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Extraction of Copper from Pregnant Leach Solution (PLS) and Reduction of Crud Formation

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ABSTRACT

Presented universal recommendations for the reduction of crud formation, reviewing various aspects affecting the loss of diluent and extractant due to the formation of a third phase (crud), encountered in many hydrometallurgical plants using copper solvent extraction. In this paper introduce the reasons of the crud formation , description of the stable emulsions containing solid particles and choice of technological scheme. An analysis of operations to be considered in the operation of copper solvent extraction plants is presented, due to the deterioration of copper grade below 0.5% in ore and the increase in aluminum content up to 20–25%. Results of use of extraction properties of modified extractants of ACCORGA series and unmodified extractant Lix984N on pregnant leached solution of the most important deposits (Almaly and Aktogay) are given. It is established that for solutions of Almaly deposit, ACCORGA5640 and unmodified Lix984 extractants have high selectivity to copper. Distribution of iron, silica, and copper ions during extraction was studied, and it was found that high selectivity to copper/iron and copper/silica is possessed by extractant Lix 984N, ACCORGA5640. It was found that for solutions of the Aktogay deposit, the ratio of interphase suspension in both extractants is the same, and phase separation in experiments with the use of extractant Lix 984N was 10 s shorter with the use of extractant ACCORGA5640. It was found that the addition of ACCORGACR60 reagent in the amount of 5-10 ppm also leads to a decrease in the volume of crud by 13%, for a stronger suppression of crud.

KEYWORDS

Hydrometallurgy; copper; solvent extraction; chemical and physical properties; crud

Introduction

Due to the depletion of copper ore deposits globally, poor oxide and transition ores are now increasingly being used in copper production. The copper grade of the deposits currently being mined in Kazakhstan averages 0.36–0.45% compared to the global average of 0.95%. To extract copper from such poor raw materials, it is necessary to apply new effective technologies and processes (Petersen 2016; Ritcey 2006). Such methods, in particular, include the technology of 'solvent extraction – electrowinning' (SX-EW) with the use of modern extractants with high technological properties. Copper production by SX-EW technology in the world has already reached to 30% of total copper production and this is due to the development of selective extractants industry (Movahhedi et al. 2023). Solvent extraction occupies a significant place in the processes of selective extraction, separation, and concentration of metals, as well as in chemical, radiochemical, petrochemical, and other industries (Baba et al. 2018; Jha et al. 2012; Zhu and Cheng 2011). The advantage of solvent extraction is, first of all, in the organization of a continuous high-performance process, and, consequently, in the reduction of capital and operating costs (Golaghaei et al. 2023). Kinetic and mechanism studies using shrinking core model for copper leaching from chalcopyrite in methanesulfonic acid with hydrogen peroxide are considered in (Wu, Ahn, and Lee 2021).

For the extraction of copper from sulfuric acid leaching solutions, the most effective and industrially used are chelate reagents, the main components of which are hydroxyoximes (Tanaydın and Demirkıran 2019). Selecting leaching methods of copper from copper smelter slag and kinetics process were considered in (Roy et al. 2016). In recent years, the market has received a wide range of effective copper chelate extractants; reagents such as LIX and ACCORGA have found widespread use in the copper industry (MCT 2007; Ruiz et al. 2021; Wilson and others 2014).

A significant number of studies have been devoted to the extraction of copper from leaching solutions with extractants such as LIX and ACCORGA (Alguacil, Cobo, and Alonso 2002; Chepushtanova et al. 2022; Cole 2016; Ferreira et al. 2010; Nicholson et al. 2017; Nobahar et al. 2022; Panda et al. 2012; Shakibania et al. 2020; Sridhar and Verma 2011). Among them, the extractant LIX 984N (which is a mixture of equal amounts of 5-nonyl salicyl aldoxime (aldoxime) and 2-hydroxy-5-nonyl acetophenoxime (ketoxime)) and ACCORGA M5640 (containing 5-nonyl salicyl aldoxime and a fatty acid ester as a modifier) are most effective in extraction of copper from acidic solutions with low pH values (1.3–2), at low copper concentrations (from 1 to 7 g/dm3) in the initial solutions; promote rapid separation of the organic and

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aqueous phases; have high selectivity to copper, good re-extraction ability, high mass transfer; are nontoxic, easily diluted in aviation kerosene; and are not expensive extractants (Agarwal et al. 2010; Ruiz, Risso, and Seguel 2020; Wang et al. 2019). In addition to the use of modern highly selective extractants, the performance of liquid extraction depends on many factors, such as the acidity (pH) of the solution, the duration of mixing and settling, the ratio of organic and liquid phases, temperature, etc (Petersen 2016).

As the experience of operating copper enterprises shows, the performance of liquid extraction, in addition to the above factors, strongly depends on the formation of the third phase (steal), which leads to a sharp decrease in the degree of extraction of the target metal and a suspension of the process, and sometimes even a complete stop. The formation of steal is also accompanied by the loss of a significant amount of extractant (organic phase), which greatly increases the cost of the process (Liu and Lan 2002; Virnig et al. 1999).

Crud is a semi-stable mixture of organic, aqueous phases, air and fine solid particles and can be formed in mixer and accumulate at the interface between two phases – organic and aqueous (interphase or interphase); at the bottom of the settler; on the surface of the organic phases (Ritcey 1980). Crud is inevitable and present in all plants where SX-EW processes are developed. As studies show, the main reasons for the formation of theft are degradation of the extractant, the presence of harmful impurities in the productive solution, such as silica (David, Fletcher and Gage 1985; Readett and Miller 1995), aluminum, iron, manganese, etc (Bednarski 2008), as well as solid suspensions (Zheng 2007) and organic components (Sperline et al. 1998).

To reduce and prevent the formation of steal, researchers used various methods – selection of an organic phase with the addition of various modifiers (Liu and Lan 2002; Sastre and Szymanowski 2004), selective precipitation, removal of harmful metal impurities (Cupertino et al. 1999; Miller 2011; Moya et al. 2018), addition of special surfactants, addition of flocculants, blowing air with in order to prevent the formation of dense suspension, changing the flow rate of organic and aqueous phases, etc. (Chepushtanova et al. 2020; Valenzuela-Elgueta, Delgado, and Ahualli 2021), reconstruction of equipment (Miller, Readett, and Hutchinson 1997), and mechanical removal of theft (Ritcey 1980). It was found in (Jääskeläinen, Paatero, and Nyman 1998) that an increase in the aromaticity of the diluent and the addition of an aqueous phase reduce the adsorption of the extractant on the main component of krat – silicon dioxide, and may lead to a decrease in the formation of krat and the loss of the extractant. However, an increase in the composition of the organic phase of aromatic hydrocarbons is undesirable due to their tendency to substitution reactions and high polarity, as they can cause degradation of the extractant.

To reduce extractant costs due to the formation of steal, it is recommended to periodically process the interfacial suspension (Wang 2005), followed by processing it with an acidic solution in order to extract the extractant and return it to the extraction process, use polysaccharides (Derranji et al. 2023), such as guar gum, xanthan gum, gum arabic, and starch. The results showed that guar gum is an effective additive that allows the extraction of the organic phase from gum with a yield of up to 95%.

Technical review – copper solvent extraction in hydrometallurgy was introduced in (Littlejohn and Dreisinger 2007). Leaching of copper from a flash furnace dust using sulfuric acid is described in (Ríos et al. 2022). Effect of mechanical activation on pressure leaching of Küre Massive-rich copper ore is introduced in (Hosseinzadeh, Petersen, and Azizi 2022; Perek and Arslan 2010). A review on recovery of copper and cyanide from waste cyanide solutions was described in (Xie, Dreisinger, and Doyle 2013).

Typical crud treatment process flowsheet Kazakhstan's plants are introduced in Figure 1.

The analysis of literary sources has shown, so far, that there is no single method for preventing and/or removing crud in the SX – EW technology and conducting research in the direction of choosing and using a selective extractant with a study of the distribution of harmful impurities of metal ions and silica remains an urgent problem. The urgency of this problem is confirming in (Lawson, Cheng, and Lee 1992; Shahcheraghi, Mousavi, and Dianatpour 2022).

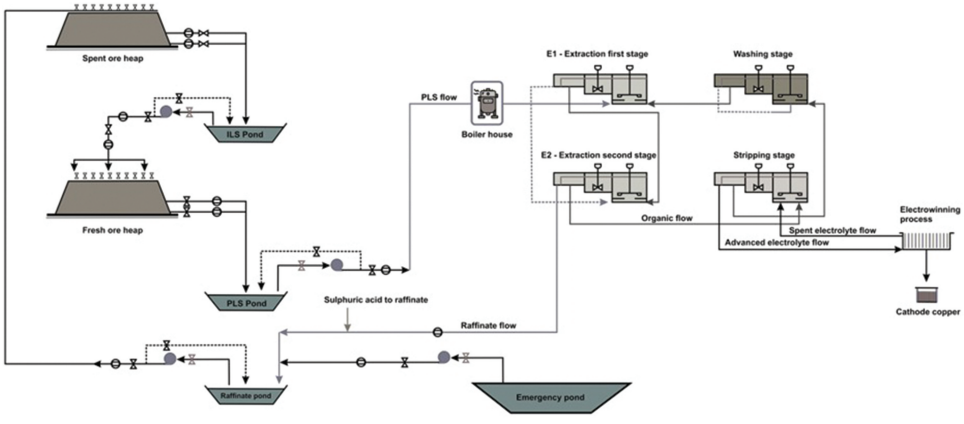


Figure 1. Typical crud treatment process flowsheet at Kazakhstan's plants.

The purpose of this work was to study the process of copper extraction from the pregnant leach solution (Chepushtanova et al. 2023),,

study of crud-formation components with extractants of the ACCORGA M5640 (with modifier) and Lix 984N (without modifier) for Almaly and Aktogay deposits, also elaborating of universal recommendations for reducing of the crud formation.

Materials and method

Materials

The object of the study was the solutions of heap leach of the Almaly and Aktogay deposits (Kazakhstan), as well as reagents of the organic phase: extractant ACCORGA M5640, Lix 984, and kerosene as a diluent, CR 60 – as an additive. Sulfuric acid and sodium hydroxide solutions were used to adjust the pH of the solution. All reagents used to prepare the model solutions had a grade: chemically clean – high purity reagent. Pulp density is S:L = 1:0.5 or 66.67% solid by weight.

The analysis of the initial model and pregnant leach solutions, as well as aqueous phases obtained in the process of extraction/stripping, was carried out using chemical and photocolorimetric analyses. Solid samples of the original ore, solid sediment after evaporation of the pregnant leached solution, crud were studied using X-ray fluorescence, X-ray phase analyses. X-ray diffraction imaging was performed on a D8 Advance apparatus (Bruker), Cu Kα radiation, tube voltage 40 kV, current 40 Ma. Processing of the obtained diffractogram data and calculation of interplanar distances were performed using EVA software.

Sample interpretation and phase search were carried out by Search/match program using the PDF-2 Powder Diffractometry Database (crystal phase ratio). To study the surface microstructure of solid samples–microscopic scanning analysis and to determine the main elemental composition of the sample of the pregnant leached solution, a complete evaporation was carried out until the formation of dry salts. The resulting salts were crushed to a particle size of not more than 0.1 mm and used for X-ray fluorescence analysis. Ray fluorescence semi-quantitative analysis was carried out on a wave-dispersive X-ray fluorescence spectrometer Axios 1 kW of PANalytical company (The Netherlands). The obtained data were processed in the Super Q software using the Omnian 37 software package (according to the FP model). Based on the results of the analysis, the qualitative semi-quantitative elemental composition of the samples was determined.

Solvent extraction experiments using the extractants ACCORGA5640 and Lix984N were carried out in pilot extraction unit, (Figure 2) under the following conditions: volume of productive solution 5000 ml. Lix formula is a combination of ketoxime (R = C_9H_{19}), aldoxime (R = C_9H_{25} or $C_{12}H_{25}$); ACCORGA5640 is a representative of modified aldoximes (5-nonyl salicyl aldoxime). Reagent CR60 is the structural formula of the compound sodium poly(4-styrenesulfonate), its chemical formula is $(H_2C{=}CHC_6H_4SO_3Na)_n$. Poly(sodium 4-styrenesulfonate) is a monomeric polymer. The sulfonate ion contains the functional group $-S(=O)_2-O-$. The general formula is RSO_2O-, where R is a radical. Salts of sulfonic acids – alkali metal sulfonates (mainly sodium alkylsulfonates) as surfactants have found as widespread use. Thus, the ACORGA CR60 is a surfactant; so in the future, it was of interest to study the process of reducing theft formation using the CR60 reagent.

The ratio O:A was set by means of fluxes and was equal to 1:1, number of stages 3, pH of the solution 1.7, and temperature –25°C. Stripping of components from the organic phase was carried out with sulfuric acid solution of 200 g/L concentration. The extraction of metals was calculated from the balance of the distribution of metals between the organic and aqueous phases.

The organic solution and aqueous solution from the respective stages are fed into the mixing chamber. Two mixing stages are used for copper extraction with a turbine pump in the first stage mixer and an auxiliary turbine in the second stage mixer. After mixing, the resulting emulsion flows by gravity to a settling chamber where the organic and aqueous phases are separated by gravity. The lighter organic phase rises upward, the heavier aqueous phase – downward. From the settling chamber, the phases are fed to other extraction or re-extraction stages.



Figure 2. Pilot extraction unit with 2 stage of extraction and 1 stage stripping.

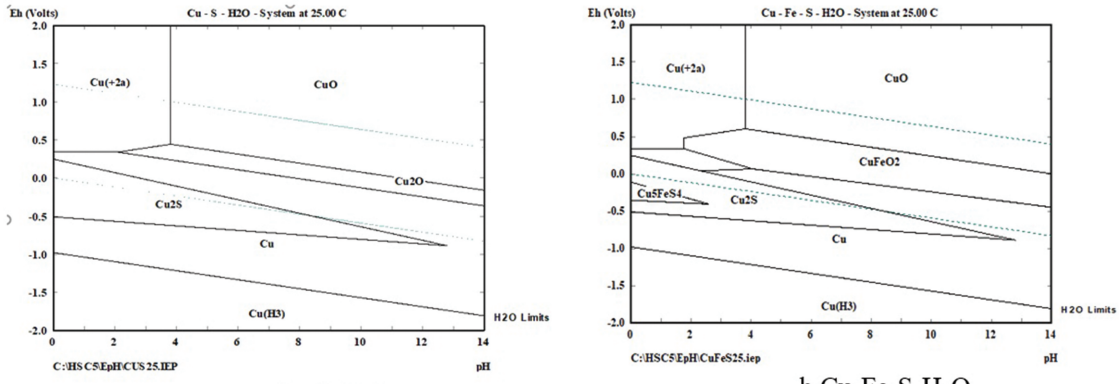


Figure 3. Diagram "potential - pH" of the Cu-S-H_2O and Cu-Fe-S-H_2O systems.

Results

Thermodynamics results of Eh-Ph diagram (HSC-Chemistry)

A thermodynamic prediction fulfilled using the HSC-Chemistry program for the probable occurrence of leaching, extraction, and stripping reactions. Thermodynamic analysis of leaching of oxidized copper ore showed that the minerals malachite, azurite, cuprite, and copper sulfates are effectively dissolved in solutions of sulfuric acid H_2SO_4 at pH 0 to 4 in an acidic environment. Minerals such as chrysocola, chalcocite, covellite, and chalcopyrite dissolve in the presence of oxidizing agents. The obtained Gibbs energy values indicate the thermodynamic possibility of copper extraction using the selected extractants. As the pH of the environment increases from 1.5 to 4, the Gibbs energy changes from – 10.5 to –26.5 kJ. Dissolution of copper sulfides is only possible during oxidative leaching (Figure 3a,b). The existence of copper ions Cu^{2+} is possible only at an oxidation potential of at least 0.45 V, in the pH range 0–4.5. As can be seen from Figure 3b in an aqueous solution in the pH range 0–4 and an increased potential, E > 0.4, in the 'Cu-Fe-S-H_2O' system copper exists in the form of the Cu^{2+} cation. With a decrease in pH, in the pH range 4–14, copper is oxidized and turns into CuO.

Results of chemical analysis

The results of the chemical analysis of the composition of the oxide ores Almaly and Aktogay are shown in Table 1 below.

After leaching of ores of Almaly and Aktogay mines with sulfuric acid solution of 30 g/L concentration, the productive solutions were obtained, the compositions of which are shown in Table 2.

Table 1. Results of chemical analysis of average samples of oxidized ores from Almaly and Aktogay mines.

	Content, %	
Components	Almaly mine	Aktogay mine
Cu	0.36	0.4
$Cu_{soluble}$	0.34 (94.44%)	0.31 (77.4%)
Fe	1.61	2.75
Al	6.94	7.25
Mg	1.03	0.99
Ca	1.41	1.08
Na	2.18	2.99
K	3.16	2.63
Mo	0.0010	0.0075
Mn	0.018	0.012
Zn	<0.02	<0.02
Pb	<0.02	–
Cr	0.016	0.0011
Sn	0.00036	0.00025
Cd	<0.004	<0.004
Ni	0.0012	0.00047
Co	0.00071	0.00084
TiO_2	0.40	0.73
Sb	0.0033	0.003
As	<0.030	<0.030
Cl	<0.05	<0.05
Au, g/t	<0.2	0.064
Ag, g/t	19.3	0.66
SiO_2	66.18	63.48
S_{total}	<0.10	<0.10
S_{SO4}	<0.10	<0.10
C_{total}	0.56	0.11
C_{CO3}	0.37	<0.10

Discussion

There are many porphyry copper deposits in Kazakhstan. One of them is the Aktogay deposit, which is a large open-pit mine in southeast Kazakhstan with an average copper content of 0.8%. The Aktogay ore body consists of an oxide ore deposit overlying a sulfide deposit.

Table 2. Results of chemical analysis (pregnant solutions) PLS.

	Elements, g/l						
PLS of ores	Cu	Fe	Mn	Al	Mg	Si	pH
PLS Aktogay	1.25	3.10	1.47	14.5	12.98	0.51	1,7
PLS Almaly	2.32	17.97	1.68	12.65	13.25	0.36	1,7

The Almaly field is located in the Karaganda region of Kazakhstan, 130 km south of the city of Karaganda. The Almaly deposit belongs to the linear porphyry type and includes three types of ores: oxidized, secondary, and sulfide. The average copper content of the oxidized ore is 0.38%.

SX-EW technology is effective for processing oxidized ores from Aktogay and Almaly (Littlejohn and Dreisinger 2007; Petersen 2016; Prasad, Kenyen, and Assar 1992).

According to the results of physical-chemical analysis of initial ores of Almaly and Aktogay, it was found that the content of copper in the ores is low and ranges from 0.36–0.40%, silica 63.48–66.18%, iron 1.61–2.75%, aluminum 6.94–7.24%. High silver content is observed in the Almaly ore (19.3 g/t), in the Aktogay ore – only 0.66 g/t. XRD analysis of ores showed that copper in ores is contained in the form of malachite, azurite, chrysocolla, and cuprite minerals, which are easily subjected to sulfuric acid leaching.

Leaching of the oxide ore from the Aktogay deposit was carried out with a 30 g/l sulfuric acid solution in columns. The leaching solutions flowed by gravity through the ore. The acid solution dissolves oxidized copper-bearing minerals in the column, resulting in a saturated copper-bearing product solution that flows into collection ditches and product solution ponds. Malachite, azurite, tenorite, and chrysocolla dissolve quite easily under the influence of sulfuric acid solutions without oxidizing agent (Mark 2021).

Chemically, the leaching process can be described by the following equations:

$$CuCO_3{\cdot}Cu(OH)_2 + 2H_2SO_4 = 2CuSO_4 + CO_2 + 3H_2O \quad (1)$$

$$2CuCO_3n{\cdot}Cu(OH)_2 + 3H_2SO_4 = 3CuSO_4 + 2CO_2 + 4H_2O \quad (2)$$

$$CuO + H_2SO_4 = CuSO_4 + H_2O \quad (3)$$

$$CuSiO_3{\cdot}nH_2O + H_2SO_4 = CuSO_4 + SiO_2 + (n+1)H_2O \quad (4)$$

$$CuSiO_3{\cdot}nH_2O + H_2SO_4 = CuSO_4 + H_2SiO_3 + nH_2O \quad (5)$$

The ore contains iron mainly in the form of hydroxides and sulfides, which, when interacting with sulfuric acid, can go into solution in the form of Fe^{2+} ions:

$$Fe(OH)_2 + H_2SO_4 = FeSO_4 + 2H_2O \quad (6)$$

$$Fe1 - xS + 2H+ + 2xe = (1-x)Fe^{2+} + H_2S\uparrow. \quad (7)$$

The components of the waste rock, these are mainly silicates $(Mg{\cdot}Ca)O{\cdot}Al_2O_3{\cdot}4SiO_2{\cdot}nH_2O$ (where $n = 2, 3, 4 \ldots$) and $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$, dissolve in sulfuric acid according to the reactions:

$$Me_2(SiO_3)_n + H_2SO_4 = Me_2(SO_4)_n + H_2SiO_3 + nH_2O \quad (8)$$

$$H_2SiO_3 = SiO_2 + H_2O, \quad (9)$$

as a result of which sulfates $CaSO_4$, $MgSO_4$, $Al_2(SO_4)_3$, and gel-like silica particles are formed.

The resulting production solutions contain sufficient copper (2.62 g/l in the Almaly PLS solution and 1.25 g/l in the Aktogay PLS solution) to be suitable for the solvent extraction process. However, along with copper, the solution contains undesirable impurities such as iron, silica, manganese, and others, which lead to a formation of third phase and deterioration quality of copper.

Experiments carried out using ACCORGA 5640 (5 and 10%) and Lix 984 reagents (10%) were chosen as extractants for selective extraction of copper from the obtained pregnant leached solutions, ACCORGA CR60 additive – to ACCORGA 5640 (10%) to suppress crud formation during extraction (Chepushtanova et al. 2023).

Figures 4 and Figure 5 show plots of metal extraction dependencies on the type of organic phase (ACCORGA 5640 (5% and 10% with addition ACCORGA CR 60) and Lix 984 (10%)).

Final transfer of Cu, Fe, and Si from the PLS to the electrolyte during the extraction/stripping process shown at Figure 6.

The results show rather high efficiency of extraction properties of ACCORGA 5640 component, at 10% concentration the extraction of copper from solution into organic phase is 97.7%, at the same time reduction of extractant concentration to 5% (in order to reduce the transfer of impurities from solution) allows to extract only 48.5% of copper.

Extractant Lix 984 (10%) extracted 85.1% of copper into organic phase from the solution. In spite of rather high extraction of copper, the extractant ACCORGA 5640 (10%) is associated with a rather large amount of iron compounds – 12.6%, the use of 5% concentration of ACCORGA 5640 with additional introduction of additive ACCORGA CR60 allows to reduce this figure to 7%.

The best selectivity for iron at the extraction stage is demonstrated by Lix 984 (10%), the transition of Fe^{2+}/Fe^{3+} ions is only 3.5%. As for silicate impurities, the lowest absorption was recorded when using 10% ACCORGA 5640 extractant – 27.8%, when using Lix 984 (10%), as well as 5% concentration of ACCORGA 5640, 38.2% of dissolved silicates get into the organic phase.

A significant part of silicate compounds, when conducting extraction with ACCORGA 5640 (5%) with the addition of additive ACCORGA CR60, remains in the organic phase –0.92 g/l. This significantly contributes to the formation and accumulation of crud at extraction and stripping stages.

In the case with application of 5% ACCORGA 5640 extractant and additive ACCORGA CR60, the minimum transfer of silicate compounds from solution to stripping is observed – 4.4%, the transfer of iron is 4.5%. In addition to SiO_2 in the organic phase at this combination of organic phase and additive, a rather high concentration of iron –4.3 g/l is formed.

Thus, the concentration of the initial main elements in Almaly solution was Cu –2.32 g/dm^3, Fe –17.97 g/dm^3, and Si –0.36 g/dm^3. The concentration of the main elements in the solution after liquid extraction with the addition of ACCORGA5640 + CR60 has been achieved: Cu –8.66 g/dm^3, Fe –7.69 g/dm3, and Si –0.11 g/dm^3.

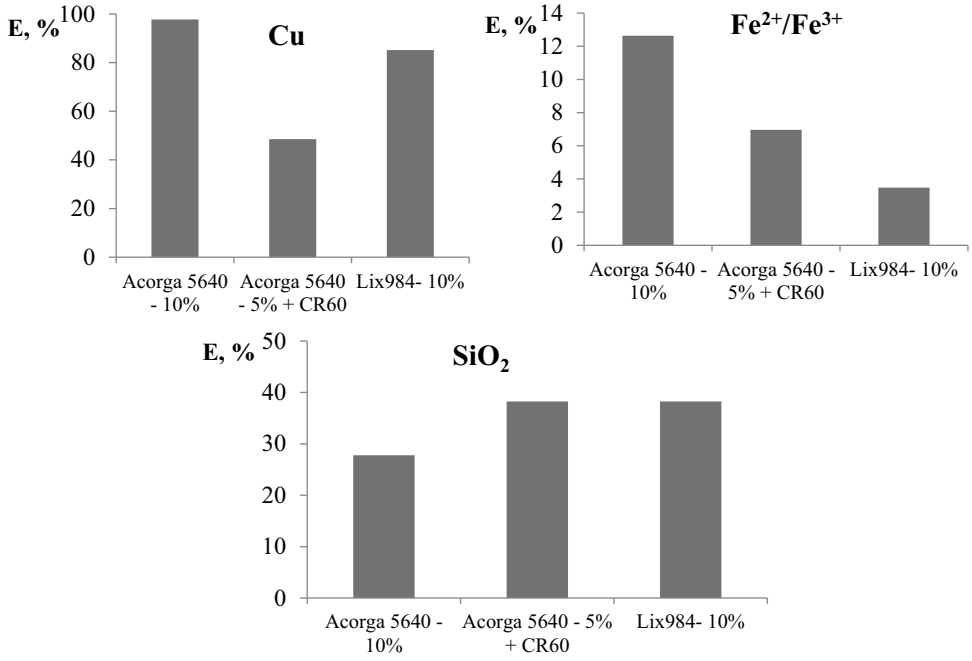


Figure 4. Extraction of copper and impurities from PLS with different extractants.

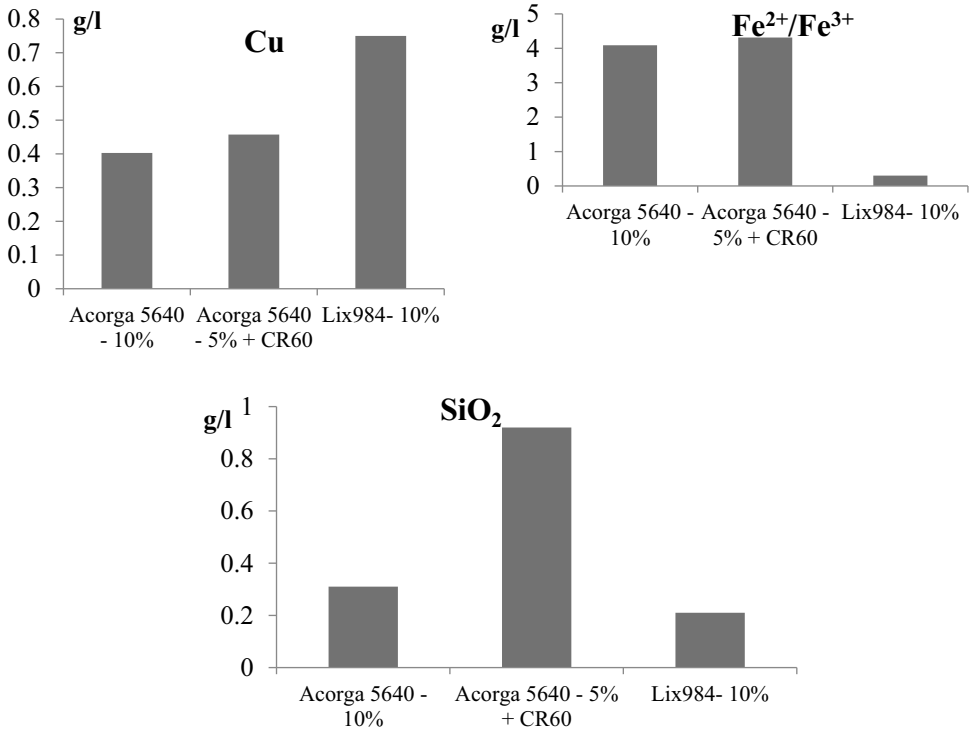


Figure 5. Residual content of Cu, Fe and Si in organic phase after stripping stage.

Balance calculation shows that in the process of extraction due to the high content of iron in the PLS, part of it begins to transfer to the organic phase. Therefore, the concentration of iron in saturated organic matter, when using extractants ACCORGA 5640, reaches 10–12 g/l while the Lix 984 does not exceed 3 g/l.

The results of extraction of copper and impurities with these extractants from the PLS Aktogay were similar.

Copper extraction isotherms

During the extraction process, on the one hand, the proton of the functional group of the reagent is replaced by the extracted metal, and on the other hand, there is additional coordination of the metal by donor atoms of the extractant molecule. The molecules of the chelating extractants Akorga and Lix contain the functional group =NOH, which belongs to 1) the group from which the extracted metal cation displaces hydrogen

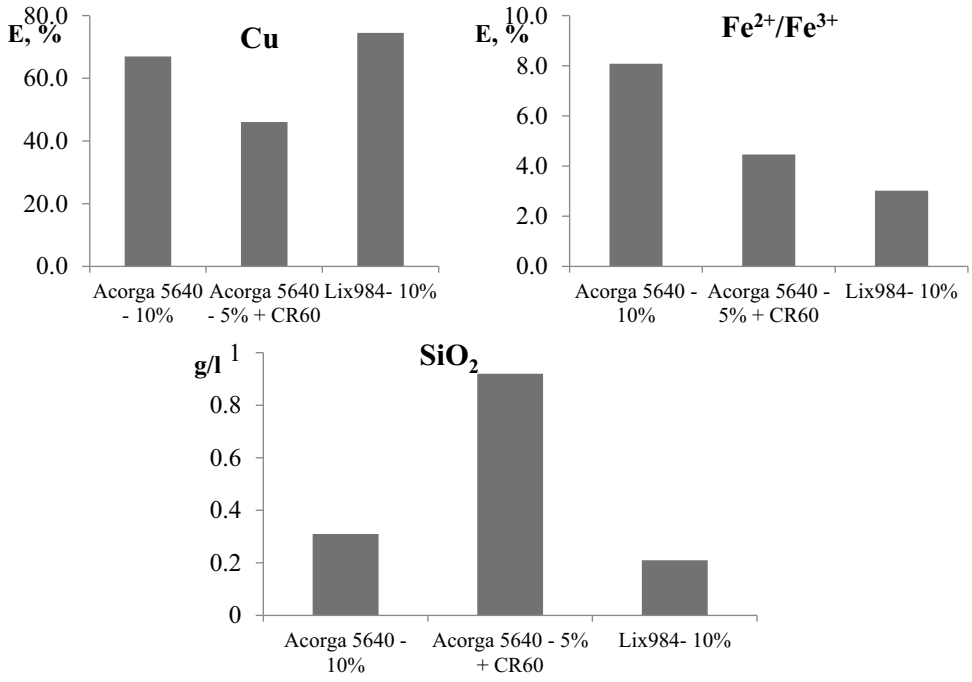


Figure 6. Final transfer of Cu, Fe and Si from the PLS to the electrolyte during the extraction/stripping process.

and 2) the group containing a nitrogen atom, which has an increased donor ability and forms a donor-acceptor bond with the metal connection. For this reason, extractants easily form a chelate complex with copper ions.

The process of copper extraction with oxyoxime extractants can be described by the following equation (Lazarova and Lazarova 2005):

$$Cu^{2+} + 2HR = CuR_2 + 2H^+ \quad (10)$$

When the aqueous and organic phases come into contact, iron extraction can occur according to the reaction:

$$Fe^{3+} + 3HR \rightarrow FeR_3 + 3H^+ \quad (11)$$

The formation of FeR_2 occurs quite quickly, however, the addition of a third extractant molecule to form FeR_3 is a rather slow process. Subsequently, iron is displaced from the complex with the extractant and replaced with copper (Arslan et al. 2004):

$$2FeR_3 + 3u^{2+} \rightarrow 3uR_2 + 2Fe^{3+} \quad (12)$$

However, with an excess of Fe^{2+} ions and extractant, some of the unsubstituted radicals can add iron ions, which will negatively affect subsequent processes. Therefore, solutions must be more thoroughly cleaned of iron before extraction. Extraction of magnesium, aluminum, and manganese ions is impossible due to the low stability of their complexes with oxyoxime extractants and their high selectivity to copper.

The most convenient graphical tool for analyzing and calculating the technological characteristics of the extraction system is isotherms McCabe-Tiele. Isotherms change characteristics of system (concentration of extractant, concentration of copper in organic and aqueous phases, pH value of initial aqueous phase, concentration of acid in aqueous phase, etc.) and depend on conditions of their structure.

To determine the number of stages of extraction and stripping for PLS, Almaly and Aktogay ore performed 12 experiments at the ratio of phases from O:A from 10:1 to 1:10. Copper extraction isotherms from two PLS were plotted based on the data on copper content in the organic phase and copper content in the aqueous phase (Figure 6a,b). The maximum saturation of organic phase with copper after three stages of extraction was 5.2 g/l for Almaly ore and 6.53 g/l for Aktogay ore.

To model the stripping isotherm, experiments were carried out at different O:A ratios using model sulfuric acid solution containing 35 g/l copper, sulfuric acid 170 g/l, and maximum copper-loaded organic solutions. After stripping at the ratio of organic and aqueous phases 5:1, we obtained a rich electrolyte with copper content of 50 g/l, which corresponds to the composition supplied for copper electrowinning.

To clarify the obtained data on isotherms, the modeling of copper extraction process was carried out according to the scheme of extraction stripping.

It was found that for PLS obtained during leaching of ores of Almaly (containing copper −2.32 g/l with pH 2.0) and Aktogay (containing copper −1.25 g/l with pH 2), it is necessary to carry out 3 stages of extraction and 1 stage of stripping (3E + 1S). Carrying out of processes on scheme 3E + 1S allows reaching through extraction of copper 78.54% from Almaly ore and 90.80% from Aktogay ore (Figure 7).

Modeling of extraction and stripping on PLS sample from Almaly mine is introduced in Figure 8.

McCabe-Tiele isotherms on PLS sample from Aktogay mine is introduced in Figure 9.

Modeling of extraction and stripping on PLS sample from Aktogay mine is introduced in Figure 10.

Crud formation. In the process of copper extraction by 3E + 1S scheme from both PLS, the formation of

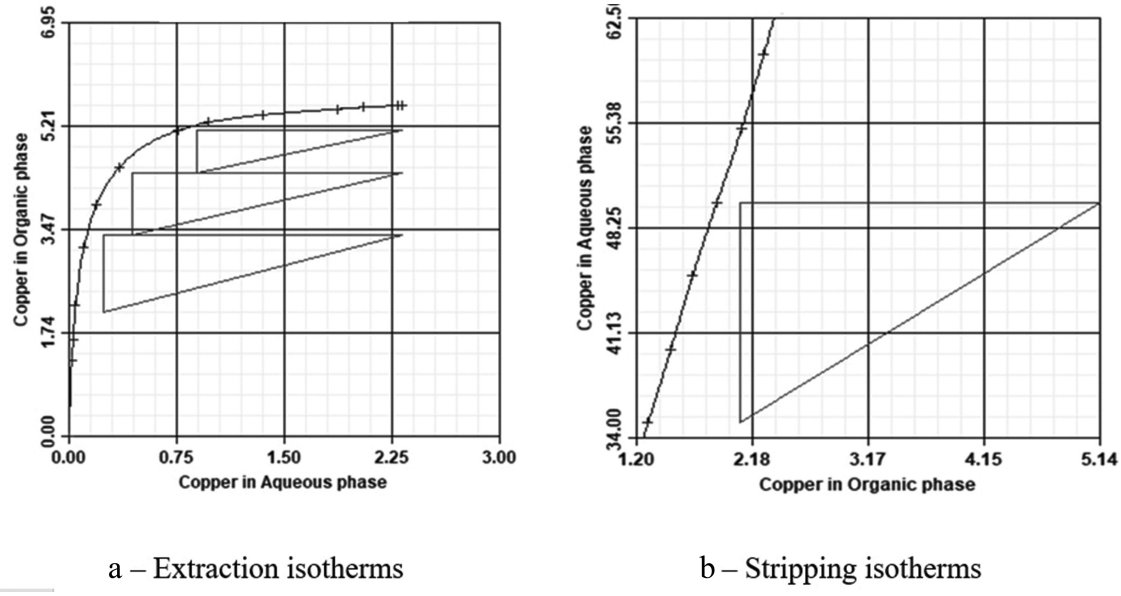


Figure 7. McCabe-Tiele isotherms on PLS sample from Almaly mine.

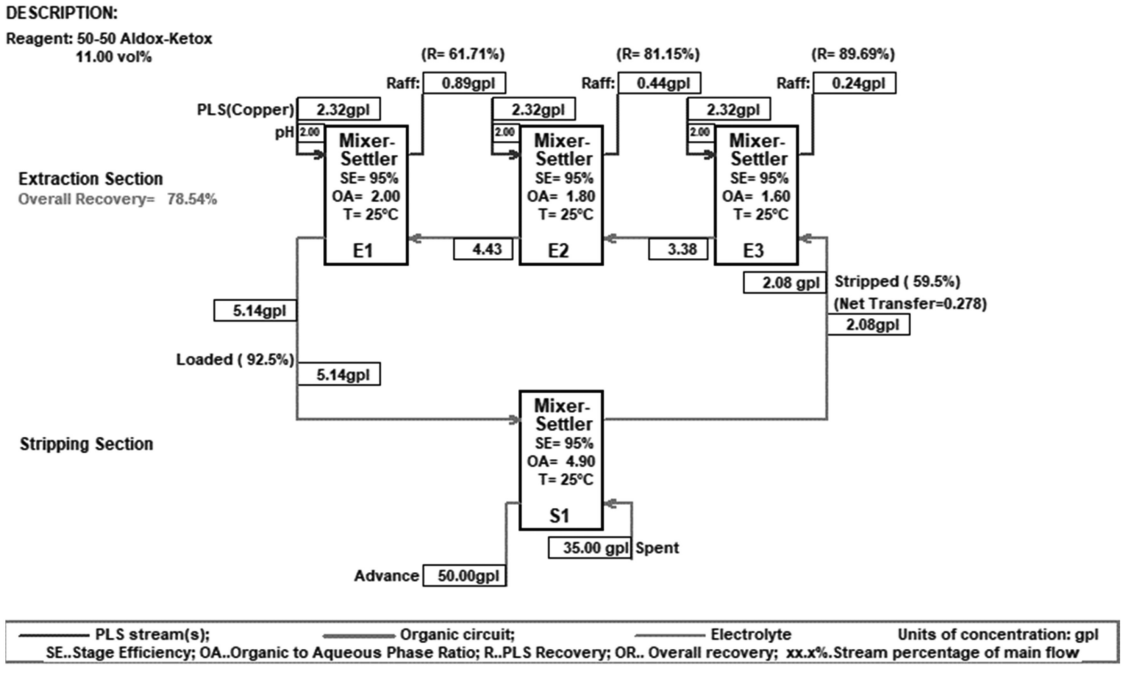


Figure 8. Modeling of extraction and stripping on PLS sample from Almaly mine.

interfacial suspension is observed (Figure 11). On visual observation, the structure of the crud was found to be amorphous, heterogeneous, light brown in color with organic phase content. The amorphous crud was filtered and dried at 120°C for 3 h and abraded to 1 mm for X-ray diffraction and microscopic analysis.

Detailed X-ray diffraction and chemical analyses of crud samples from PLS of Almaly and Aktogay ores confirmed the above conclusions that the main components are silica, sulfate, and oxyhydrate compounds of aluminum, magnesium, iron-bearing minerals magnetite and hematite, and others. (Table 3, Figures 12 and Figure 13).

The study of microstructures of samples of crud of Almaly and Aktogay mines by the method of electrodisperse electroscopy of characteristic X-ray phase radiation showed that indeed they contain quartz, aluminosilicates, and gypsum in greater quantities.

The presence of more silica in crud is due to the fact that the soluble form of silica is its monomer containing only one silica atom $Si(OH)_4$. At higher concentrations, monosilicic acid first forms polysilicic acids with low molecular weights with diameters less than 50A, and then polymeric varieties with higher molecular weights in the form of colloidal particles with diameters greater than 50A. The mutual

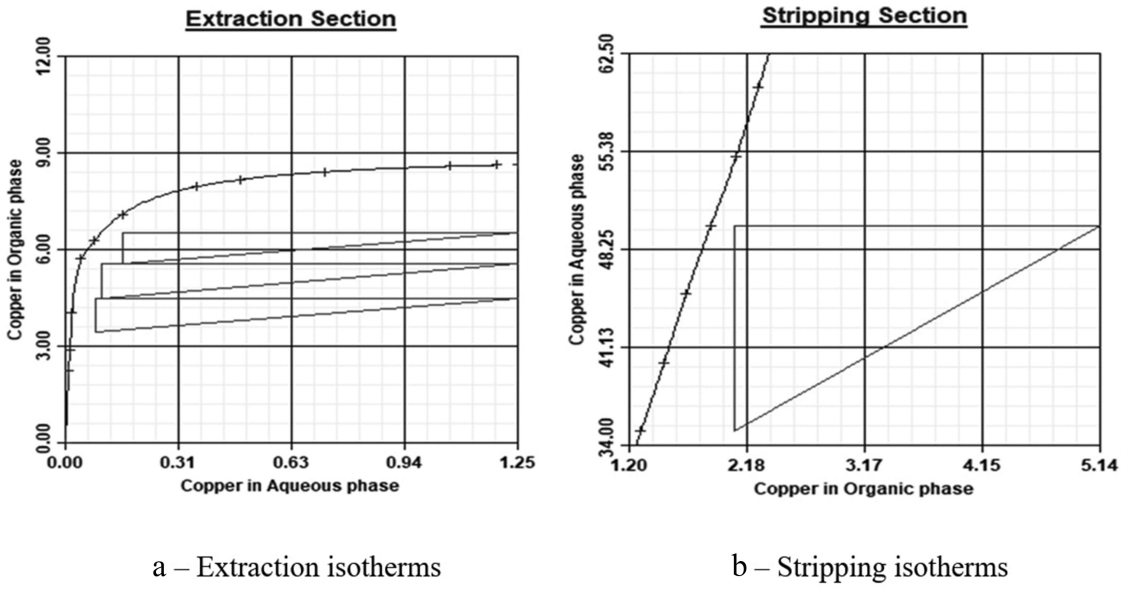


Figure 9. McCabe-Tiele isotherms on PLS sample from Aktogay mine.

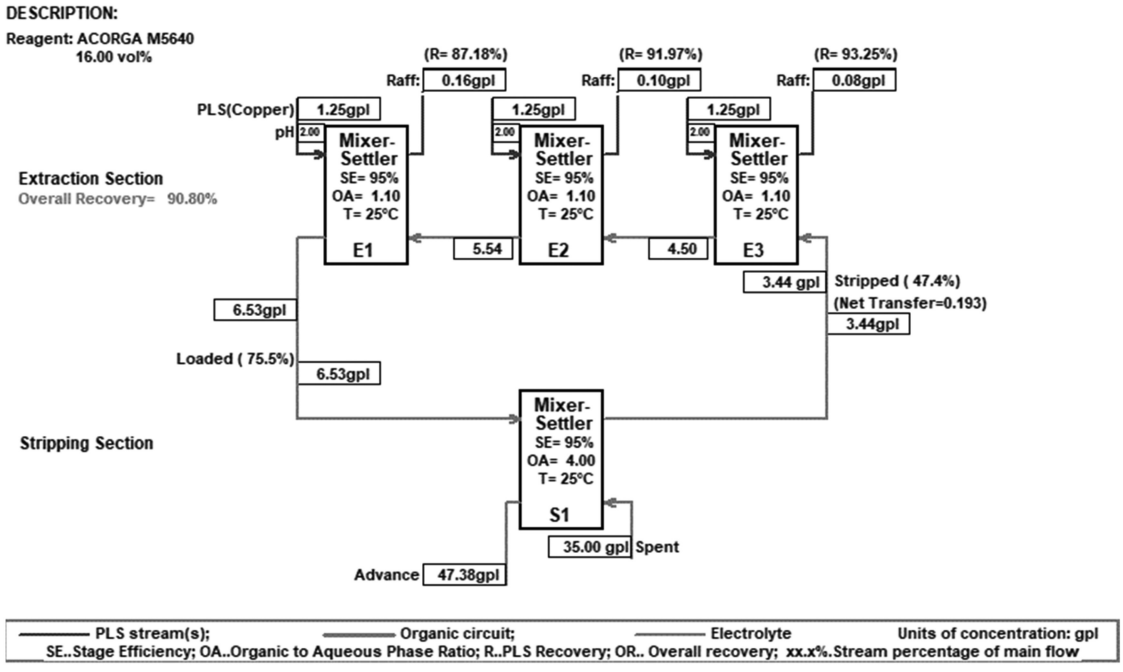
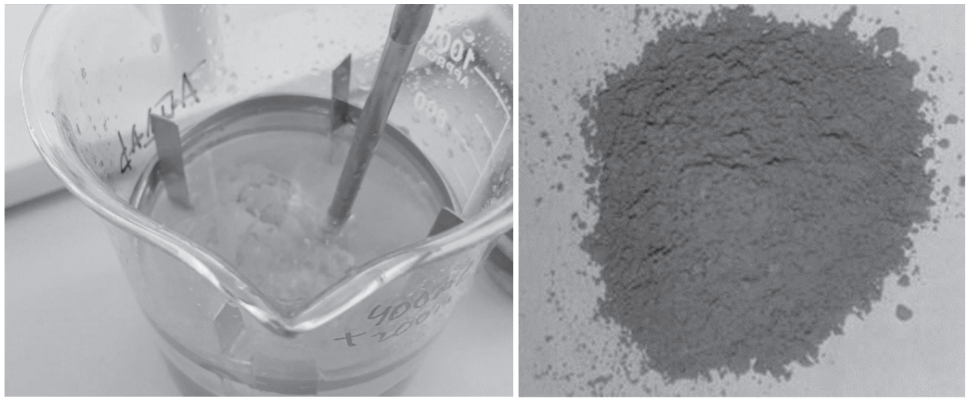


Figure 10. Modeling of extraction and stripping on PLS sample from Aktogay mine.

condensation of the monomer and low molecular weight silica polymers results in the formation of new small nucleated particles. Silica is deposited on them as well until the supersaturated ones are reduced. Because of this process, colloidal silica particles are formed during leaching and extraction, which in turn are able to aggregate to form a gel with a developed inner surface containing SiOH groups. Thus, 'hydrated' forms of silica are formed and very slow deposition leads to the formation of quartz. It was found that the rate of polycondensation of silica strongly depends on the pH of the system, the minimum value of the rate of polycondensation corresponds to the region of pH 2–3, and at pH below 2–3 the reaction is accelerated by H^+ ions, and at pH above 2–3 - by OH- ions (Autef et al. 2012; Eiler 1982).

The presence of oxi- and hydrate compounds of aluminum and magnesium in the crud composition is associated with the ability of their chemisorption on the surface of silica (Liu and Lan 2002).

Monosilicic acid also depending on the pH of the medium is able to combine with metal ions to an increasing extent, which explains the reason for the presence of copper and iron in the crud (Goss and Oliver 2023; Juhri et al. 2022; Stein et al. 2020).



a – crud formation during extraction stage b – crud after filtration and abrading

Figure 11. Crud formation and sample.

Table 3. Crud X-ray diffraction analyses from Almaly and Aktogay mines.

Compound Name	Formula	Almaly mine, %	Aktogay mine, %
Quartz. syn	SiO_2	76,11	73,02
Rostite	$Al(SO_4)(OH)\cdot 5H_2O$	12,30	13,34
δ-AlO(OH)	AlO(OH)		
Aluminum Oxide Hydroxide		7.52	6.68
Magnesium hydrosulfate	$Mg_3S_2O_8(OH)_2$	0.5	2.76
Iron oxides	FeO	1.43	1.19
Copper	Cu	1.6	2.11
Other		0.5	0.3

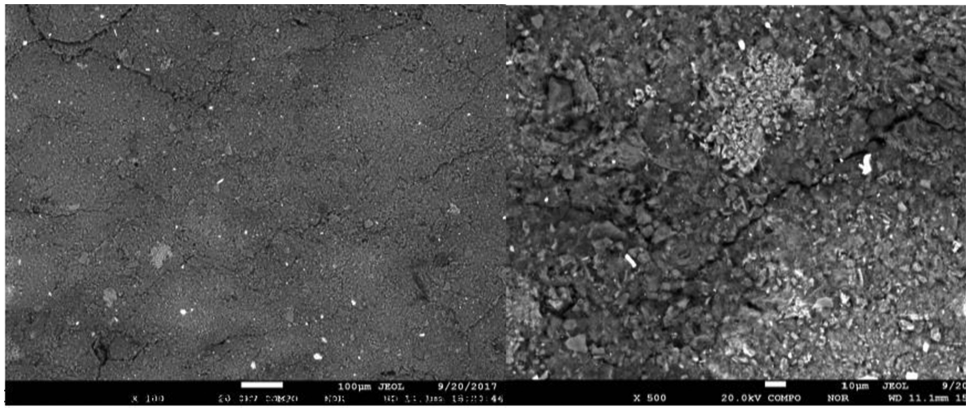


Figure 12. Microscopic structure of the crud. Image in secondary electrons at zoomed x100.

Gypsum is present in all the samples. This results in such a dense, viscous, and difficult to separate suspension, which directly affects copper recovery.

Organic compounds can either inhibit dissolution by coating the silica surface with a strongly adsorbed film, or accelerate it by binding the $Si(OH)_4$ monomer, which is in equilibrium with the surface, into a soluble complex.

The presence of a significant amount of extractant in the crud can be explained by the fact that the oxyoximes are able to form a chelate bond with the silica atom, or a hydrogen bond with the $Si(OH)_4$ and SiOH groups in polysilicic acid.

To suppress the crud, enlarged extraction experiments of copper extraction with ACCORGA5640 extractant were carried out using ACCORGA CR60 reagent.

As the results showed, the reduction of crud formation is noticeable already when it is added in the amount of 1 ppm and crud formation reduced up to 18–25%.

IR spectrometric studies of ACCORGA CR60 reagent showed (Figure 13), the presence of water absorption bands ν (OH) – 3428 cm^{-1}, δHOH –1647 cm^{-1}, sulfonate ion RSO_2O^- –1186, 1127, 1051, 1036, 1008, 672, 588 cm^{-1}, and Poly(sodium 4-styrenesulfonate) type compounds – 1496, 1451, 1411, 1186, 1127, 1036, 1008, 833, 773, 672, 588 cm^{-1} (Stuart 2004).

Polysodium 4-styrenesulfonate in terms of its properties refers to a cation-exchange polyelectrolyte that forms a soluble compound, sodium silicate (Figure 14a,b). The formation of this compound disrupts the polymerization of silicic acid, thereby leading to the conversion of crud solids into soluble forms (Figure 14b).

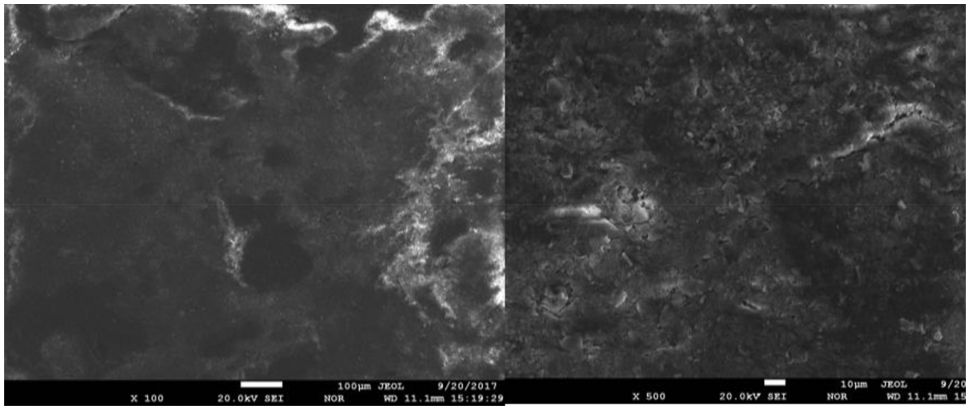


Figure 13. Microscopic structure of the crud. Backscattered electron image at x100 zoomed.

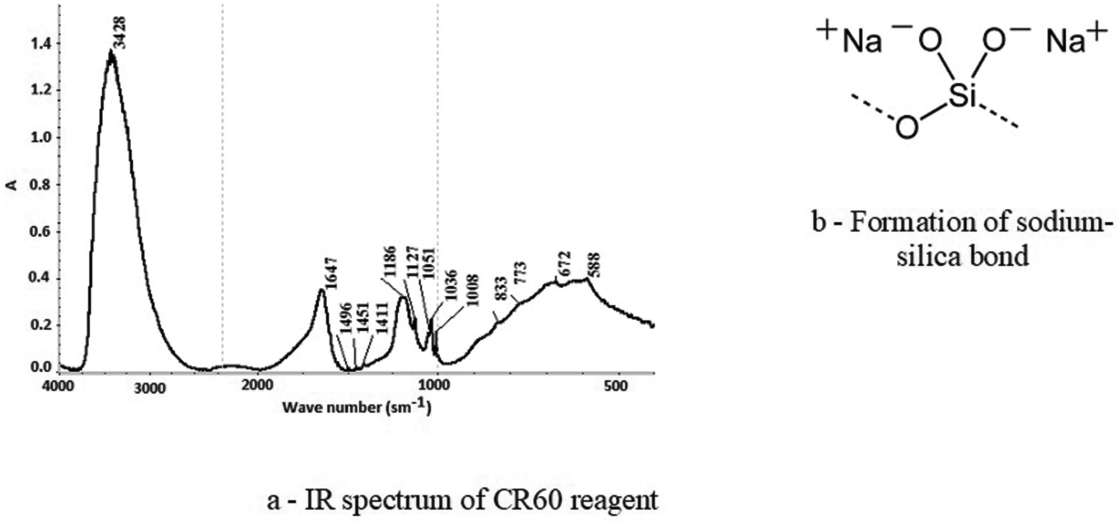


Figure 14. IR spectrum of CR60 reagent and formation of sodium-silica bond.

Table 4. Extraction of PLS solution with the addition of CR 60 reagent.

Extractant name	O:A	Raffinate volume, sm^3	Volume extract, sm^3	Concentration Cu in raffinate, g/dm^3	Extraction into extract, %
LIX 984 N	1:2	82	43	1,250	–
ACORGA M 5774	1:2	82	43	1,060	15
ACORGA M 5640	1:2	82	43	0,947	24

The final results of studying the process of copper extraction with various extractants in the presence of the CR 60 additive to reduce the formation of thefts are presented in Table 4.

As can be seen from Table 4, the best indicator for the extraction of copper into the extract corresponds to the extractant ACORGA M5640 and is 24%, followed by ACORGA M5774–15%. At the same time, the additive reduces the formation of thefts. The use of ACORGA CR60 reagent in an amount of 5 cm^3 in a productive sulfuric acid solution before its submission to the liquid extraction operation leads to a significant reduction in the formation of interfacial steal. The optimal technological parameters of the extraction process were determined: O:A ratio = 1:2, temperature 20 ± 5°C, CR60 additive volume – 5 sm^3, process duration 5 min, phase settling time 1 day. ACORGA M5774 (10 vol.%, diluent – kerosene) is used as an extractant. It is recommended to carry out countercurrent extraction, the number of stages is 2–3.

Conclusions

For extraction of copper from leach solutions of Almaly and Aktogay deposits, the optimal extractant is ACCORGA 5640.

According to the final extraction and stripping the transfer of the main components of the productive solution (copper ions, iron and silica), the extractants can be arranged in the following sequence:

for copper: ACCORGA5640 (5%) + CR60 < ACCORGA5640 (10%) < Lix 984N(10%)

for Fe: 10%Lix 984N < ACCORGA5640 (5%) + CR60 additive < ACCORGA5640 (10%)

by SiO_2: ACCORGA5640 (5%) + CR60 < ACCORGA5640 (10%) < Lix984N (10%)

For effective concentration and extraction of copper from PLS of Almaly and Aktogay mines, it is necessary to carry out 3 stages of extraction and 1 stage of stripping;

It is established that in the processes of solvent extraction of copper from PLS, sample from Almaly and Aktogay mines crud is formed, which create challenges during operation. The crud of both mines contain silica from 73 to 77%, copper from 1.6 to 2.11%, aluminum, magnesium, iron oxides, and organic phase.

It is possible to intensify the extraction of copper from PLS by solving the problem of crud formation with the use of hydrosulfate-salt mixture – edge-suppressing reagent ACCORGA CR 60 in the amount of 1 ppm, which leads to passivation of colloidal silica, by reducing polymerization and the formation of structure with oxygen.

By removing the waste mass from extraction, the saturated solution flow can be increased to 262,800 m^3 per year and an additional 525.6 tons more copper cathode can be produced. In monetary terms, 525.6 tons of copper cathode will amount to about 3 million 700 thousand US dollars. The practical significance of the research results lies in the intensification of the processing processes of copper heap leaching solutions at SX-EW enterprises in Kazakhstan and abroad. The reduction in copper costs reaches up to 40% when using a theft suppression mechanism. Research is aimed at achieving the goal of strategically increasing annual copper production by 15–20% under the SX-EW scheme.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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