Investigations of extraction of copper and crud formation components of productive solution of Almaly deposit

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The SX-EW technology is more effective for the production of copper from refractory oxidized ores for the present day. A wide range of modern extractants is currently offered on the market for the extraction of copper from leaching solutions and its choice is a very important issue in the production of copper using the SX-EW technology. The aim of this work was to study the extraction properties of modified extractants of the Acorga series (5747, 5910, 5640) and unmodified extractant Lix 984N. It has been established that extractants Acorga 5640 and unmodified Lix984 have high selectivity to copper.
During the extraction of copper from the productive solution with the use of all extractants, the formation of a third phase, cruda, is observed. Physical and chemical studies have established that the steak contains a large amount of silica, magnetite, hematite and anglesite.
The distribution of iron, silica, and copper ions during extraction was studied and it was found that the extractant Lix 984 N (10%), then Acorga5640 (10%), has a high selectivity to copper/iron and copper/silica.
Acorga 5640 (10%) is an effective extractant of copper from the productive solution of the Almaly deposit. It is observed that the amount of crud formed during extraction also depends on the rate of phase mixing, the number of revolutions of the stirrer, at a speed of 350-450 rpm, the formation of crud is 0.73%. The addition of the Acorga CR60 reagent in the amount of 5-10 ppm leads to a 3-3.2-fold decrease in the volume of the crud.

Key words: copper, SX-EW technologies, extraction, extractants Acorga, Lix 984 N, selectivity, crud.

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Introduction

Currently, the development of the ore base throughout the world is associated not only with the commissioning of new rich deposits, but, first of all, with the involvement in the processing of previously unprocessed poor oxidized ores, dumps of substandard ores, overburden mineralized rocks, enrichment tailings, waste from metallurgical production and so on. using cost-effective SX-EW technology consisting of leaching, extraction and re-extraction, electrolysis stages [1, 2].

Currently, extraction processes are widely used in hydrometallurgy, especially on a large scale — in the production of copper [3], as well as radioactive elements, but also metals such as zirconium, hafnium, niobium, tantalum, tungsten, molybdenum, indium, rhenium, as well as rare earth and noble metals [4–7]. The share of copper produced using SX-EW technology in the world has already reached 30% of the total copper production and this is due to numerous developments in the field of synthesis of selective extractants. In the production of cathode copper using the SX-EW technology, chelate extractants based on oxyoximes with and without modifiers are mainly used [8].

In Kazakhstan, the first copper production using SX-EW technology was introduced in 2004. Major projects implemented in recent years include the exploitation of oxidized ore dumps at the Kounrad deposit [9], heap leaching of open pit oxidized ores at the Aktogay and Bozshakol deposits, and heap leaching of crushed ore at the Ayak-Kodzhan, Ai and Aktogay deposits [10]. As the practice of operating enterprises shows, productive solutions obtained by leaching copper ores contain a number of elements, compounds and suspended solids, some of them can create problems during extraction [11, 12] or electrolysis [13], one of which is the formation and accumulation of the third phase (crud) in the liquid extraction unit. The formation of a crud often leads to a suspension, sometimes even to a complete stop, of the extraction process. Studies have established that in the processes of liquid extraction, harmful impurities of metals in the productive solution, namely, iron, silica, manganese ions [13], etc., solid suspensions, which were formed during leaching and insufficient settling of water flows [14], lead

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to the formation of crud. improper selection of the organic phase (extractant and diluent) [15], operating mode of the extraction unit, etc. [16]. Various methods were used to suppress and remove crud: precipitation and removal of harmful metal impurities [17], selection of the organic phase with the addition of various modifiers [18], addition of flocculants [19], air blowing to prevent the formation of a dense suspension, changing the flow rate of organic and aqueous phases [19], etc. To prevent and remove crud, selective extractants, dilution of the aqueous phase, or the addition of surfactants can be used [18–20]. The authors of [21] found that the processes of settling and pumping out the interfacial suspension were effective for the removal of silica-based thief; processing it periodically, as it accumulates. Then, in order to separate the liquid phase and break the emulsion, the crud was diluted with an acidic solution, filtered, and the liquid phase was pumped out and returned to the extraction process. The remaining suspension with a small content of the extractant was stored for further disposal.

As the analysis of literary sources has shown, so far there is no single method for preventing or removing theft in SX-EW technology. Conducting research in the direction of the selection and use of a selective extractant with the study of the distribution of harmful impurities of metal ions and silica remains an urgent problem.

The purpose of this work is to study the process of copper extraction from the productive solution of the Almaly deposit with the study of crud-formation components with extractants of the Acorga and Lix984N group.

Methodology

Leaching experiments

The object of the study were solutions of heap leaching of the Almaly deposit, as well as reagents of the organic phase: extractant Acorga M 5910, Acorga M 5747, Acorga M 5640, Lix 984; lighting kerosene brand KO-30 (as a solvent for extractants).

Samples of oxidized copper ores from the Almaly deposit with a copper content of 0.38% were chosen as the feedstock for obtaining a productive copper solution.

The extraction and re-extraction processes were carried out in a laboratory extractor of the EL-1 brand and on a pilot extraction plant of the Cytec Solvay Group Company.

In order to determine the selectivity of each type of extractant, as well as a sample for comparing the duration of phase separation, in addition to the productive solution from the field, a prepared model solution was used. The specified concentration of copper in the model solution was 1 g/l, total iron was 2.4 g/l (Fe^{2+} : $Fe^{3+} \approx 1 : 1$), the pH was adjusted to 1.7 by adding 0.1 N sulfuric acid (according to pH = 1.7 in the productive solution) and with constant control of the pH of the solution with a 160 MP ionomer. To prepare a model solution, copper sulfate $CuSO_4$ $5H_2O$ was used in terms of the molecular fraction of copper (25%) – 4 g/l of copper sulfate to achieve 1 g/l of Cu^{2+} ions. Iron salts $FeSO_4$ $5H_2O$ were dissolved in a similar way to achieve the specified concentration of Fe^{2+}/Fe^{3+} ions = 2.4 g/L. 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: clean for analysis or chemically clean – high purity reagent.

The analysis of initial model and productive solutions, as well as aqueous phases obtained in the process of extraction/re-extraction was carried out using chemical, photocolorimetric analyses. Solid samples of the original ore, solid sediment after evaporation of the productive solution, as well as crud were examined using *X*-ray fluorescence, *X*-ray phase analyses; determination of the viscosity of organic phases and aqueous phases was carried out on a laboratory viscometer.

To determine the main elemental composition of the sample of the productive solution, a complete evaporation was carried out until the formation of dry salts. The resulting salts were crushed to a particle size of no more than 0.1 mm and used for *X*-ray fluorescence analysis.

X-ray fluorescence semi-quantitative analysis was carried out on a wave-dispersive *X*-ray fluorescence spectrometer Axios 1 kW from PANalytical (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.

The extraction of metals was calculated from the balance of the distribution of metals between the organic and aqueous phases.

Results and discussion

Physical and chemical analysis of porphyritic oxidized copper ore from the Almaly deposit showed that the copper content in the ore is low and amounts to 0.38%. The main copper minerals are, %: chalcanthite 7.9; malachite and azurite – 65.8; chrysacolla 18.4; primary and secondary copper sulfides (chalcocite, covellite) – 5.3; chalcopyrite – 2.6. The main component of the waste rock was silica – 66.18%, oxides of iron and mica.

As is known, for the processing of this type of ore, non-oxidizing leaching using mineral acids [22] is quite acceptable, and copper extraction with a high degree is a combination of reagents [23]. Due to the low content of copper sulfide minerals (7.9%) in the ore, sulfuric acid non-oxidizing leaching was chosen. To obtain a productive solution, a countercurrent multi-stage leaching of oxidized ore with a solution of sulfuric acid with a concentration of 25 g/l was carried out, as a result of which a productive solution was obtained, composition, g/dm^3: Cu – 2.62; Fe –17.97 and SiO_2 – 0.36.

Chemical analysis of the productive solution shows that the copper content in the solution is low, the amount of iron exceeds the copper content by almost 7.5–8.25 times, which is a problem in the extraction of copper [24].

The content of manganese (0.386%), nickel (0.016%) and zinc (0.006%) is very low, in connection with this, only the behavior of iron and silicon ions in the extraction and re-extraction processes was studied.

The efficiency of the metal extraction process is affected by many factors, such as the selectivity of the extractant, the pH of the medium, the duration of mixing and phase separation, the concentration of extractants, the ratio of aqueous and organic phases, etc. [25].

In order to determine the selectivity of each type of extractant, preliminary studies were carried out to determine the selective extractant using the Acorga (5747, 5910, 5640) and Lix 984 reagents. Lighting kerosene of the KO-30 brand served as a diluent.

Studies on the extraction of metals from solutions were carried out under the following conditions: the concentration of extractants was 10%, the ratio of the aqueous and organic phases $O : A = 1 : 1$, the duration of mixing of the organic and aqueous phases was 5 minutes, the temperature was 20 °C, pH was 1.7.

In the course of primary experiments to determine the selectivity of extractants, a longer separation time of the aqueous and organic phases was noted during the extraction of copper from the productive solution. Depending on the composition of the extractant and the productive solution, the duration of the separation of the organic and aqueous phases can be different, the longer the duration, the higher the probability of reducing the efficiency of the process. Complete separation of the aqueous and organic phases was observed only after more than 5–7 minutes, while on a model solution, complete phase separation was achieved in 20 seconds. At the same time, the phase separation time recommended for hydrometallurgical production of cathode copper using the SX-EW technology should not exceed 30 seconds. In addition to the long-term separation of the phases, the fuzziness of the interfacial interface was also observed – in the upper layer of the aqueous phase, there were noticeable traces of the organic phase, by analogy with the interfacial suspension described in [3] – crud. A visual phase separation during the extraction process is shown in **Fig. 1**.

The research results are shown in **Fig. 1** and **Table 1**.

The studies carried out to determine the duration of phase separation after extraction led to the following results: complete separation of the aqueous and organic phases in productive solutions **(Fig. 2, *a*)** occurred over a longer time (after more than 5-7 minutes), while complete separation of the phases on the model solution was reached in 20 seconds **(Fig. 2, *b*)**. In addition to a longer time separation of phases in productive solutions, an indistinct interfacial separation was also observed — in the upper layer of the aqueous phase, there were noticeable traces of the third phase, i. e. interfacial suspension crud.

During the subsequent re-extraction of the organic phase with a solution of sulfuric acid with a concentration of 200 g/dm^3 and regeneration of the electrolyte by washing the organics with a 20% solution of sulfuric acid, phase separation occurred within the required duration of no more than 30 seconds. At the same time, the re-extract obtained during the re-extraction of the loaded organic

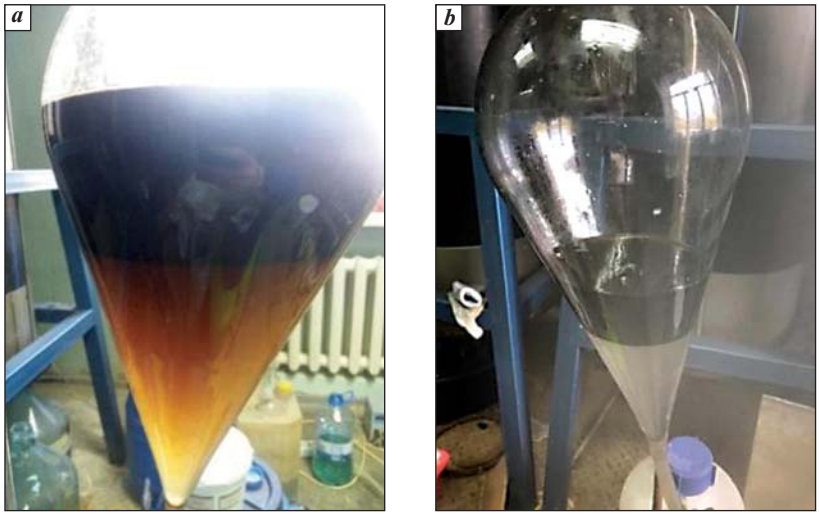


Fig. 1. Separation of organic and aqueous phases, productive and model solutions in a separating funnel:
a – productive solution; *b* – model solution

Table 1
Extraction of copper with various extractants from model solutions

Extractant	$C_{(Cu)p.s.}$*	$V_{p.s.}$*	$C_{(Cu)raf.}$*, g/l	$O : A$*	Number of stages, n	$E_{(Cu)ext.}$*, %
Acorga 5910 – 10%	1.0	0.6	0.15	1 : 1	3	85.0
Acorga 5747 – 10%	1.0	0.6	0.15	1 : 1	3	85.0
Acorga 5640 – 10%	1.0	0.6	0.09	1 : 1	3	91.0
Acorga 5640 – 5%	1.0	0.6	0.06	1 : 1	3	94.0
Lix984N – 10%	1.0	0.6	0.07	1 : 1	3	93.0

* $C_{(Cu)p.s}$ – concentration of copper in the productive solution; $C_{(Cu)raf.}$ – concentration of copper in the raffinate (in aqueous solution after extraction); $V_{p.s.}$ – volume of productive solution; $O : A$ – ratio of organic and aqueous phases; $E_{(Cu)ext.}$ – the degree of extraction of copper during extraction.

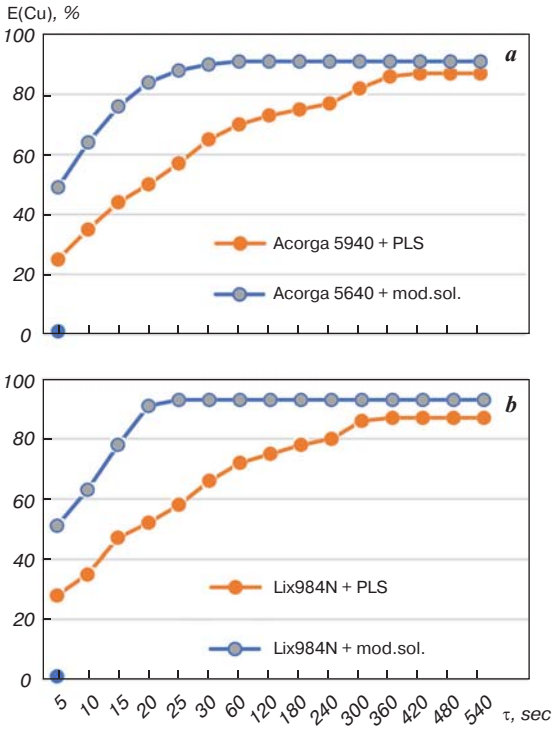


Fig. 2. The dependence of the degree of extraction of copper on the duration of the separation of the organic and aqueous phases during the extraction of copper Acorga 5640 (*a*) and Lix984N(*b*)

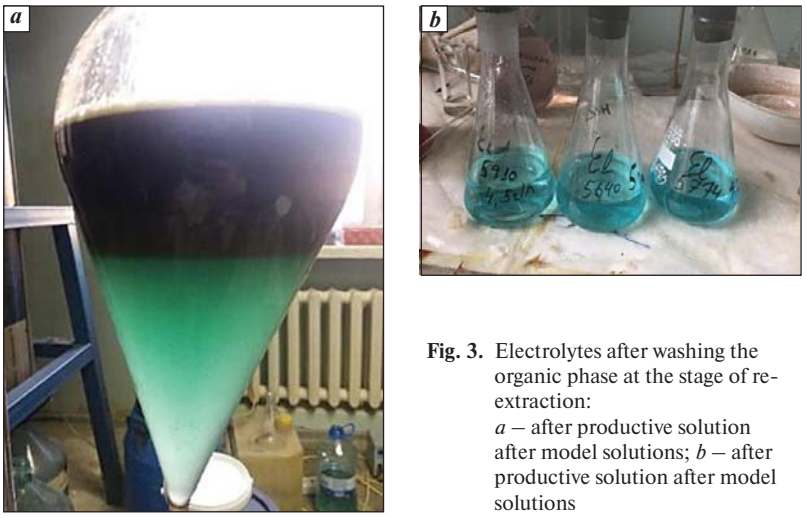


Fig. 3. Electrolytes after washing the organic phase at the stage of re-extraction:
a – after productive solution after model solutions; *b* – after productive solution after model solutions

phase after the extraction of the productive solution differed markedly in color from the electrolytes obtained during the processing of model solutions. The green color indicated the possible transfer of a significant amount of iron ions into the reextract; in the model solutions after the re-extraction, the blue color more characteristic of copper sulphate prevailed **(Fig. 3)**.

In practice, the freshly prepared organic phase is translucent with a slight yellowish tint, changing to a light brown color when it is first introduced into the liquid-extraction cycles. In the organic phase after the stripping step there will always be some amount of copper from 0.2 to 0.5 g/l. This amount of copper is quite acceptable, and there should be no tendency to increase the concentration of constantly present copper.

The results of copper extraction from model solutions are shown in **Table 1**.

As the results of copper extraction from the model solution show, the maximum extraction of copper (94%) is observed when using the extractant 5% Acorga 5640, while the extractants 10% Acorga 5910 and 10% Acorga 5747 did not provide a high degree of extraction – the extraction of copper does not exceed 85% in both cases. 10% Acorga 5640 and 10% Lix984N showed relatively high copper recovery of 91% and 93% respectively.

The re-extraction of copper from the organic phase was carried out with a solution of sulfuric acid with a concentration of 200 g/dm^3, at a ratio of organic and aqueous phases $O : A = 2 : 1$, in 3 stages, the duration of stirring was 5 minutes, and the temperature was 20 °C.

The results of copper stripping from the organic phase and the residual concentration of copper in the organic phase using each extractant are shown in **Table 2**.

The results of the back-extraction process show that a high degree of copper extraction from the organic phase (90.2% or more) was ensured when using extractants 10% Lix984N and 10% Acorga 5640, the minimum was achieved with 10% Acorga 5910 (88.2%). To select the optimal extractant, we calculated the residual

Table 2
Results of stripping and residual concentration in the organic phase

Extractant	$C_{(Cu)o.ph.}$*, g/l	$V_{o.ph.}$*, l	$C_{(Cu)re.}$*, g/l	$V_{el.}$*, l	$O : A$*	Number of stages, n	$E_{(Cu)re.}$*, %	$E_{(Cu)e.}$*, %
Acorga 5910 – 10%	2.55	0.2	4.5	0.1	2 : 1	3	88.2	75.0
Acorga 5747 –10%	2.55	0.2	4.6	0.1	2 : 1	3	90.2	76.7
Acorga 5640 –10%	2.73	0.2	5.0	0.1	2 : 1	3	91.6	83.3
Lix984N – 10%	2.79	0.2	5.14	0.1	2 : 1	3	92.1	85.7

*$C_{(Cu)o.ph.}$ – concentration of copper in the organic phase; $V_{o.ph.}$ –volume of organic phase; $C_{(Cu)re.}$ – concentration of copper in the re-extract (in aqueous solution after stripping); $V_{el.}$ – volume of electrolyte; $O : A$ – ratio of organic and aqueous phases; $E_{(Cu)re.}$ – degree of extraction of copper during re-extraction; $E_{(Cu)e.}$, % – end-to-end extraction of copper after extraction and re-extraction.

Table 3
Residual concentration of copper in the organic phase

Extractant, organic phase	Acorga 5910 – 10 %	Acorga 5747 – 10 %	Acorga 5640 – 10%	Lix984N – 10%
$C_{(Cu)r.c.}$*, g/l	0.30	0.25	0.23	0.22

*$C_{(Cu)r.c.}$ – residual concentration of copper in the organic phase

Table 4
Results of copper extraction from a productive solution with an extractant 10% Acorga 5640

Components	$C_{Cu^{2+}}$ in p.s.*, g/l	$C_{Cu^{2+}}$ in raffinate, g/l	E*, %	D*	β*
Cu	0.262	0.006	97.7	42.67	–
Fe	17.97	15.7	12.6	0.14	305
SiO_2	0.36	0.26	27.8	0.38	112

*p.s. – productive solution, E – extraction degree, D – distribution ratio, β – separation factor.

Table 5
Results of stripping and residual concentration of components in the organic phase

Components	$C_{Cu^{2+}}$ in p.s.*, g/l	V organic phase, l	$C_{Cu^{2+}}$ in reextract, g/l	E*, % (from organic phase)	D*	E, % (through)
Cu	1.28	1	0.877	68.5	2.20	66.9
Fe	11.35	1	7.26	64.0	1.77	8.1
SiO_2	0.5	1	0.19	38.0	0.61	10.6

*p.s. – productive solution, E – extraction degree, D – distribution ratio.

Table 6
Residual concentration of components in the organic phase with Acorga 5640 extractant

	Cu	Fe	SiO_2
Residual concentration in the organic phase, g/l	0.4	4.09	0.31

concentration in various organic phases. The residual concentration of copper in the organic phase with various extractants is shown in **Table 3**.

Based on the results of comparing the residual concentrations of copper in organic phases, the following efficiency series for the use of extractants can be established: 10% Lix984N > 10% Acorga 5640 > 10% Acorga 5747 > Acorga 5910.

Thus, the data in **Table 1** shows the greatest efficiency when using 10% Lix984N and 10% Acorga 5640.

Further studies on the extraction of copper from a productive solution of the composition g/l: Cu^{2+} 0.262; $Fe^{2+/3+}$ 17.97; colloidal insoluble silicates 0.36 were performed using extractants Acorga 5640 and Lix984N in kerosene.

For concentration and refining of such a composition of the productive copper solution, extraction with a reagent having high selectivity is acceptable. For research, we chose Acorga 5640 brand extractants (consists of mixtures of aldoximes and a modifier) and Lix984N (a mixture of equal parts of aldoximes and ketoximes), which have high selectivity to copper, fast extraction and phase separation kinetics, high flash point, etc.

The total volume of the solution supplied for extraction was 5000 ml. The O:B ratio was set using streams and was equal to 1 : 1, the number of stages was 3, the pH of the solution was 1.7. The results of experiments on the extraction of the components of the productive solution are shown in **Table 4**.

Experimental results **(Table 4)** shows a high selectivity of the extractant 10% Acorga 5640 to copper ions. Despite the high degree of copper extraction (97.7%), 12.6% of iron and 27.8% of silicate compounds passed into the organic phase from the productive solution.

The re-extraction of copper, iron and silica was carried out with a solution of sulfuric acid with a concentration of 200 g/dm^3 The results of stripping and the residual concentration of the components in the organic phase are shown in **Table 5**.

The residual concentration of the components in the organic phase with the Acorga 5640 extractant is shown in **Table 6**.

At the stage of re-extraction **(Table 5)**, 64% of iron from the organic phase passed into the electrolyte with an iron concentration of 7.26%. The residual concentration of iron in the organic phase was 4.09 g/L. The silicate compounds extracted from the productive solution subsequently also passed into the re-extract (38%), the rest (62%) contaminating the organic phase, formation an interfacial third phase – crud. The residual content of silicate compounds in organic matter was 0.31 g/l, **Table 6**.

In addition to the accumulation of crud, an incomplete transition of copper into the electrolyte was also observed at the stage of re-extraction. Part of the copper simultaneously with the ions of silica and iron entered the formed crud.

Table 7
The results of the extraction of components from the productive solution with the extractant Lix 984N (10%)

Components	$C_{Cu^{2+}}$ in ave. solution, g/l	*V* productive solution, l	C_{Me} in raffinate, g/l	*V* raffinate, ml	*O : A*	*E*, %	*D*	β
Cu	0.262	0.6	0.04	0.6	1:01	85.1	0.85	–
Fe	17.97	0.6	17.34	0.6	1:01	3.5	0.04	24.31
SiO_2	0.36	0.6	0.22	0.6	1:01	38.2	0.38	2.23

Table 8
Results of stripping and residual concentration of components in the organic phase of Lix 984 (10%)

Components	C_{Me} in the organic phase, g/l	*V*, organic phase, l	C_{Me} in re-extract, g/l	*V* re-extract, l	*O : A*	*E*, %	Through extraction, *E*, %
Cu	6.0	0.2	7.0	0.15	2 : 1,5	87.5	74.5
Fe	2.25	0.2	2.6	0.15	2 : 1,5	86.7	3.0
SiO_2	0.39	0.2	0.24	0.15	2 : 1,5	46.2	17.6

Table 9
Residual concentration of components in the organic phase with Lix 984N extractant (10%)

Residual content of components in the organic phase Lix 984-10%, g/l	Cu	Fe	SiO_2
	0.75	0.3	0.21

Table 10
Phase composition of the crud

Phase name	Chemical formula	Content, %
Quartz	SiO_2	63.98
Englishite	$Pb(SO_4)$	14.94
Magnetite	Fe_3O_4	13.73
Hematite	Fe_2O_3	7.35

Table 11
The result of *X*-ray fluorescence analysis theft (formation of interfacial waste)

Components	Content,%	Components	Content, %
O	40.08	Co	0.010
Na	0.329	Cl	0.168
Mg	0.608	K	0.256
Al	2.037	Ca	0.175
Si	23.46	Ti	0.228
P	0.078	Cr	0.021
S	5.829	Br	0.006
Mn	0.058	Zn	0.008
Fe	1.357	W	0.335
Ni	0.073	Mo	0.016
Cu	2.686	Sr	0.007
Zr	0.006	Pb	0.009

In parallel, as a comparative sample, studies were performed on the extraction and re-extraction of copper using the extractant Lix 984N (10%) on the studied productive solution. The research results are shown in **Tables 7–9**.

The residual concentration of the components in the organic phase with the extractant Lix 984N (10%) is shown in **Table 9**.

As the results of the extraction of copper and impurities with Lix 984N extractant (10%) show, the final degree of copper extraction is high (74.5%) compared with Acorga 5640 extractant (10%) (69.9%).

To clarify the transition of copper, iron and silica ions into an interfacial suspension, we carried out physical and chemical studies to establish the phase composition of the crud, the results of which are presented in **Table 10**.

As the results of *X*-ray phase analysis show **(Fig. 4)**, the crud is dominated by quartz 63.98%, a certain amount of lead mineral anglesite – 14.94%, iron-bearing minerals magnetite – 13.73% and hematite – 7.35%.

X-ray fluorescence analysis showed **(Table 11)** that the content of silicon and oxygen prevails in the crud sample, which confirms the presence of a large amount of oxygen, sulfur, iron and silicon.

Comparing the analyzes of the elemental composition of the solid sediment of the productive solution and the crud, it can be noted that the composition of the crud contains high levels of oxygen, sulfur, iron and silicon.

The results obtained demonstrate a rather high efficiency of the extraction properties of the Acorga5640 component (10%), the extraction of copper from solution into organics is 97.7%. The extractant Lix 984N (10%) extracts 85.1% copper from the solution into the organic phase. Despite the rather high extraction of copper, the extractant Acorga 5640 (10%) simultaneously binds with a fairly large number of iron compounds – 12.6%, Lix 984N (10%) demonstrates the best selectivity for iron at the extraction stage, the transition of Fe^{2+}/Fe^{3+} ions is only 3,5 %. For silicate impurities, the lowest absorption was recorded when using Acorga5640 (10%) – 27.8%, and when using Lix 984 (10%), the highest – 38.2%. But the residual concentration of silica in the organic phase when using Acorga 5640 (10%) is 1.5 times higher compared to Lix 984 N and is 0.31 and 0.21 g/l, respectively.

The concentration of iron in saturated organics, when using Acorga 5640 (10%) extractants, reaches 10–12 g/l, while in Lix 984N (10%) it does not exceed 3 g/l.

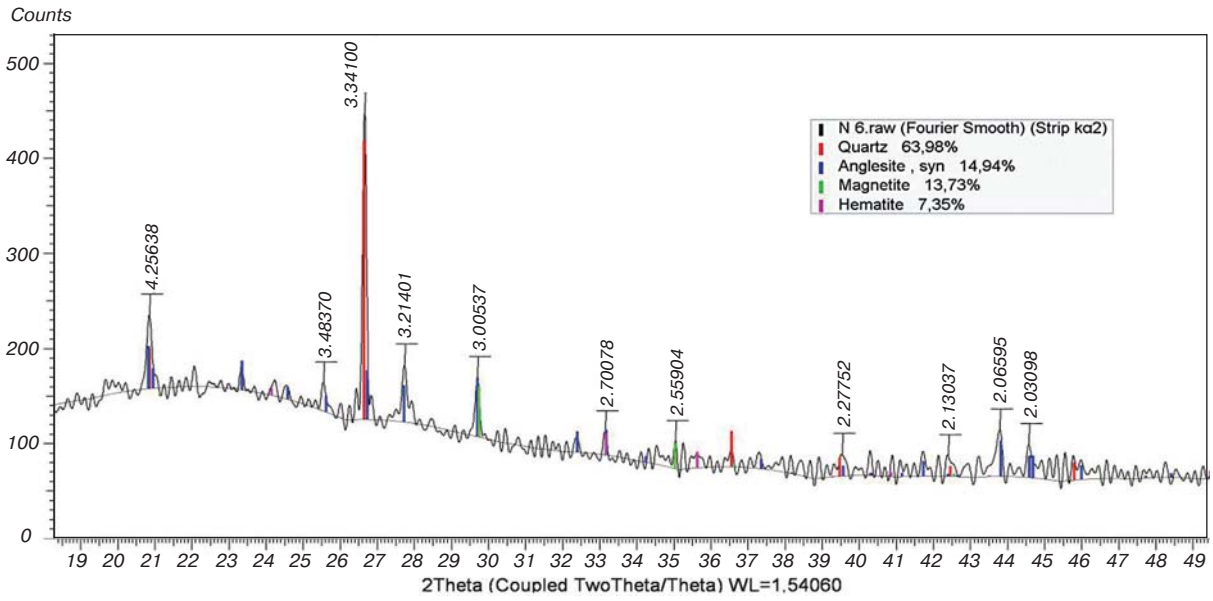


Fig. 4. Diffractogram of the crud

According to the residual concentrations of the main components of the productive solution (copper, iron and silica ions) in the organic phase, the extractants can be arranged in the following sequence:

for Cu: Lix 984N (10%) > Acorga 5640 (10%) ;

for Fe: Lix 984N (10%) > Acorga 5640 (10%);

for SiO_2: Acorga 5640 (10%) > 10% Lix 984N.

As a result of comparison of experimental data on the extraction of copper from the productive solution of Almaly, it was found that for efficient extraction of copper, it is preferable to use the extractant Acorga 5640 (10%). However, when using this extractant, the formation of a crud is possible, since the accumulation of silica in the organic phase is observed. To prevent the formation of crud, further experiments were carried out using the new Acorga CR60 crud suppression reagent from Solvay.

Study of the formation of crud and the effect of Acorga CR60 on the reduction of crud

Studies of the volume of crud formation depending on the intensity of mixing were carried out under the following conditions: pH – 1.7, temperature – 22 °C. Extraction was carried out by supplying the productive solution to the extraction unit and 10% solution of Acorga 5640 in kerosene brand KO-30, in the ratio $O : A = 1 : 1$. The speed range of the agitators on the plant is from 250 to 900 rpm. The volume of the organic phase is 100 ml, the ratio $O : A = 1 : 1$, the number of extraction stages is 6. At the end of each experiment, the organic phase was filtered, and the resulting steak was weighed on an analytical balance. The results of tests on the mass yield of crud at different phase mixing rates (the number of revolutions of the stirrer, rpm) are presented in **Table 12**.

As the results of experiments show, with an increase in the phase mixing rate from 250 rpm to 850 rpm, the volume of crud formation increases almost 2 times — from 0.70 to 1.31%.

The influence of the phase mixing rate on the process of crud formation is largely determined by the design features of the structure of the extraction chambers and mixer blades. The increase in speed in most cases contributes to the creation of vortex flows that form funnels on the surface. As a result, air is captured and drawn into the process of mixing the organic and aqueous phases. This leads to the formation of additional conditions for the formation of crud — foaming and acceleration of oxidative processes in the organic phase due to atmospheric oxygen. At increased speeds, the formation of finely dispersed crud fragments also occurs, which are invisible at the initial stages, but over time, during settling, form clusters in the form of emulsions in the interfacial layer. **Fig. 5** shows the process of crud formation in the pilot extraction plant at minimum 5a (250 rpm) and maximum 5b (850 rpm) revolutions.

At low speeds, the process of formation of crud is somewhat slower, but at the same time, the extraction efficiency also decreases. Thus, for this type of extraction chambers, the best optimal mode for the phase mixing rate is the range of 350–450 rpm.

Table 12
Influence of the phase mixing rate (the number of revolutions of the stirrer, rpm) on the process of crud formation

No. of experiment	ω, rpm	$E_{(Cu)}$, %	Quantity crud, C_{cr}, %
1	250	87,6	0,70
2	450	91,0	0,73
3	650	93,2	1,12
4	850	93,8	1,31

Table 13
Influence of Acorga CR60 reagent on the process of crud formation at 350 rpm

No. of experiment	Concentration AcorgaCR60, *C*, ppm	The degree of extraction of copper, $E_{(Cu)ext}$, %	Quantity crud, E_{crud}, %	Phase separation time, τ, s
1	0	97.70	0.720	420
2	5	97.98	0.240	280
3	10	98.84	0.225	180
4	100	98.86	0.226	180
5	1000	98.88	0.227	180

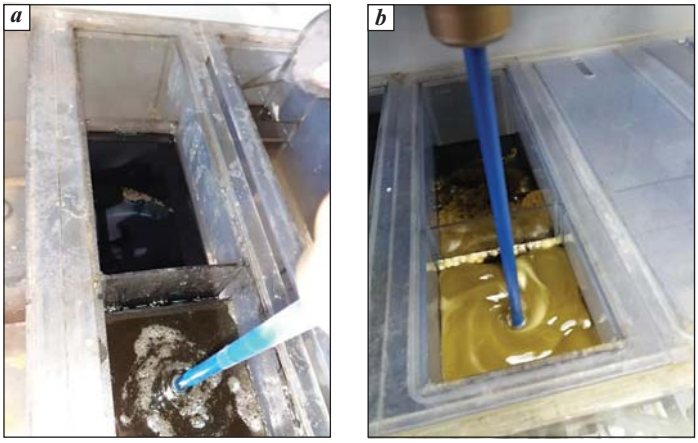


Fig. 5. The process of formation of the crud at the minimum and maximum speeds of the agitator:
a – 250 rpm; *b* – 850 rpm

Influence of Acorga CR60 reagent on crud formation

To suppress the formation of crud during extraction, we conducted studies to study the effect of the additive Acorga CR60, developed by Solvay. It is known that Acorga CR60 showed positive results in reducing of crud formation at enterprises in Asia and North America [26, 27].

The studies were carried out with the Acorga 5640 (10%) extractant with the addition of the Acorga CR60 additive in a laboratory extractor under the following conditions: the ratio of the organic and aqueous phases is 1:1, the temperature is 20 °C, the mixing intensity is 350 rpm, the contact time of the phases is 180 sec., pH of solutions – 1.7, volume of productive solution 1.6 l, number of stages – 2. The re-extraction of metals was carried out with a solution of sulfuric acid with a concentration of 200 g/dm^3. The research results are shown in **Table 13.**

According to the results of experiments on the extraction of copper in the presence of the additive Acorga CR60, it was found that the addition of a crud suppressing reagent from 0 to 10 ppm leads to a significant increase in the extraction of copper from 97.70 to 98.84%, to a decrease in the volume of crud from 0.720 to 0.225%, to reduction of phase separation time from 420 to 180 sec. An increase in the amount of Acorga CR60 additive by 10–100 times led to an increase in the degree of extraction by 0.02–0.04%, the volume of formation of crud 0.01–0.02%. The phase separation time did not change and amounted to 180 sec.

Thus, the effective concentration of Acorga CR60 additive is 5-10 ppm.

Conclusion

For the processing of productive solutions obtained by leaching of refractory oxidized ores of the Almaly deposit, the SX-EW technology is the most suitable.

Effective extractants of copper from sulfate solutions are the modified extractant Acorga 5640 and unmodified Lix984N, from the productive solution of the Almaly deposit composition, g/l: Cu 0.262; Fe 17.97; SiO_2 0.36 – Acorga 5640 extractant.

The best selectivity for $Cu^{2+}/(Fe^{3+/2+})$ ions is shown by 10% Lix984N and 10% Acorga 5640 estragents.

During the extraction of copper from the productive solution of the Almaly deposit, a third phase is formed – an interfacial suspension (crud). The main harmful impurities that lead to the formation of crud during the extraction of copper from the productive solution are iron ions and dissolved silica.

The extractant Lix 984N (10%) and Acorga 5640 (10%) have a high selectivity to the copper-iron and copper-silica systems.

During the extraction of copper from productive solutions with 10% Acorga 5640, the formation of crud is inevitable, the amount of which increases with increasing phase mixing rate.

The additive addition of 5-10 ppm Acorga CR60 to the productive solution during the extraction of copper with 10% Acorga 5640 leads to an increase in the degree of extraction by 1.18%, a decrease in the volume of the crud and the time of phase separation (by 3.2 and 2.3 times, respectively).

The research results can be applied in the selection of extractants and additives in the processing of similar copper-containing productive solutions by liquid extraction.

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