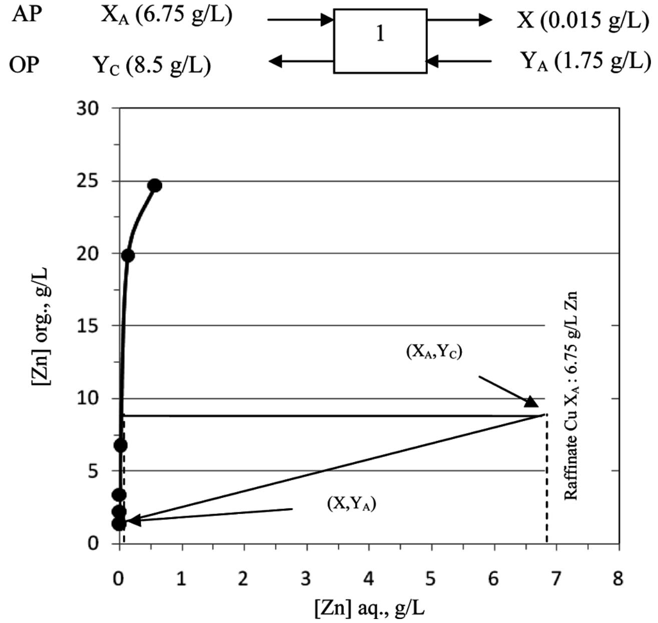

FIG. 5. McCabe-Thiele diagram for determination number of stages for zinc extraction at equilibrium pH 2.5 with D2EHPA 30% (v/v) ESCAID 100.

Stripping of the Metals from the Loaded Organics

The objective of this part has been to determine the operational conditions for stripping copper and zinc from the loaded extractants. In general, the stripping cycle should produce advance electrolytes with concentration of metals as higher as possible.

The stripping studies of copper from the loaded organic after the extraction have been realised with solution simulating spent electrolyte containing 33 g/L Cu and 150 g/L H_2SO_4. Mixing of the loaded organic with this stripping agent at O/A ratio of five, has resulted in almost complete stripping (99%) of the loaded metal in a single stage. Rich advance electrolyte with 48.5 g/L copper has been obtained after the stripping cycle. In a similar manner zinc has been stripped from the loaded organic with solution resembling lean electrolyte after zinc electrolysis – 60 g/L Zn and 150 g/L H_2SO_4. After the single stage stripping at O/A ratio of three, zinc concentration in the electrolyte has advanced to 85.5 g/L. The relatively high O/A ratios for the stripping of copper and zinc have been intentionally chosen with the aim to concentrate to a maximum possible extent the metals of interest in the advance electrolyte solutions.

CONCLUSIONS

In this paper we demonstrate that it is feasible to couple a solvent extraction circuit to the bacterial leaching of re-floated sulphide tailings in view of the ultimate recovery of the remaining copper and zinc.

Copper could be quantitatively extracted from the bioleach pregnant leach solution (PLS) in two stages by the use of 15% LIX984N (v/v) in kerosene without adjusting the solution pH. Stripping of copper to the aqueous phase could be realized with solution containing 150 g/L sulphuric acid in a single stage at O/A ratio of five.

Zinc extraction from the raffinate after copper extraction necessitates preliminary elimination of the ferric iron due to the lower selectivity of D2EHPA. The studies showed that following iron precipitation, zinc could be extracted in a single stage with efficiency higher than 99% at equilibrium pH between 2.5 and 3.5. The loaded zinc could be subsequently stripped in a single stage with solution containing 150 g/L sulphuric acid at O/A ratio of three.

After solvent extraction of copper and zinc under the chosen conditions, relatively lean raffinates with 65 mg/L copper and 15 mg/L zinc could be obtained. Following extraction and stripping, the concentration of copper and zinc in advance electrolytes has reached 48.5 g/L and 85.5 g/L respectively, which make them highly suitable for electrolytic treatment.

In order to confirm prediction data about copper and zinc extraction, studies under semi-continuous conditions for simulation the extraction in the mixer-settler mode are underway.

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