

MINISTRY OF SCIENCE AND HIGHER EDUCATION
OF THE REPUBLIC OF KAZAKHSTAN

Non-profit Joint Stock Company Kazakh National Research Technical University named
after K.I. Satpayev

Mining and Metallurgical Institute named after O.A. Baykonurov

Department of metallurgical processes, heat engineering and technology of special
materials

Mukangalieva Araylym Omirzakizi

Technological study of copper heap leaching solutions

MASTER'S THESIS

7M07204 - Metallurgy and mineral processing

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Araylym Omirzakizi Mukangalieva

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Supervisor

Ph.D., Candidate of Technical Sciences, Associate
Professor, head of the Department MPH&TSM

 Chepushtanova T.A.

«08» 06 2023 year

Reviewer

Candidate of Technical Sciences, head of
Pyrometallurgy Laboratory JC «IMOB»

 Kyatkovsky S. A.

«06» 06 2023 year

Normocontrol

Candidate of Technical Sciences, Senior Lecturer

 Konyratbekova S.S.

«08» 06 2023 year

ДОПУЩЕН К ЗАЩИТЕ
НАО «КазНТУ им.К.И.Сатпаева»
Горно-металлургический институт
им. О.А. Байконурова

ADMITTED TO THE DEFENSE

Ph.D., Candidate of Technical Sciences,
Associate Professor, head of the Department
MPH&TSM

 Chepushtanova T.A.

«08» 06 2023 year

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Department of metallurgical processes, heat engineering and technology of special
materials special materials

7M07204 – «Metallurgy and mineral processing»

APPROVED

Head of the Department

MPH and ToF SM,

Ph.D. Candidate of Technical
Sciences Associate Professor

[Signature] T.A. Chepushtanova

07 2022 year



REQUEST

for a master's thesis

Graduate student Araylym Mukangalieva Omirzakyzy

Subject Technological research of heap leaching solutions for copper

Approved by the *order of the Rector of the University № 1779-M from "02" 11. 2021 year.*

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Input data to the master's thesis: scientific, educational and methodical literature on the topic of the thesis, methods of analysis of technogenic raw materials (liquid copper extraction cradle, productive solutions), data on the copper deposit of Almalı and Aktogay.

Summary of the Master's thesis:

a) the current state of the considered problem of mottling in liquid copper extraction;

b) analysis of the composition of the initial mineral raw materials, oxidized copper ore, the composition of the melt, the definition and study of impurities in the productive copper extraction solutions.

The list of graphic material: not less than 23 slides with the results of research.

Recommended basic literature:

1 Ritcey G.M. Principles and applications to process metallurgy (second edition). – 2006. – Vol. 1. – 563 page.

2 Elshkaki A. Resource Demand Scenarios for the Major Metals – 2018.–52.

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Signatures

of the advisors and the supervisor on the completed master's thesis, indicating the relevant sections of the work

Name of sections	Consultants, Full name. (academic rank)	Date of signature	Signature
Introduction	T.A. Chepushtanova Ph.D., Candidate of Technical Sciences, Associate Professor	02.06.2022	<i>T.A.</i>
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Normo-controller	S.S. Konyratbekova Candidate of Technical Sciences, Senior Lecturer	08.06.2023	<i>S.S.</i>

Supervisor *T.A.* Chepushtanova T.A.

The task was accepted for execution by the learner *A.O.* Mukangaliyeva A.O.

Data

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АҢДАТПА

Магистрлік диссертация 71 беттен тұрады, 3 бөлімнен, 17 кестеден, 18 суреттен, 1 қосымшадан және 47 әдеби көзден тұрады.

Диссертациялық жұмыс Алмалы кен орнының мысты үймелі шаймалау ерітінділерін зерттеуге, өнімді ерітінділердің химиялық құрамын анықтауға, сұйық экстракция әдісімен мысты алуға, Acorga CR60 сияқты экстрагенттердің жаңа түрлерін қолдана отырып, крад түзілу проблемаларын зерттеуге арналған.

Жұмыстың мақсаты Acorga 5640 және Acorga CR60 (Cytex) экстрагенттерін сұйық мыс экстракциясында өнеркәсіптік қолданудың техникалық-экономикалық негіздемесі үшін сынау болды, атап айтқанда меншікті ағынды анықтау, араластыру жылдамдығының, температураның осы реагентті пайдалана отырып крадтың түзілу процесіне әсері, PLS ерітінділерінен мыс алудың оңтайлы жағдайларын әзірлеу.

Зерттеу объектілері құрамында $\text{Cu} - 2,35 \text{ г/дм}^3$ бар Алмалы кен орнының үймелі шаймалау ерітіндісі (PLS) және құрамында 1 г/дм^3 мыс бар модельдік ерітінді болды.

Жұмыста CR-60 крадты басатын қоспаны қолдану крадтың пайда болуының төмендеуіне ықпал ететіні анықталды, CR60 қоспасының басты артықшылығы - шұңқырларда крадтың пайда болуының төмендеуі, осылайша PLS және органикалық ағындар үшін көлемнің ұлғаюы, бұл зауыттардың өнімділігінің артуына тікелей әкеледі. PLS ерітінділерінде кремний диоксиді болған кезде сұйықтықты алу процесі қиынға соғады, бірақ ACORGA CR60LT реагентінің қоспасымен процестің тұрақты жұмысы байқалады.

Жұмыста Acorga CR60 (CYTEC) крадты басатын қоспасы бар Acorga 5640 экстрагентімен мыс алу процесінің математикалық моделі құрастырылған.

АННОТАЦИЯ

Магистерская диссертация изложена на 71 страницах, содержит 3 раздела, 17 таблиц, 18 рисунков, 1 Приложение и 47 литературных источников.

Диссертационная работа посвящена изучению растворов кучного выщелачивания меди месторождения Алмалы, определению химического состава продуктивных растворов, извлечению меди методом жидкостной экстракции, изучению проблем крадообразования с применением новых типов экстрагентов, таких как Acorga CR60.

Целью работы являлось испытание экстрагентов Acorga 5640 и Acorga CR60 (СУТЕС) для технико-экономического обоснования их промышленного применения в жидкостной экстракции меди, а именно определение удельного расхода, влияние скорости мешалок, температуры на процесс образования крада с использованием данного реагента, разработка оптимальных условий экстракции меди из PLS растворов.

Объектами исследований являлись раствор кучного выщелачивания (PLS) месторождения Алмалы с содержанием $\text{Cu} - 2,35 \text{ г/дм}^3$ и модельный раствор с содержанием меди 1 г/дм^3 .

В работе установлено, что применение крадоподавляющей присадки CR-60, способствует снижению образования крада, основное преимущество присадки CR60 - это снижение образования крада в отстойниках, тем самым увеличение объёма для потоков PLS и органики, что напрямую ведет к увеличению производительности заводов. Процесс жидкостной экстракции в присутствии диоксида кремния в растворах PLS затрудняется, но с добавкой реагента ACORGA CR60LT наблюдается стабильная работа процесса.

В работе построена математическая модель процесса экстракции меди экстрагентом Acorga 5640 с крадоподавляющей присадкой Acorga CR60 (СУТЕС).

ANNOTATION

The Master's thesis is presented on 71 pages, contains 3 sections, 17 tables, 18 figures, 1 Appendix and 47 literary sources.

The dissertation work is devoted to the study of solutions for heap leaching of copper from the Almaly deposit, the determination of the chemical composition of productive solutions, the extraction of copper by liquid extraction, the study of the problems of crud with the use of new types of extractants, such as Acorga CR60.

The aim of the work was to test the extractants Acorga 5640 and Acorga CR60 (CYTEC) for a feasibility study of their industrial use in liquid copper extraction, namely, to determine the specific flow rate, the effect of the speed of agitators, the temperature on the process of formation of the crud using this reagent, to develop optimal conditions for the extraction of copper from PLS solutions.

The objects of research were a heap leaching solution (PLS) of the Almaly deposit with a Cu content of 2.35 g/dm^3 and a model solution with a copper content of 1 g/dm^3 .

The paper found that the use of the CR-60 anti theft additive helps to reduce the formation of theft, the main advantage of the CR60 additive is to reduce the formation of crud in settling tanks, thereby increasing the volume for PLS and organic flows, which directly leads to an increase in the productivity of plants. The process of liquid extraction in the presence of silicon dioxide in PLS solutions is difficult, but with the addition of the ACORGA CR60LT reagent, stable operation of the process is observed.

A mathematical model of the copper extraction process with the extractant Acorga 5640 with the anti crud additive Acorga CR60 (CYTEC) is constructed in the work.

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INTRODUCTION

Current state of the scientific and technical problem. At the present stage of economic development, the problem of effective and rational development of copper ore raw material base of the Republic of Kazakhstan has extremely important national economic significance. The urgency of this problem consists in limited and irreplaceable reserves of copper-containing deposits, higher cost of extraction, deterioration of quality composition of extracted ores, negative effect of production wastes on the environment and so on. The solution to this problem lies in the development and implementation of modern methods of geotechnology and hydrometallurgy into industrial practice on the basis of heap leaching of new low-grade ores or pre-leaching of spent deposits, extraction extraction of copper from productive leaching solutions and electrochemical production of complex (commercial) metal from re-extracts. The content of copper in ores of the oxidized zone is high enough for their processing by heap leaching methods with further extraction of the target metal from productive solutions by extraction and electrolysis (SX-EW process). Critical analysis of existing technologies, patent search, analysis of the technology market was performed. It is determined that many organic compounds can be used to extract copper from aqueous solutions, but the number of selective reagents is limited due to: The selectivity and degree of extraction depend largely on the structure of the extractant and the composition of aqueous solution; extractants containing in their structure hydroxyl I (OH) and oxime (NOH) groups are more selective towards copper in a wide range of pH of aqueous leaching solution, this eliminates the consumption of reagents for neutralization of aqueous solutions and positively affects the economics of the process. Technologies aimed at search of new types of extractants with the highest copper selectivity as well as reagent regimes of their application (ratio of organic and aqueous phases during extraction, composition of the organic phase, neutralization of crude, etc.) are topical.

The aim of the work was to test the extractants Acorga 5640 and Acorga CR60 (CYTEC) for feasibility study of their industrial application in liquid copper extraction, namely to determine the specific consumption, the effect of stirrer speed, temperature on the process of crude copper formation using this reagent, the development of optimal conditions for extraction from PLS solutions.

Work objectives:

- study of the chemical composition of productive solutions;
- carrying out laboratory research of heap leaching solutions of Almaly deposit on the pilot plant (pilot extraction plant of Cytec Solvay Group) using CR60 additive;
- determination of the optimal extractant, which does not affect the formation of interfacial waste (crud);
- definition of chemical-physical analysis of CR60 additive reagent and development of alternative reagent regimes which contribute to suppression of inter-phase waste formation and reduction of organic drops carried away together with aqueous solution (raffinate);

- definition of the optimal technological parameter of extraction in the condition of which will be less formation of interfacial waste (crud);
- determination/calculation of the volume of the formed interphase suspension (crud) in the extraction settling tank.

The scientific novelty of the work lies in the development of methods for the application of the additive Acorga CR60 (CYTEC) for copper extraction, by which, it is possible to reduce the formation of crude to 30 % due to the action of sulfur - hydrochloric acid - heptane mixture and hydro-sulfate-chloride salt mixture in the additive.

It has been established that for the optimal extraction of copper in the Almalı deposit with the copper content in PLS solutions up to $\text{Cu} - 2.35 \text{ g/dm}^3$ it is expedient to use the extractant Acorga 5640 – 5 %; the best result showed that at 900 rpm extraction of copper was 91.0 %.

Topicality of the problem. The topic of research is relevant because reducing the weight of the crud significantly affects the economic performance of the technology of liquid copper extraction, especially the costs and expenses of the reagents of the process. The accumulation of solids in solvent extraction (SX) loops can cause problems with the physical and economic performance of the operation. These solids are responsible for the formation of a solid stabilized emulsion containing organic, aqueous, air, and fine solids. Accumulation of steal in SX sumps can limit SX operation performance, require plant downtime, result in higher organic losses, or lead to higher water entrainment of organics (all of which can have significant negative economic consequences). Existing methods of steal management are usually reactive in nature. The steal is physically removed after excessive amounts have been fed into the circuit and is treated mechanically using centrifuges or filtration. A new proactive solution has been developed to prevent the formation and accumulation of interfacial suspensions.

Theoretical and methodological basis for writing the paper. Performance of this work is based on knowledge of the extraction of metals from aqueous solutions, the ability to work with aqueous and organic reagents, knowledge of the basic methods of determining the copper content in aqueous solution, engineering methods of processing research results and the ability to create and optimize mathematical models built by the method of complete factor experiment.

Practical basis for writing the work. Researches were carried out in laboratory of special courses (classrooms 302 and 312 of GMK building) of department "Metallurgical processes, heat engineering and technology of special materials" with use of modern laboratory equipment and qualitative chemical reagents, physicochemical researches of samples were carried out in laboratories of JSC Institute of Metallurgy and Mineral Processing.

Rationale for the need to carry out the work. Kazakhstan occupies 6th place in the world on stocks of copper. In view of this fact sale of copper for the Republic is the second most important source of formation of GDP. Kazakhstan produces about 4 % of world copper production and about 50 % of copper production among CIS countries. Production of copper from oxide ore only in Aktogay Kazminerals

will be about 20 thousand tons per year by 2024. New extraction techniques are in demand both for Kazakhstani enterprises and for foreign countries such as: Australia, Canada, Zambia and others.

Performance of work on the project GF № AP14871587 – "Development of a comprehensive technology to reduce mottling in liquid copper extraction" for 2022–2024, this master's thesis is the expected result of the project.

1 Critical analysis of literary and patent data

1.1 Raw material sources of copper in the Republic of Kazakhstan

The content of copper in different types of ores varies from 0.3-5 %. The content of the main by-product components varies over a wide range. The main method of copper ore mining is open pit, which accounts for about 65 % of the world metal production. The annual capacity of the largest copper-ore enterprises exceeds 30 million tons of ore and 200 thousand tons of metal (Chuquicamata and El Teniente in Chile, Bingham in the U.S., Panguna in Papua New Guinea). The largest reserves of copper ores are concentrated in the Urals, Kazakhstan, Central Asia, Africa and America [1], [2], [3]. China, Chile, Japan, the USA and Russia are the leaders in world production of copper. In total, most copper is produced in Asia (43 %), America (32 %) and Europe (19 %). Africa produces only 4 % of copper, and Australia and Oceania produce 2 %. In turn, such countries as Chile, Peru, USA, China, Indonesia and Australia became world leaders in copper production [4]. Kazakhstan produces about 4% of world copper production and about 50 % of CIS production. At the same time, consumption of copper in the republic is 8 % of its total production, 22 % is exported to neighboring countries and 70 % is exported to foreign countries.

Kazakhstan ranks high in the world market of non-ferrous metals in terms of reserves, mining and production of refined copper: 7th in refined copper production [1-5] 9th in the world in terms of copper reserves, 11th in terms of production. Zhezkazgan and Balkhash copper are registered as benchmarks on the London Non-Ferrous Metals Exchange [9]. Extraction of copper in Kazakhstan, including production of copper in concentrate, production of refined copper, is growing steadily [7], [8], [11].

The deposits of cuprous sandstone, copper-porphyritic, and colchodan-polymetallic are mainly used [10]. In 2017, the production of copper ores in Kazakhstan was almost 78.5 million tons and 5.77 million tons of copper-zinc ores [10]. Of these, 26 million tons were mined in the Karaganda region, 28.5 million tons in the Pavlodar region, and 18.3 million tons in the East Kazakhstan region. In total, 10.5 million tons of copper concentrate and 408435 tons of refined copper were produced [10], the production of which is mainly concentrated in the Karaganda region. Global demand for refined copper is growing and in 2017 was 24.4 million tons according to UBS Global Research [14]. Global population growth and continued urbanization require significant investments in infrastructure, the main raw material for which is still copper. The observed increase in copper prices on the London Metal Exchange (LME) shows the feasibility and further investment in the development of the copper industry in the Republic of Kazakhstan is shown in figure 1.



Figure 1 – Copper prices in US dollars (USD) per ton over the last year

The current official data of the London Metal Exchange (LME) on the quotations of non-ferrous metals used in the electrical industry. The cost of metal is specified in US \$ per ton. Analyze the dynamics of copper prices (LME Copper) over the past year.

The price on the London Metal Exchange today is: US\$8227.86 per ton [14]. The main copper producers in Kazakhstan are Kazakhmys (0.23 million tons of production in 2016, commercial products copper, zinc), Kaz Minerals (0.18 million tons, commercial products copper), Kazzinc (0.5 million tons, commercial products zinc, lead, copper, aluminum) [14]. Reliably proven copper reserves in Kazakhstan are estimated at about 36.6 million tons [15], [16].

The largest corporation mining copper-containing ores in Kazakhstan, and one of the top ten copper companies in the world, is Kazakhmys Corporation LLC, which produced 233.77 thousand tons of copper cathode equivalent in 2017 [17]. The division includes the Balkhash copper smelter, Zhezkazgan copper smelter.

This company accounts for about 85 % of copper concentrate produced in the country and 90 % of refined copper. The main raw material base of Kazakhmys Corporation LLC still remains Zhezkazgan deposit. Now the plants work with ore

containing 0.7 – 0.8 % of copper. Therefore, off-balance reserves of operating mines, including mixed ores in caving zones, in broken pillars, in protective pillars, in ore body flanks, and accumulated technogenic formations represented by poor oxidized and mixed ores in ore dumps and ore enrichment wastes in tailings storages are considered as a reserve replenishment of raw material base of PO "Zhezkazgantsvetmet" of "Kazakhmys" Corporation [18], [19].

The total volume of the balance reserves and deposits of copper [7] is concentrated in the Eastern and Central Kazakhstan, with their most part concluded in poor copper-porphyry deposits. The reserve for strengthening of mineral-raw-material base is a number of колчедано-polymetallic deposits in the east of the republic (Artemyevskoe, Kosmurun, Akbastau, etc.). In Central Kazakhstan the Nurkazgan copper and porphyry deposit with high quality ores has been prepared for exploitation, in South Kazakhstan the Shatyrol copper deposit, and in the Zhezkazgan mining district one of the largest deposits in the country, Zhaman-Aybat [7]. The copper-porphyry type deposits, such as Aktogay, Aidarly, Koksay and Bozshakol, also have significant potential [7].

The main growth projects of Kaz Minerals Corporation are the development of the Bozshakol and Aktogay deposits. The full design capacity of the Bozshakol processing plants will be 30 million tons of ore per year [19]. The term of operation of the mine - more than 40 years, the content of copper in ore – 0,36 %. Reserves of copper in Aktogay deposit are estimated at 5.8 million tons of copper and 115 thousand tons of molybdenum. The Aktogay mine will operate for over 50 years, at a copper content of 0.37 % in the oxide ore and 0.33 % in the sulphide ore. The annual capacity of the enrichment plant to process sulfide ore will be 25 million tons [19]. Copper production of Kaz Minerals Group in the coming years is expected in the range of 270-300 thousand tons of finished products [19].

1.2 Hydrometallurgical methods of copper-containing raw material processing

Copper is one of the main non-ferrous metals in terms of production volume, the need for which and its price is constantly increasing. Copper has long been successfully used in various branches of technology. Today this is quite an extensive range of use: radio engineering, power engineering, chemical technology, metallurgy. Therefore, issues of expanding the raw material base, availability and improving the quality and technology of copper have always been given close attention, both in Kazakhstan and abroad. Thus, the search for new technological solutions for the chemical separation of pure copper from copper-containing solutions is now an urgent task. An alternative to the electrochemical, as well as sorption and extraction method of obtaining pure copper are methods of its chemical recovery from solutions.

Hydrometallurgical methods of copper recovery are in principle suitable for processing of any types of ore raw materials. However, they are usually used to

extract copper from oxidized ores or preburned sulfide ores. The share of hydrometallurgical processes in the total copper production abroad is constantly increasing and now amounts to about 12 – 15 %. The limited use of hydrometallurgical methods in the copper industry is mainly the result of small reserves of oxidized ores and the difficulty of associated extraction of gold and silver. For this reason, hydrometallurgy is mainly used for processing of poor ores with unprofitable content of noble metals, whose waste rock does not react chemically with the solvent. For hydrometallurgy to be practical, it is also necessary for copper to be in the form of an easily soluble compound or to be converted to a soluble form without significant costs.

Leaching is defined as "the treatment of complex substances, such as a mineral, with a specific solvent capable of separating its soluble parts from the insoluble parts" [20]. The method is used to obtain a concentrated solution of a valuable solid material or to remove an insoluble solid from a soluble material with which it is contaminated. The method used for extraction is largely determined by the fraction of soluble component present, its distribution in the solid, the nature of the solid, and its particle size [21]. If the solute is evenly dispersed in the solid, the material near the surface will dissolve first, making the process much more difficult. Consequently, the solvent will have to penetrate through this outer layer before it can reach more dissolved material, and the process will become progressively more difficult. The extraction rate will decrease.

The following leaching methods are used to produce copper ores and concentrates: agitation, autoclave, percolation, underground and heap leaching.

The heap leaching method is the most promising for copper raw materials, as it allows processing the dumps of old and new pits of deposits, for which the method of enrichment is unprofitable [22].

The technology of heap leaching of copper ores has turned into a giant operation [22]. Combined with solvent extraction and electrolysis, it now accounts for about 20 % of copper production and is expected to grow. It has replaced the cementation process with scrap iron. Hydrothermal oxidation of sulfide concentrates has the great advantage of producing elemental sulfur, which solves the SO₂ and sulfuric acid problems of smelters. In the case of copper, hydrogen deposition occurs without the need to

neutralization of the acid produced, which is a great advantage and can be an excellent substitute for electrolysis. Recent advances in the engineering aspects of pressure equipment design are widely opening up possibilities for a wider range of applications.

Heap leaching was first introduced in 1752 in Riotinto (Spain) and is still used today. In pre-revolutionary Russia, the heap leaching method was used at Kedabek (Caucasus) and Gumeshki (Urals). The main solvent in copper leaching is sulfuric iron oxide, which is formed due to the weathering of pyrites. Then, as part of the industrial application of mineral leaching, there is the heap leaching technology, a technology that was developed in the United States, however, it is in Chile that this technology has been significantly improved, reaching practical application on a large

scale (mainly in the copper metallurgical industry), and where the hydrometallurgical process is now the most commonly used. In the hydrometallurgical process, the crushed material is transported (usually by conveyor belts) to a location where a pile will be formed. In this process, the material is first sprayed with an aqueous solution and sulfuric acid (H_2SO_4), known as the curing process, to begin the copper sulfation process in oxidized minerals or sulfated minerals (cured with mixed solutions of sulfuric acid and chlorides [25]). The mineral is discharged using a spreader machine, depositing it in a very organized manner and forming a continuous 6 to 8 m high embankment: Heap leaching. A drip irrigation system is installed over this pile, and sprinklers cover the entire open area. A watertight membrane is installed under the leach pile to provide a drainage system (corrugated pipes) to collect the saturated leaching solution (PLS) that can seep through the pile [26].

Then, depending on the characteristics (physical and/or chemical) of the mineral, industrial percolation leaching can be grouped into the following categories In situ leaching (ISL), (underground), dump leaching (DL), (mined) ground mineral), heap leaching (HL), (figure 2) (ground and/or agglomerated mineral); vat leaching (VL) (ground mineral or concentrates); and heap leaching of agglomerated fine fraction (AFHL) (ground mineral or concentrates) [28].

Heap leaching does not require the construction of expensive plants; huge masses of ore can be processed at one time; and it does not require large amounts of highly skilled labor.

However, the application of heap leaching is limited by certain requirements to the composition and preparation of ores: the ore should be as porous as possible, with microscopic channels contributing to the penetration of solutions, the rock should crack, crumble under the action of the solution.

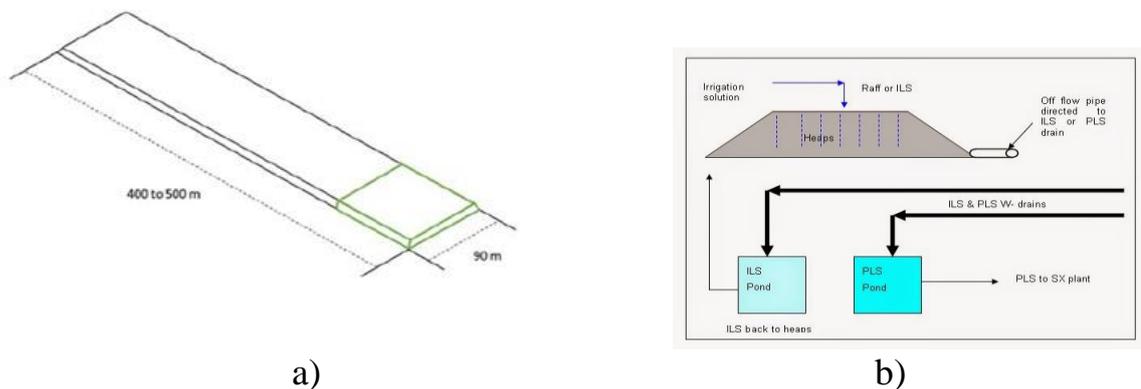


Figure 2 – Dimensions (a) and cross section (b) of a conventional leach heap

Secondary sulphides (chalcocin and covelin) are successfully processed. Primary pyrite, on the other hand, cannot be dissolved. The process requires favourable climatic conditions – dry climate and high average annual temperature.

It is important to prepare an impermeable bed under the dump. Experiments show that extraction of copper can decrease by 30 – 40 % in case of bad bed. The soil is prepared with a slope of 3.5° to 8° . The bed is usually prepared from a layer of clay or silt from enrichment plants, moistened with oil and then dried (this operation is repeated several times). Only in such conditions an impermeable layer is obtained.

Gradually the size of the heaps increased from 10 to 300 metres, and the dump trucks originally used for smaller heaps were replaced by huge stackers. As heap leaching became a major construction undertaking, requiring the movement of tens of thousands of tonnes of ore per day, a thorough knowledge of the fluid flow through the layers, and material and heat balances, complex mathematical modelling equations were introduced to fully automate the process.

It involved not only civil engineers, but also microbiologists and metallurgists.

Two methods are currently in operation:

- a short pile 10 – 20 metres high, which is then removed after depletion and dumped into a tailings pond. A new heap is then introduced in its place;

- new ore stacks are continuously added to the short pile, reaching a height of about 300 metres. Once dry, the pile remains in place and is prepared for vegetation.

Each system has its own advantages and disadvantages. In a short pile system, the metal stockpile in the plant is low, but there are costs involved in transporting the ore for disposal. In a high pile system, or movement is under control, but stacking machines are expensive.

Site preparation is an important part of heap leaching technology. To avoid solution loss and groundwater contamination, the site must be cleared of debris, compacted with a layer of clay and then covered with an impermeable membrane over a layer of asphalt. Perforated plastic pipes are then installed to collect the leachate. A pile is then created. For high piles there is always a risk of these pipes breaking. All precautions must therefore be taken to ensure that the pipes are strong and able to withstand the heavy load of the pile.

For good results, the ore must be leached periodically and dried completely. If the surface of a piece of ore having the favourable properties listed above is moistened with the solution, it will penetrate into the pores of the piece, pass through the capillaries (if the capillaries are open at both ends) and have a dissolving effect on the copper minerals. When the lump dries, the soluble salts (copper sulphate crystals) from the capillary will emerge on the surface under the force of reverse capillarity.

The next time the ore is wet, this salt will be transferred to the solution and washed off with water. It is necessary to use only the amount of water necessary for washing off the CuSO_4 , as a great excess of water is useless the solution is only flattened and no more copper is extracted.

Therefore, after moistening of ore it is necessary to dry it only under this condition quick and full enough leaching of copper is possible.

Gradually the size of the heaps increased from 10 to 300 metres, and the dump trucks originally used for smaller heaps were replaced by huge stackers. The operation of the unit as heap leaching became a major construction undertaking,

requiring the movement of tens of thousands of tonnes of ore per day, a thorough knowledge of fluid flow through the beds and material and heat balances, complex mathematical modelling equations were introduced to fully automate the process.

Heap leaching, heap leaching and vat leaching have been widely used in the last three decades in the copper and gold mining industry. In the case of copper, this technology has been used to:

- waste copper oxide production and low-grade ores;
- rich copper oxide ores;
- relatively high grade sulphide copper ores (1– 2 % copper).

A huge advantage obtained in sulphide processing is related to bypassing the milling and flotation stages in the treatment of huge volumes of milled material [28].

However, this technology cannot be applied to the following material:

chalcopyrite raw material as it is, for all practical purposes, insoluble in ambient conditions;

sulphides containing precious metals as these would be lost in piles.

1.3 Liquid copper extraction

Solvent extraction is a process in which a compound is transferred from one solvent to another due to the difference in solubility or distribution coefficient between the two immiscible (or poorly soluble) solvents [29]. Compared to other separation methods it gives a better separation effect than chemical precipitation and a higher degree of selectivity and faster mass transfer than the ion exchange method. Compared to distillation solvent extraction has advantages like low energy consumption, high production capacity, fast operation, simple continuous operation and easy automation.

Extraction is the first step to separate the desired natural products from the raw materials. Extraction methods include solvent extraction, distillation method, pressing and sublimation according to the extraction principle. Solvent extraction is the most widely used method. Extraction of natural products goes through the following steps:

- solvent penetrates the solid matrix;
- the dissolved substance dissolves in solvents;
- the dissolved substance diffuses from the solid matrix;

the extracted solutes are collected. Any factor that increases diffusivity and solubility in the above steps will facilitate extraction. Extraction solvent properties, raw material particle size, solvent/solids ratio, extraction temperature and extraction time will affect extraction efficiency.

The choice of solvent is crucial for solvent extraction. When selecting solvents, selectivity, solubility, cost and safety must be considered. According to the law of similarity and miscibility (like dissolves in like), solvents with a polarity value close to that of the dissolved substance are likely to perform better, and vice versa.

In metal recovery operations, the valuable component is usually a metal ion or metal ion complex contained in an aqueous solution. This aqueous solution is mixed with an immiscible organic phase containing an active extractant, with the active extractant transferring the desired component from the aqueous phase to the organic phase. The aqueous-organic mixture, called dispersion, then passes from the mixer to a settling tank where the phases are separated. "Loaded organic" phase, now containing the extracted metal, is then transferred from the extraction section of the SX circuit to the reextraction section where the extracted metal is separated from the organic phase. The "purified organic phase" is then reused for extraction [30]. In most cases the separation of the extracted particles from the saturated organic matter is done by mixing the saturated organic matter with an aqueous solution. After the re-extraction operation, the final extraction of the metal from the aqueous solution takes place. Extraction of the metal directly from the loaded organic phase is also possible, but is not currently used commercially. Because the solvent extraction process resembles the extraction of metals from solid ion exchange resins, it is sometimes referred to as liquid ion exchange.

In the LX/SX/EW copper production process, crushed oxidised copper ore is piled in a heap which is irrigated with a sulphuric acid solution. The copper is leached from its minerals using a leaching agent to produce a saturated leaching solution (PLS). The solution is diverted from the base of the heap via a pipeline.

The PLS contains impurities that need to be removed. The solution is purified and concentrated in the solvent extraction process. In the extraction stage, copper ions are selectively transferred from the aqueous phase to the organic phase using an organic extraction chemical in an organic solvent. The loaded copper-containing organic solution is washed with water to remove impurities. During the stripping step, copper ions are transferred from the loaded organic phase back to the aqueous phase to form a rich electrolyte. The empty organic solution is recycled back for extraction. The concentration of sulphuric acid in the aqueous solution leaving the extraction stage (raffinate) is brought to an appropriate level by adding water or sulphuric acid [31].

The mixture of raffinate, water and sulphuric acid has formed a leaching agent and it is returned back to the leachate. The rich electrolyte leaving the stripper is mixed with the spent electrolyte when mixing the electrolytes to achieve the correct concentration of copper in the

High purity copper cathodes are produced by electrolysis. The spent electrolyte is recycled back for stripping.

The choice of the level of variables to be controlled during the extraction process is influenced by factors which are responsible for limiting the extraction rate. There are many factors that influence the extraction rate. Among the most important are particle size, solvent, temperature and liquid agitation [32]. Then, if diffusion of the solute through the porous structure of the residual solids is considered the main controlling factor, the material must be small in size so that the distance that the solute must travel is small. In addition, if diffusion of dissolved

solids is the controlling factor, a high degree of liquid agitation is required. The process flow diagram is shown in figure 3.

1.4 New types of solvent extractants for copper extraction

Although a large number of molecules with a wide range of extraction functions have been proposed as extractants for copper extraction from sulphuric

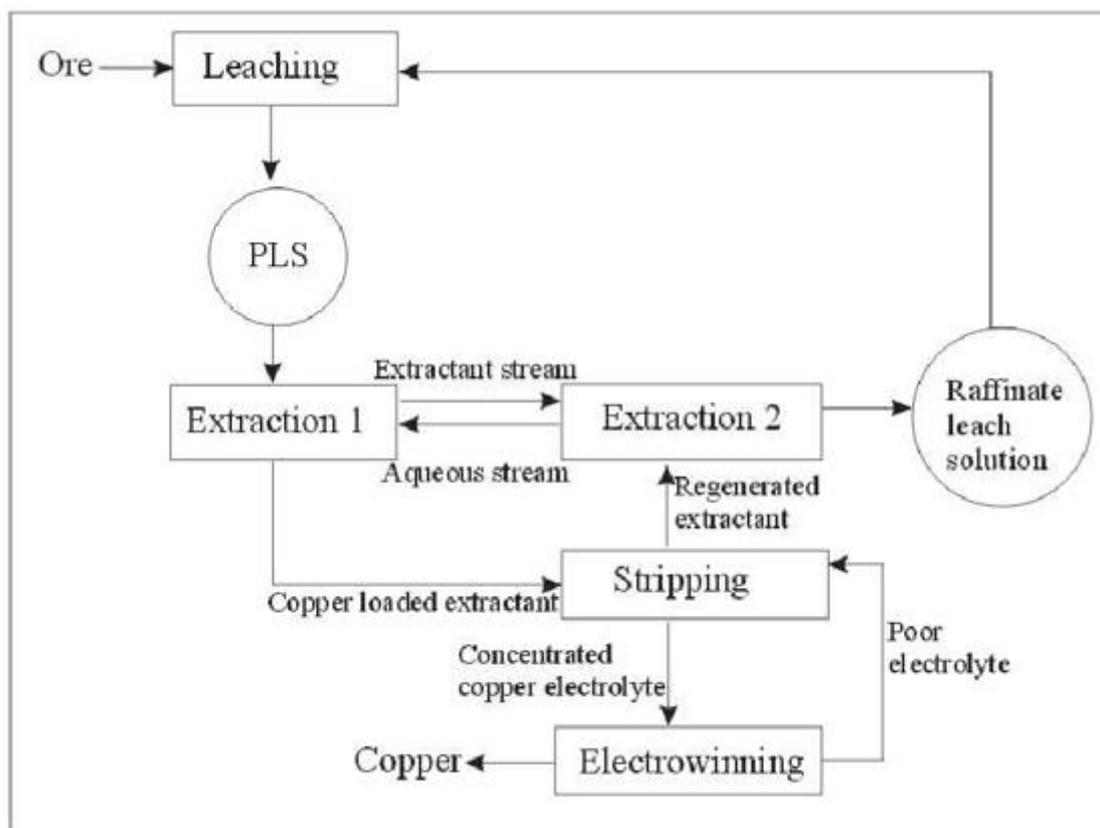


Figure 3 – Basic Process Scheme for Extraction and Re-extraction of Copper-bearing Ore

acid leaching solutions, only hydroxy oximes have been used in industrial SX-EW plants for copper [32].

General structure extractants can be divided into two different classes depending on their structure and properties: ketoximes, which are usually medium strength copper extractants, and salicylaldoximes, which are very strong copper extractants. The strength of the copper extractant is based on the degree to which the previously shown copper extraction equilibrium is shifted towards extraction by the reagent. Simply put, very strong copper extractants extract a significant amount of copper at pH values less than 1.0, while medium strength copper extractants are most useful at pH values above 1.6 to 1.8.

Another class of extractants combines salicylaldoxime with ketoxime in an approximate molar ratio of 1/1. This "third" class is not based on structure, but rather on the distinct and advantageous properties of the blends. These proprietary blends are classified as strong copper extractants and as such are applicable at low pH values such as 1.2.

Ketoxime: Ketoxime was the first hydroxy oxime extractant to be used commercially to extract copper from dilute sulfuric acid leach solution, and ketoxime was used exclusively for approximately 11 years. The most outstanding feature of the ketoximes represented by LIX 84 is the good physical characteristics they exhibit under a wide variety of conditions, particularly with respect to aqueous solutions, which are known to be sensitive to certain organic solutions. One example would be stirred leaching solutions which contain colloidal silica, some solids and/or residual flocculants. A second example is leaching solutions with dissolved organic matter, often present due to decaying vegetation. The ketoximes exhibit excellent phase separation, low carry-over losses to raffinate and do not contribute excessive crud. Since ketoximes are only moderately strong extractants for copper and are kinetically slow at low temperatures, the number of SX installations using exclusively ketoxime extractants is limited. However, in circuits designed to use ketoximes, the operator obtains a cheap and reliable copper extractant.

Salicylaldoximes: Salicylaldoximes were developed to overcome the perceived drawbacks of ketoximes. Their outstanding characteristics include fast copper transfer kinetics and high extractability. However, salicylaldoximes themselves are such strong extractants of copper that they are most often used in combination with an equilibrium modifier or with ketoxime so that they can be effectively removed with an acidic copper solution from which high quality copper can be obtained.

The use of equilibrium modifiers directly leads to some disadvantages as some modifiers are known to accelerate the decomposition of the reagents. It has also been reported that equilibrium modifiers contribute significantly to the amount of fouling produced in some solvent extraction loops.

Another problem sometimes associated with modified reagents is electrolyte contamination due to excessive entrainment of the leaching solution into the loaded organic stream. Finally, nonylphenol is known to have harmful effects on some structural materials.

Since the salicylaldoxime group is less stable than the ketoximes, and in the salicylaldoxime subgroup the nonyl derivative is less stable than the dodecyl derivative. In working circuits at normal temperatures, the cleavage of the reagent by 5-nonylsalicylaldoxime is calculated to be about 10% of the total reagent composition. The actual degradation results of the working circuits have not been published; however, it is known that for some plants the degradation is higher than the calculated value depending on the modifier, temperature and acid content in the aqueous desorbing solution.

In heated circuits the degradation of reagents can be even more significant and must be determined experimentally. Nevertheless, the total reagent loss in a

well-functioning plant is quite low, so losses due to degradation are not excessive in any case.

Despite their drawbacks, reagents with modified salicylaldoxime, such as LIX 622, have proved very successful in commercial schemes that are designed for their use and where the leaching solution is compatible with the reagent.

Henkel solvent copper extraction reagents. Henkel manufactures three oxime extractants: 5-nonylsalicylaldoxime, 5-dodecylsalicylaldoxime and 5-nonyl-2-hydroxyacetophenoxime. These three oximes form the basis for a wide range of reagents which are obtained by mixing the oximes in different ways, for example with a diluent, with each other or with a modifier, to obtain LIX copper solvent extraction reagents with the properties best suited for the particular leaching solution and the plant design under consideration.

In addition, there are existing SX copper plants that purchase individual reagent components separately and mix these components to best suit the individual needs of a particular leaching solution, plant or time of year

Table 1 – Composition of some copper hydroxime extractants available from Henkel

Extractant/Category	Composition
LIX 84/Ketoxime	Mixture of predominantly 2-hydroxy 5-nonylacetophenoxime with small quantities of 5-dodecylsalicyl doxime in a hydrocarbon diluent with a high flash point, required for handling purposes
LIX860N/Aldoxime	Mixture of predominantly 5-dodecylsalicyl-aldoxime with small quantities of 2-hydroxy-5-nonylacetophenoxime in a hydrocarbon diluent with a high flash point, required for handling
LIX 860N/Aldoxime	Mixture of essentially 5-nelicalcylacylphenoxime with small amounts of 2-hydroxy-5-nonylacetophenoxime in a hydrocarbon diluent with a high flash point, required for the purposes of handling
LIX 984/Mixture	Diluted mixture of LIX 84 with LIX 860.
LIX 973/Mixture	Mixture of LIX 860 and LIX 84 by 7/3 volume
LIX 622/ Salicylaldoxime	Mixture of 5-dodecylsalicylaldoxime and tridecanol in a hydrocarbon diluent with a high flash point, necessary for handling

Henkel offers both conventional reagents and concentrated reagents [33]. Concentrated reagents contain the same oximes as conventional reagents. However, because concentrated reagents contain less diluent in order to reduce packaging,

transport and handling costs, concentrated reagents are more viscous than reagents in the conventional formulation and they do not flow well at temperatures below about 5 °C.

We can recommend the optimum reagent composition for your specific conditions and applications.

ACORGA® OPT solvent extraction reagents are proprietary formulations specifically designed to increase copper transfer compared to unmodified aldoxime: ketoxime systems.

- improved copper transfer;
- improved Cu, Fe selectivity.

Table 2 shows the content of some of the aldoxime copper extractants available from Solvay.

Table 1 shows the content of some oxime copper extractants available from Henkel.

Oxime copper extractants sold by Henkel Corporation, alone or in blends, are highly selective for copper over iron when mixed with almost all copper leaching solutions. As a result, minimal bleeding from the electrolysis plant is required for iron control.

ACORGA copper solvent extraction reagents. ACORGA® copper extractants are well established in the industry and used by the largest copper mines in the world [33]. Solvay's extensive product line includes a range of modified aldoxime M extractants, a range of modified aldoxime: ketoxime OPT extractants, a range of nitration resistant NR extractants and a range of oxidation resistant OR extractants.

Table 2 – Composition of some aldoxime copper extractants available from Solvay

Extractant/Category	Composition
ACORGA® M5640	modified ester, fast kinetics, high Cu/Fe selectivity, high grade PLS, low medium pH, strong aldoxime
ACORGA® M5774	modified ester, fast kinetics, high Cu/Fe selectivity, medium pH, medium PLS, medium aldoxime
ACORGA® M5910	modified ester, fast kinetics, high Cu/Fe selectivity, high pH, weak aldoxime, low average PLS
ACORGA® NR-10	modified ester, fast kinetics, high Cu/Fe selectivity, medium pH, medium PLS, nitration resistance
ACORGA® NR-20	modified ester, fast kinetics, high Cu/Fe selectivity, high pH, nitriding resistant, low medium PLS
ACORGA® OPT5540	aldoxime/ketoxime blend, modified ester, fast kinetics, high Cu/Fe selectivity, high quality PLS, medium PLS
ACORGA® CR60 LT	They are process additives designed to assist in solvent extraction operations to reduce the formation of crud due to turbidity in leaching solutions.

1.5 Possible causes of crud formation

Common to all or most solvent extraction operations in the mining industry is the problem of stable emulsions (crud) and possible sludge formation. Sludge can cause significant losses of solvent in the circuit and consequently have a negative effect on operating costs. As there can be many causes for sludge formation, each plant may have a sludge problem unique to that operation.

Factors such as the type of ore, solution composition, solvent composition, presence of other organic components, design and type of agitation, etc. can adversely affect the chemical and physical operation of the solvent extraction circuit and lead to sludge formation.

The nature of the feedstock composition can be a major determining factor as to whether or not sludge will form during subsequent extraction operations.

Solids should be absent from most solvent extraction schemes, and clarification is usually aimed at reaching about 10 parts per million solids. One of the main reasons for the lack of good clarification, resulting in solids entering the solvent extraction circuit. The presence of colloids, such as silica, can lead to the formation of stable emulsions and sludge during phase mixing to achieve mass transfer. Aged feeds may present a greater potential stealing problem than fresh leaching solutions [34]. In plants dominated by bacteria, sludge was formed due to favourable environmental conditions and costly modifications to the circuit were subsequently required. Removal of air from such circuits is often necessary to minimise bacterial and fungal growth. In some systems, hydrolysed compounds may precipitate out of solution and thus a crude mass is obtained. In some extraction systems, the anionic strength of the aqueous stock solution may not be sufficient, so stable emulsions are formed when the two phases are mixed. If sufficient agitation is applied over a period of time, sludge may form. Another important cause of sludge formation in solvent extraction plants is dust from the air if it is allowed to mix in the mixer-sump circuit. Thus, the vessels must be sealed to prevent dust accumulation. Organic substances in the feed, such as lignin or humic acids, can also contribute to sludge formation.

Nature of solvent. The choice of extractant and solvent composition is an important aspect of a successful solvent extraction operation, but the possibility of sludge formation due to solvent composition should not be overlooked. Many systems require a modifier to improve phase separation, promote solubilisation of organometallic compounds and reduce the tendency for third phase and emulsion formation. If the solvent tends to form emulsions when mixed with the aqueous feedstock solution, which can lead to sludge formation, if colloids or suspended solids are present in the aqueous feedstock, several factors may be responsible. Perhaps the system requires the addition of a modifier, replacement with a different modifier or a higher concentration of modifier is required. It may also be that the type and composition of the diluent may be incompatible with the system. An aromatic diluent or an aliphatic diluent with some aromatic content may be more desirable than a fully aliphatic diluent for that particular process. Often unreacted

chemicals from the production process or possibly impurities from the containers used to transport the solvent components are present in the solvent. The problems associated with such contaminants become particularly evident if their effects are not considered in laboratory studies [35]. Their presence in the solvent system can lead to sludge formation, good or poor phase separation and improved or degraded loading characteristics. Such effects can lead to the rejection of a particular solvent due to its poor chemical and physical characteristics.

Equipment selection. There is no universal contact equipment suitable for all solvent extraction operations. Even in a plant, it can be quite wrong to choose the same type of contactor for all stages of the extraction process. Thus, each plant has to make a choice; the final choice is determined by the type of aqueous raw material and its composition, the type and composition of the solvent, and how the relevant physical characteristics affect the mixing process, flow structure and coalescence. Naturally, the efficiency of mass transfer must also be taken into account. With an adequate understanding of all the physico chemical variables present in the process, which will thus affect the extraction as well as minimise emulsion and sludge formation, suitable equipment for this plant can be selected [35]. That is, the type of equipment and the mixing method used to achieve mass transfer are important if the tendency for emulsion formation is to be minimised. Solvent degradation due to the chemical system [36] may have to be considered when selecting equipment. In one plant, centrifugal contactors were chosen over mixing sumps because of the lower solvent degradation.

Method of operation. In solvent extraction, one of the main concerns must be the technique by which mass transfer is achieved. That is, the physical design and operation can contribute not only to high solvent losses, such as entrainment, but also to the formation of stable emulsions and slurries. The physical aspects of the process relate to the dispersion of the two mixing phases, the type of droplet formation and the speed and completeness of coalescence. These are important aspects in choosing the right contact equipment and in the design and operation of the plant. Depending on the type of contact equipment chosen and the energy input to the system, different types of dispersion will be created for a particular system. The differences will be indicated by mass transfer rates, droplet size distribution, surface wetting, deposition and coalescence rates, and entrainment.

Depending on the physical and chemical properties of the two dispersible phases, such as viscosity, surface tension, presence of solids, colloids, etc., with more mixing and smaller droplet sizes an unstable region will be reached followed by a stable emulsion. If solids or colloids are also present, the result will be a crude mass [34]. This is shown in figure 1 showing the operating range of pulsed columns. This information can easily be correlated to excessive turbulence in settling tank mixers, especially in pump mixer design, and in some stirred columns where there is a lot of agitation [36].

The chemical and physical aspects of the feedstock may vary for each individual operation and will vary in inorganic composition, organic content, colour, density, etc. The composition of many slurries appears to have common components

such as Si, Al, Fe, P etc. Together with solvent, gypsum, clay and other fine particles there is often a direct relationship between raw liquor and sludge compositions, indicating possible water transport as well as ineffective clarification prior to solvent extraction.

A resin-like substance is formed on some South African plants and is defined as aliphatic carboxylic acids. There is evidence of the presence of dodecanoic acid from the oxidation of the modifier dodecanol. More than one plant in North America has experienced some stealing problems at more than 3 % isodecanol. It is possible that the vortex created by agitation is a contributing factor to the sludge produced by the breakdown of isodecanol. Trivalent iron as an oxidiser is also present. In an early plant, an animal glue flocculant used to filter leached pulp caused strong fungal growth in the solvent extraction circuit. The addition of a solvent soluble fungicide (benzothiazole derivative) reduced the amount of dirt caused by the fungus. Using an aromatic diluent instead of an aliphatic diluent is also effective in minimising the problem of dampness caused by bacteria.

In some cleaning and washing systems the crude sludge consists mainly of silica as well as inorganic sulphates. Such sludge can be treated with dilute sulphuric acid and recirculation through a pump leads to destruction of the sludge.

Crud prevention. As mottling is a phenomenon that is difficult to fully characterise, is often site-specific and can indeed vary from extraction, cleaning and partitioning operations, it is therefore difficult to cite preventive measures. The following are some of the methods that can be suggested to prevent dampness. Again, it should be stressed that since crud has a different history of formation, one or more preventive measures may be necessary [38]. Solids in the raw material have been mentioned as one of the main causes of subsequent sludge formation in the solvent extraction circuit. Consequently, good clarification is necessary in order to minimise crudity and hence operating costs. Benefits of good clarification:

- better mixing efficiency;
- less rawness and hence less solvent loss, less entrainment of organics;
- less difficulty in maintaining a continuous phase;
- reduced transfer of iron to the electrolyte (in copper processing) through suspended solids;
- improved tank farm efficiency, reduced maintenance costs.

Conclusions on Section 1:

analysis of the current state of the copper industry in Kazakhstan has shown that the development of the ore base is associated with the involvement in processing of previously unprocessed dumps of substandard ores, overburden mineralized rocks, lost reserves of extra-mine deposits, concentration tailings, metallurgical waste, etc. At the same time the most difficult objects for processing are mixed copper ores, including those stockpiled in dumps at many copper deposits in Kazakhstan;

- poor and especially oxidised copper ores are most often processed using hydrometallurgical methods, among which leaching, ion exchange and extraction processes are the most popular;
- concentration of copper in the extraction process from productive solutions occurs during the extraction re-extraction stage;
- the extraction process is influenced by many technological factors, among which the most important are: the influence of pH, the presence of impurities and solid suspended matter, temperature and the resistance of the extractant to melt;
- extraction of copper from productive solutions usually proceeds by two mechanisms – solvate and cation-exchange, in the presence of chelate-forming groups in the extractant the extraction mechanism will be associated with the formation of chelate complexes.

2 Experimental part

Extraction of copper in the extraction process is largely determined by the state of copper in aqueous solutions. Since copper extraction was carried out from solutions prepared by dissolving copper sulphate, thermodynamic analysis of copper state in aqueous solutions was performed for the following systems: «Cu-H₂O», «Cu-Fe-H₂O», «Cu-S-H₂O», «Cu-Fe-S-H₂O», «Si-S-H₂O», «Fe-S-H₂O», «Mn-S-H₂O», «Mn-H₂O», for which the corresponding Pourbe diagrams were constructed.

The construction of Pourbe diagrams for the above systems, were carried out with the software product of Outokumpu Technology Engineering Research (HSC Chemistry 5.11).

2.1 Thermodynamic analysis of the systems «Cu -H₂O», «Cu-Fe- H₂O»

The thermodynamic analysis of the "Cu-H₂O" system (figure 4) shows that in acidic media at pH = - 2 ÷ 4, copper is in solution in the form of Cu²⁺. The stable solid phases are elemental copper and its oxides Cu₂O and CuO. In addition, it forms CuFeO₂ complex.

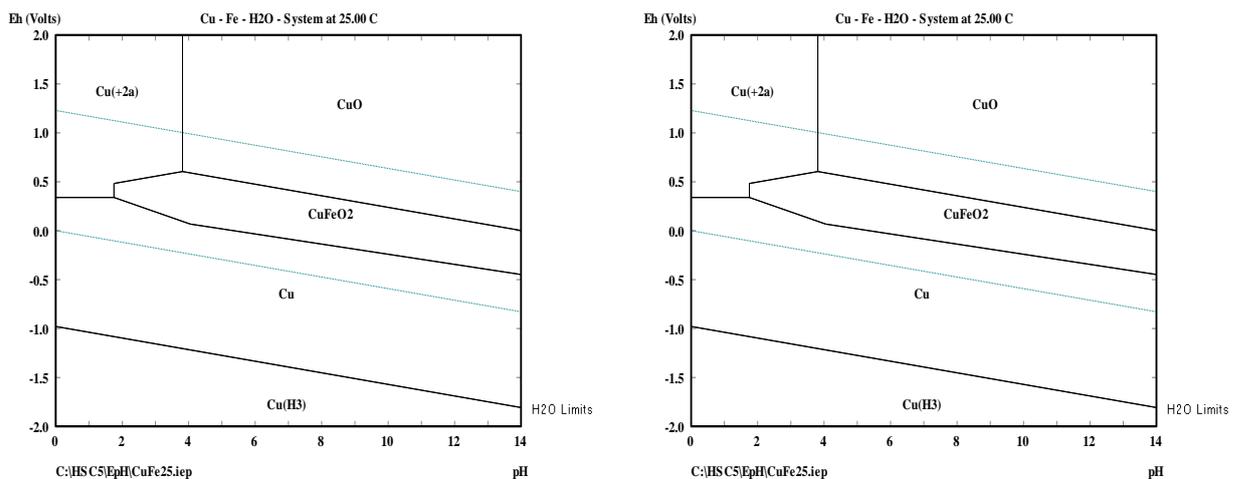


Figure 4 – «Potential-PH» diagram of «Cu-H₂O» and «Cu-Fe-H₂O» system

For example, these diagrams for the system "Cu-H₂O" and "Cu-Fe-H₂O" is plotted at 25 °C, a pressure of 1 bar and a component concentration of 1 mole per 1000 g of solution.

Areas of existence of stable condensed phases: CuO, Cu₂O, Cu, Cu(H₃), Cu-Fe-H₂O.

CuO formed at Eh 0.2 to 2.0 and pH 4 to 14 in weakly acidic, slightly alkaline and strongly alkaline media;

Cu₂O formed at Eh -0.4 to 0.5 and pH 4.8 to 14 in weakly acidic, slightly alkaline and strongly alkaline environments;

Cu formed at Eh -1.8 to 0.3 and pH 0 to 14 in acidic, weakly acidic, weakly alkaline and strongly alkaline media;

Cu(H₃) is formed at Eh -2 to -1 and pH 0 to 14 in acidic, weakly acidic, weakly alkaline and strongly alkaline environments;

CuFeO₂ formed at Eh - 0.4 to 0.75 and pH 3.5 to 14 in acidic, weakly acidic, weakly alkaline and strong alkaline media.

The domains of the stable ionic phases are: Cu(+2a)

Cu(+2a) formed at an Eh of 0.25 to 2 and a pH of 0 to 5.2 in acidic, weakly acidic media.

2.1.1 Thermodynamic analysis of the «Cu-S-H₂O» system

The dissolution of copper sulphides is only possible with oxidative leaching shown in the picture 5.

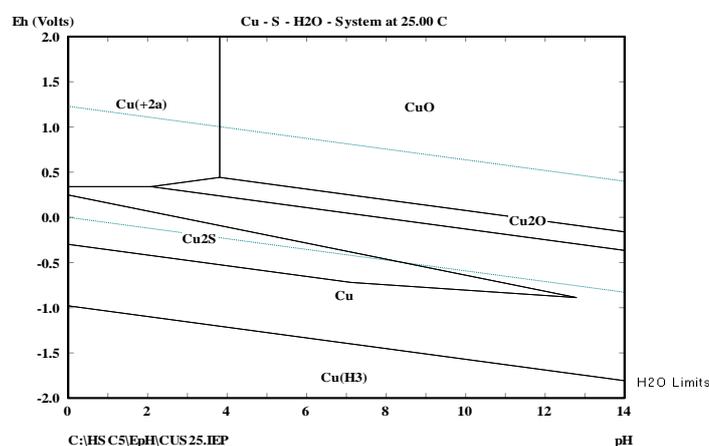


Figure 5 – «Potential-PH» diagram of «Cu-S-H₂O» system

For example, this diagram for the system "Cu-S-H₂O" is plotted at a temperature of 25 °C, a pressure of 1 bar and a component concentration of 1 mole per 1000 g of solution.

Areas of existence of stable condensed phases: CuO, Cu₂O, Cu, Cu(H₃), Cu₂S.

CuO forms at Eh from 0.2 to 2.0 and pH from 4 to 14 in weakly acidic, slightly alkaline and strongly alkaline media;

Cu₂O formed at Eh -0.4 to 0.5 and pH 4.8 to 14 in weakly acidic, slightly alkaline and strongly alkaline environments;

Cu formed at Eh -1.8 to 0.3 and pH 0 to 14 in acidic, weakly acidic, weakly alkaline and strongly alkaline media;

Cu(H₃) formed at Eh -2 to -1 and pH 0 to 14 in acidic, weakly acidic, weakly alkaline and strongly alkaline media;

Cu₂S formed at Eh -0.9 to 0.3 and pH 0 to 13 in acidic, weakly acidic, weakly alkaline and strongly alkaline media.

The domains of the stable ionic phases are: Cu(+2a)

Cu(+2a) formed at an Eh of 0.25 to 2 and a pH of 0 to 5.2 in acidic, weakly acidic media.

2.1.2 Thermodynamic analysis of the «Cu-Fe-S-H₂O» system

Many copper-bearing ores contain chalcopyrite along with the main oxidised copper minerals. As a consequence, the analysis of the "Cu-Fe-S-H₂O" system diagram helps to predict the behavior of its main components in the picture 6.

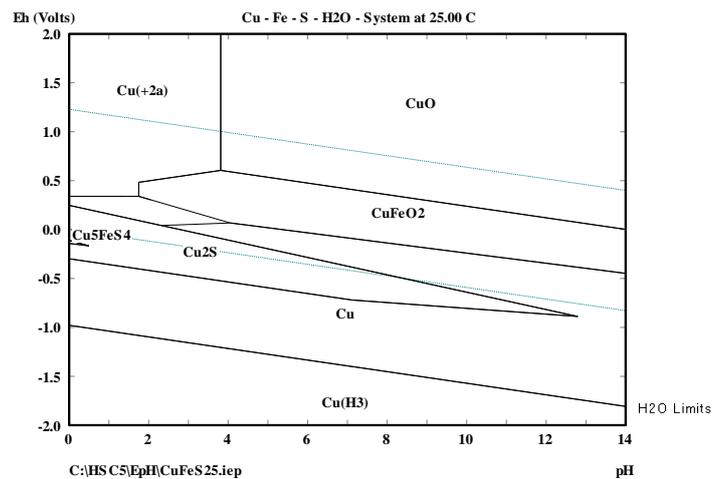


Figure 6 – «Potential-PH» diagram of «Cu-Fe-S-H₂O» system

For example, this diagram for the system "Cu-S-H₂O" is plotted at a temperature of 25 °C, a pressure of 1 bar and a component concentration of 1 mole per 1000 g of solution.

Areas of existence of stable condensed phases: CuO, Cu₂O, Cu, Cu(H₃), Cu₂S, Cu₅FeS₄.

CuO formed at Eh from 0.2 to 2.0 and pH from 4 to 14 in weakly acidic, slightly alkaline and strongly alkaline media;

Cu₂O formed at Eh -0.4 to 0.5 and pH 4.8 to 14 in weakly acidic, slightly alkaline and strongly alkaline environments;

Cu formed at Eh -1.8 to 0.3 and pH 0 to 14 in acidic, weakly acidic, weakly alkaline and strongly alkaline media;

Cu(H₃) is formed at Eh from -2 to -1 and pH 0 to 14 in acidic, weakly acidic, weakly alkaline and strongly alkaline media;

Cu₂S formed at Eh -0.9 to 0.3 and pH 0 to 13 in acidic, weakly acidic, weakly alkaline and strongly alkaline environments;

Cu₅FeS₄ forms at Eh -0.4 to -0.2 and pH 0 to 4 in acidic, weakly acidic environments.

Areas of existence of stable ionic phases: Cu(+2a)

Cu(+2a) formed at Eh 0.25 to 2 and pH 0 to 5.2 in acidic, weakly acidic media.

2.1.3 Thermodynamic analysis of «Si-S-H₂O» system

In the process of ore leaching with sulphuric acid the acid interacts with silicon oxide contained in the initial ore, the record of the interaction is shown as a reaction:



This reaction produces free orthosilicic acid. Thus, in aqueous solution under certain conditions in very small quantities orthosilicic acid (monomolecular form) is unstable, so it condenses very quickly into high-molecular forms which are insoluble in water and transform into H₂SiO₃ methacrySTALLINE acid. This can be seen from the reaction below and the Pourbaix diagram (Figure 7).

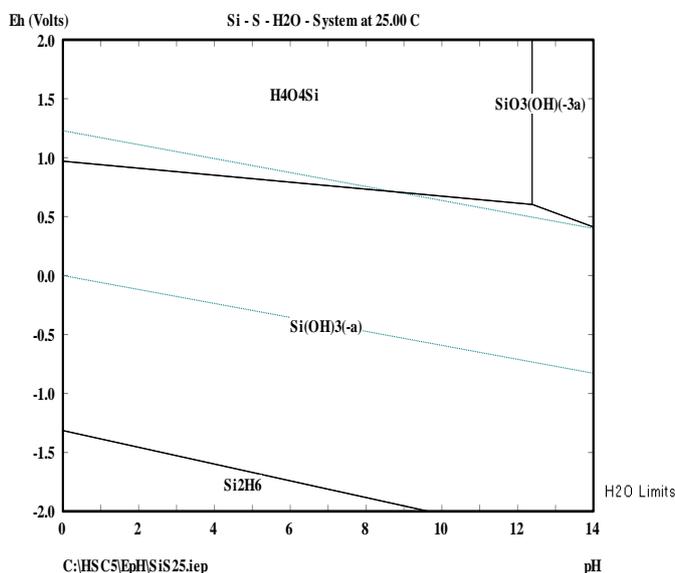


Figure 7 – «Potential-PH» diagram of «Si-S-H₂O» system

For example, this diagram for the Si-S-H₂O system is plotted at 25 °C, 1 bar and a component concentration of 1 mole per 1000 g of solution.

Areas of existence of stable condensed phases: H₄O₄Si, Si₂H₆

H₄O₄Si formed at Eh of 0.8 to 2.0 and pH of 0 to 12.5 acidic, weakly acidic, weakly alkaline and strongly alkaline media;

Si₂H₆ formed at Eh -2 to -1.3 and pH 0 to 9.5 in acidic, weakly acidic, weakly alkaline environments.

Areas of existence of stable ionic phases: SiO₃(OH)(-3a), Si(OH)₃(-a).

SiO₃(OH)(-3a) formed at Eh of 0.4 to 2 and pH of 12.3 to 14 slightly alkaline and strongly alkaline media;

Si(OH)₃(-a) formed at Eh -2 to 1 and pH 0 to 14 for acidic, weakly acidic, weakly alkaline and strongly alkaline media.

2.1.4 Thermodynamic analysis of the «Fe-S-H₂O» systems

In this system «Fe-S-H₂O» in solution there are Fe²⁺ ions, which are oxidized to Fe³⁺ by the equation $\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$.

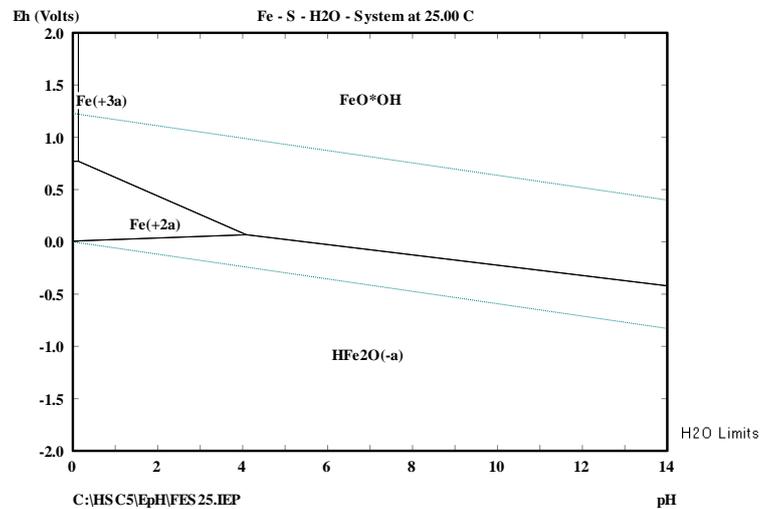


Figure 8 – «Potential-PH» diagram of «Si-S-H₂O» system

For example, this diagram for the system «Fe-S-H₂O» is plotted at 25 °C, a pressure of 1 bar and a component concentration of 1 mole per 1000 g of solution.

Areas of existence of stable condensed phases: FeO·OH

FeO·OH formed at Eh -0,4 to 2,0 and pH 0,4 to 14 acidic, weakly acidic, weakly alkaline and strong alkaline media;

Areas of existence of stable ionic phases: Fe(+3a), Fe(+2a), HFe2O(-a).

Fe(+3a) formed at Eh of 0.7 to 2 and pH of 0 to 0.4 acidic environments;

Fe(+2a) formed at Eh of 0.2 to 0.7 and pH of 0 to 4 acidic media;

HFe2O(-a) formed in Eh from -2 to 0 and pH 0 to 14 acidic, slightly acidic, slightly alkaline and strongly alkaline media.

2.1.5 Thermodynamic analysis of the «Mn-H₂O» and «Mn-S-H₂O» systems

The Pourbaix diagram of the «Mn-H₂O» system was created using the Outotec HSC Chemistry Software for solutions with an initial manganese concentration of 1 mol/L. The «Mn-H₂O» diagram shows that manganese in aqueous solution between pH 1 - 7.6 and potential 1.3 - 1.2 exists as Mn²⁺ cation. Above pH 7.6, manganese hydroxide Mn(OH)₂ is formed in solution, which is insoluble in water. Therefore, the half-reaction for the transition of manganese Mn(II)/Mn (0) up to pH 7.6 can be written in the following form:



At equilibrium pH higher than 8,6 the reaction takes place:



The potential of the first half-reaction does not change over a large pH range, while in the second half-reaction it decreases with increasing pH of the medium.

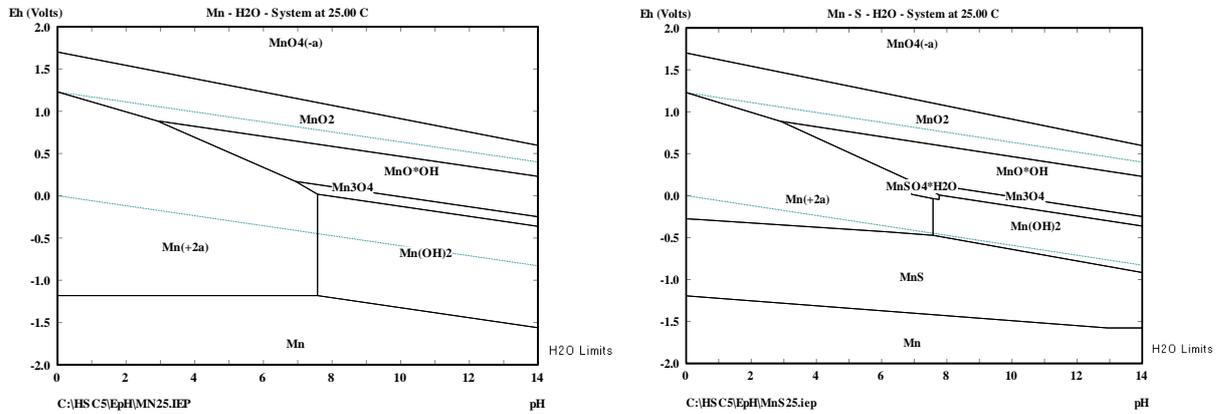


Figure 9 – «Potential-PH» diagram of «Mn-H₂O» and «Mn-S-H₂O» Systems

For example, this diagram for «Mn-H₂O» system is created at a temperature of 25 °C, a pressure of 1 bar and a component concentration of 1 mole per 1000 g of solution.

Areas of existence of stable condensed phases: Mn, Mn(OH)₂, Mn₃O₄, MnO.OH, MnO₂.

Mn formed at Eh from -2 to -1.4 and pH from 0 to 14 acidic, weakly acidic, weakly alkaline and strongly alkaline media;

Mn(OH)₂ formed in Eh from -1.5 to -0.5 and pH 8 to 14 slightly alkaline and strongly alkaline environments;

Mn₃O₄ is formed at Eh from -0.5 to -0.3 and pH 7.8 to 14 in slightly alkaline and strongly alkaline environments;

MnO.OH formed at Eh from -0.3 to 0.25 and pH 3 to 14 slightly acidic, slightly alkaline and strongly alkaline media;

MnO₂ is formed at Eh 0.25 to 1.6 and pH 0 to 14 in acidic, weakly acidic, weakly alkaline and strongly alkaline media.

Areas of existence of stable ionic phases: Mn(+2a), MnO₄(-a).

Mn(+2a) formed at Eh from -1.2 to 1.3 and pH from 0 to 7.8 in slightly alkaline and strongly alkaline environments;

MnO₄(-a) formed at Eh 0.6 to 2 and pH 0 to 14 for acidic, weakly acidic, weakly alkaline and strongly alkaline media.

For example, this diagram for the system «Mn-H₂O» is created at 25 °C, at a pressure of 1 bar and with a component concentration of 1 mole per 1000 g of solution.

Areas of existence of stable condensed phases: Mn, Mn(OH)₂, Mn₃O₄, MnO·OH, MnO₂, MnS, MnSO₄·H₂O, MnSO₄.

Mn formed at Eh from -2 to -1.4 and pH 0 to 14 acidic, weakly acidic, weakly alkaline and strongly alkaline media;

Mn(OH)₂ formed in Eh from -1.5 to -0.5 and pH 8 to 14 slightly alkaline and strongly alkaline environments;

Mn₃O₄ formed at Eh from -0.5 to -0.3 and pH 7.8 to 14 slightly alkaline and strongly alkaline environments;

MnO·OH formed at Eh from -0.3 to 0.25 and pH 3 to 14 slightly acidic, slightly alkaline and strongly alkaline media;

MnO₂ is formed at Eh 0.25 to 1.6 and pH 0 to 14 in acidic, weakly acidic, weakly alkaline and strongly alkaline environments;

MnS formed at Eh -0.4 to -0.3 and pH 0 to 14 acidic, weakly acidic, weakly alkaline and strongly alkaline media;

MnSO₄ formed at Eh 0.25 to 1.6 and pH 7.6 to 14 in acidic, weakly acidic, weakly alkaline and strongly alkaline environments;

Areas of existence of stable ionic phases: Mn(+2a), MnO₄(-a).

Mn(+2a) formed at Eh from -1.2 to 1.3 and pH from 0 to 7.8 in slightly alkaline and strongly alkaline environments;

MnO₄(-a) formed at Eh 0.6 to 2 and pH 0 to 14 in acidic, weakly acidic, slightly alkaline and strongly alkaline media.

Table 3 – Thermodynamic characteristics of the main reactions in the system

№ Reac.	Temperature, °C	ΔH°, kJ	ΔS°, J/°C	ΔG°, KJ	K	lg(K)
1	Cu+H ₂ O=CuO + H ₂					
	0,000	20,487	-11,864	23,728	1,032E-019	-18,986
	100,000	20,821	-10,831	24,862	2,737E-015	-14,563
	200,000	21,207	-9,916	25,898	1,087E-012	-11,964
	300,000	21,610	-9,144	26,850	5,764E-011	-10,239
	400,000	22,017	-8,489	27,731	9,905E-010	-9,004
	500,000	22,420	-7,930	28,551	8,484E-009	-8,071
	600,000	22,815	-7,449	29,320	4,578E-008	-7,339
	700,000	23,197	-7,035	30,043	1,788E-007	-6,748
	800,000	23,562	-6,678	30,729	5,514E-007	-6,258
900,000	23,903	-6,375	31,381	1,424E-006	-5,847	
2	Cu+Fe ₂ O ₃ =2FeO + CuO					
	0,000	142,978	54,582	128,069	3,330E-103	-102,477
	100,000	143,062	54,877	122,585	1,575E-072	-71,803
	200,000	142,876	54,443	117,116	7,928E-055	-54,101
300,000	142,533	53,790	111,703	2,526E-043	-42,597	

Continuation of table 3

№ Reac.	Temperature, °C	ΔH° , kJ	ΔS° , J/°C	ΔG° , KJ	K	lg(K)
	400,000	142,060	53,032	106,361	2,918E-035	-34,535
	500,000	141,445	52,183	101,100	2,626E-029	-28,581
	600,000	140,635	51,200	95,929	9,703E-025	-24,013
	700,000	139,586	50,062	90,867	3,902E-021	-20,409
	800,000	139,203	49,686	85,882	3,224E-018	-17,492
	900,000	138,923	49,437	80,926	8,370E-016	-15,077
3	$2\text{Cu}+\text{S}(\text{g})=\text{Cu}_2\text{S}$					
	0,000	-85,266	-27,122	-77,858	1,994E+062	62,300
	100,000	-85,138	-26,734	-75,162	1,060E+044	44,025
	200,000	-83,634	-22,900	-72,799	4,254E+033	33,629
	300,000	-83,129	-21,929	-70,560	8,088E+026	26,908
	400,000	-82,713	-21,258	-68,403	1,622E+022	22,210
	500,000	-82,151	-20,473	-66,322	5,612E+018	18,749
	600,000	-81,957	-20,237	-64,287	1,237E+016	16,092
	700,000	-81,787	-20,053	-62,273	9,691E+013	13,986
	800,000	-81,649	-19,917	-60,275	1,888E+012	12,276
900,000	-81,550	-19,829	-58,288	7,236E+010	10,860	
4	$2\text{Cu}+\text{SiO}_2=2\text{CuO}+\text{Si}$					
	0,000	143,160	-1,059	143,449	1,643E-115	-114,784
	100,000	143,429	-0,219	143,511	8,713E-085	-84,060
	200,000	143,696	0,416	143,500	5,146E-067	-66,289
	300,000	143,935	0,875	143,434	2,005E-055	-54,698
	400,000	144,128	1,185	143,330	2,895E-047	-46,538
	500,000	144,257	1,366	143,201	3,291E-041	-40,483
	600,000	144,191	1,289	143,066	1,541E-036	-35,812
	700,000	144,433	1,552	142,923	7,937E-033	-32,100
	800,000	144,671	1,785	142,756	8,412E-030	-29,075
900,000	144,400	1,526	142,610	2,695E-027	-26,569	
5	$\text{Cu}+2\text{H}_2\text{SO}_4=\text{CuSO}_4+\text{SO}_2(\text{g})+2\text{H}_2\text{O}$					
	0,000	-0,386	43,027	-12,138	5,163E+009	9,713
	100,000	-2,822	35,007	-15,885	2,016E+009	9,304
	200,000	-3,259	33,961	-19,328	8,476E+008	8,928
	300,000	-3,207	34,034	-22,713	4,588E+008	8,662
	400,000	-1,892	36,135	-26,216	3,252E+008	8,512
	500,000	-0,428	38,162	-29,933	2,897E+008	8,462
	600,000	1,045	39,954	-33,840	2,958E+008	8,471
700,000	2,524	41,558	-37,917	3,282E+008	8,516	

Continuation of table 3

№ Reac.	Temperature, °C	ΔH° , kJ	ΔS° , J/°C	ΔG° , KJ	K	lg(K)
	800,000	4,020	43,020	-42,147	3,838E+008	8,584
	900,000	5,540	44,375	-46,518	4,642E+008	8,667
	1000,000	7,078	45,632	-51,019	5,737E+008	8,759
6	$\text{Cu}_2(\text{OH})_2\text{CO}_3=2\text{CuO}+\text{CO}_2+\text{H}_2\text{O}$					
	0,000	25,629	72,333	5,871	2,004E-005	-4,698
	100,000	25,373	71,546	-1,324	5,967E+000	0,776
	200,000	24,917	70,475	-8,428	7,821E+003	3,893
	300,000	24,201	69,110	-15,410	7,522E+005	5,876
	400,000	23,195	67,499	-22,242	1,666E+007	7,222
	500,000	21,881	65,684	-28,903	1,481E+008	8,171
	600,000	20,248	63,701	-35,373	7,155E+008	8,855
	700,000	18,284	61,576	-41,638	2,248E+009	9,352
	800,000	15,985	59,329	-47,684	5,150E+009	9,712
	900,000	13,342	56,976	-53,500	9,280E+009	9,968
	1000,000	10,350	54,531	-59,076	1,387E+010	10,142
7	$\text{H}_2\text{O}+\text{SiO}_2=\text{H}_2\text{SiO}_3$					
	0,000	5,257	-21,442	11,114	1,280E-009	-8,893
	100,000	3,326	-27,445	13,567	1,131E-008	-7,947
	200,000	1,185	-32,518	16,571	2,213E-008	-7,655
	300,000	-1,110	-36,916	20,048	2,264E-008	-7,645
	400,000	-3,548	-40,834	23,939	1,687E-008	-7,773
	500,000	-6,129	-44,405	28,203	1,064E-008	-7,973
	600,000	-8,973	-47,861	32,816	6,101E-009	-8,215
	700,000	-11,568	-50,674	37,745	3,330E-009	-8,477
	800,000	-14,218	-53,265	42,944	1,793E-009	-8,746
	900,000	-17,416	-56,131	48,434	9,468E-010	-9,024
	1000,000	-20,185	-58,396	54,162	5,032E-010	-9,298

Conclusions of section 2

– on the basis of the presented thermodynamic analysis of copper in aqueous solutions, it follows that copper in aqueous solution, depending on the presence of nonmetals, can be in two main ionic forms as the simple cation Cu^{2+} and as the complex cation $\text{Cu}(\text{NH}_3)_5^{2+}$; cation-exchange and neutral extractants should be used for copper extraction from aqueous solutions; the simple copper cation Cu^{2+} exists only in the oxidation potential region, and this region also depends on the copper concentration in solution and on the presence of sulfur or chlorine in the system. This fact can be of importance, if reagents capable of reducing the oxidation potential, the so-called redox polymers, are used as extractants;

– thermodynamic analysis of leaching of oxidized copper ore has shown, that minerals malachite, azurite, kuprite and sulphates of copper dissolve effectively in solutions of sulphuric acid H_2SO_4 at pH from 0 to 4 in acid medium. And minerals such as chrysocolla, chalcocene, covelline, chalcopyrite dissolve in the presence of oxidants. The obtained values of Gibbs energy indicate the thermodynamic possibility of copper extraction when using the selected extractants. The Gibbs energy changes from -10.5 to -26.5 kJ as the pH of the medium increases from 1.5 to 4.

3 Experimental data for liquid copper extraction and mottling

3.1 Input materials

The object of the study was the heap leaching solution (PLS) of the Almalı deposit, which operates a metallurgical complex for the production of copper cathode with a capacity of 10 thousand tonnes of copper cathode per year. Specific PLS conditions (silica, high concentration of dissolved solids, high viscosity) are observed at this deposit, which favours crude formation in the lagoons, leading to crude movement and plant instability, partly and increased entrainment of organic phase with aqueous phase. Despite such specific conditions, the copper cathode production plant is operating according to design values and has the potential to increase production.

The aim of this work was to determine the compatibility and effectiveness of the new CR60 chemical additive to reduce cathode formation and its effect on the physical and metallurgical characteristics of the process, as well as the organic phase entrainment.

The concentrations of the major elements in solution were: Cu – 2.35 g/dm³, Fe – 21.55 g/dm³, SiO₂ – 0.34 g/dm³.

To determine the elemental composition of the productive solution, evaporation with obtaining a solid sediment was carried out. Evaporation of the productive solution (PLS) showed that the total concentration of salts reaches 35 %.

Preparation of the crud sample for analyses involved pre-drying the sample until it was completely dehydrated, followed by grinding to no more than 0.1 mm particle size. In order to determine the main mineral forms present in the crud, X-ray phase analysis was carried out, the results of which are presented in table 4.

Table 4 – Results of X-ray phase analysis of the crud (formation of interfacial waste)

Name	Formula	%
Quartz	SiO ₂	63,98
Anglesite	Pb(SO ₄)	14,94
Magnetite	Fe ₃ O ₄	13,73
Hematite	Fe ₂ O ₃	7,35

The result of X-ray phase analysis of the crud showed the predominance of quartz 63.98 %, also found some amount of lead mineral anglesite – 14.94 %, as well as iron minerals magnetite – 13.73 % and hematite – 7.35 %.

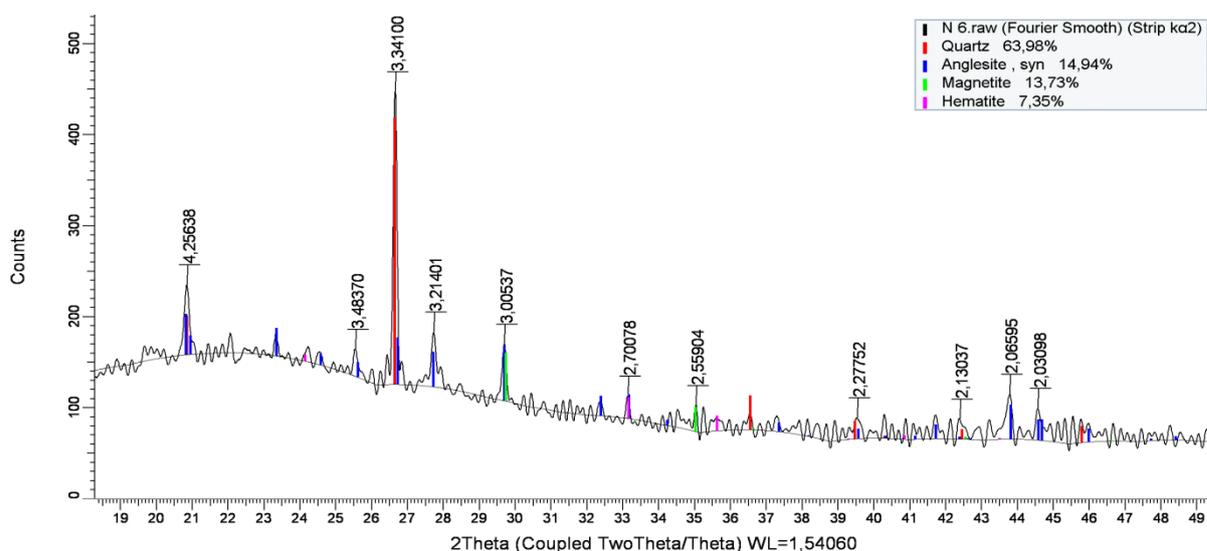


Figure 10 – XRD diffraction data

The detailed elemental composition of the krad was investigated by X-ray fluorescence analysis, the results of which are shown in table 5.

Table 5 – Results of X-ray fluorescence analysis of the crud (interfacial waste formation)

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 order to determine the basic elemental composition of a sample of 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 in table 6.

Evaporation of 100 ml of productive solution allowed to isolate 35 g of salt compounds in a solid dry state, which is a sufficiently high content. Comparing analyses of elemental composition of solid sediment of productive solution and crud, we can note quite high values of oxygen, sulphur, iron.

Table 6 – Results of X-ray fluorescence analysis of solid sediment of evaporated productive solution

Components	Content, %	Components	Content, %
O	59,394	Ti	0,067
Na	0,346	V	0,008
Mg	3,818	Mn	0,386
Al	4,883	Fe	5,048
Si	0,304	Co	0,014
P	0,296	Ni	0,016
S	14,984	Cu	0,746
Cl	0,263	Zn	0,073
K	0,019	Y	0,004
Ca	0,114	Th	0,013

The formation of "beard" (interphase suspension consisting of crud and other impurities) apart from the presence of oxidation products of organic phase is also promoted by unfavorable composition of productive solution (high content of solid slime particles, high content of silicon in solution etc.).

The rate of "bearding" for each type of mixing and stratification chambers is individual and difficult to determine in advance. To reduce the formation of this type of beard, in addition to cleaning the solution of contaminants, it is also very important to minimise any air ingress into the solution during all stages of feeding and mixing of the aqueous and organic phases.

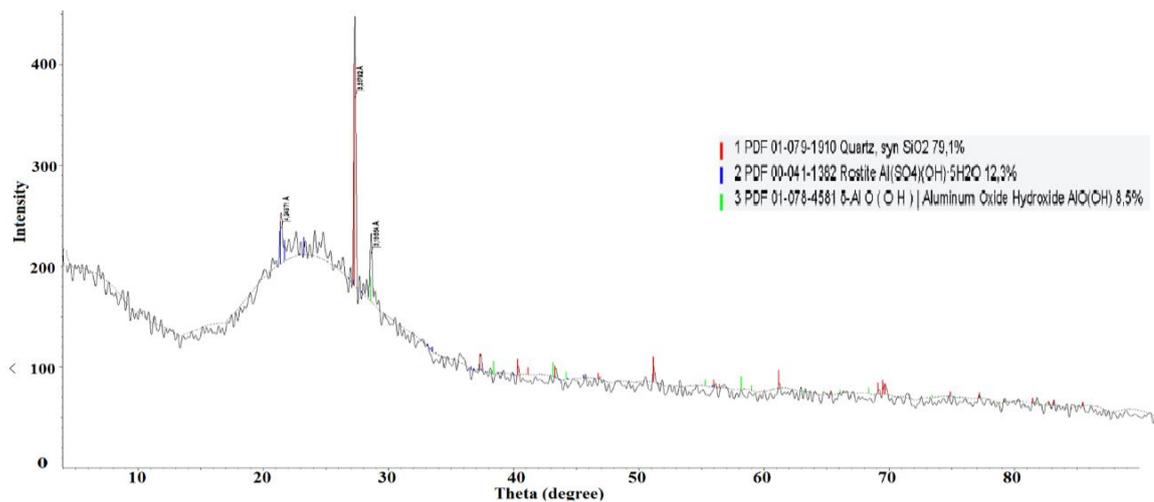


Figure 11 – Diffraction data from X-ray diffraction krad analysis

3.2 Pilot plant tests

Highlights of the pilot plant tests with the reagent. The pilot plant was located in the Department of MPT&TSM, figure 12. The test was performed with ACORGA CR60LT reagent dosing in PLS with 1E+1S configuration (1 extrusion stage and 1 reextraction stage), the raffinate and rich electrolytes were drained into the drainage system.



Figure 12 – SOLVAY pilot extraction plant

The reagent dosage (ACORGA CR60LT) was chosen to be 10 ppm or ml/m³ of solution and increased to 15 ml/m³ as the tests progressed.

The first 72 hours of the tests were conducted in parallel two circuits as one extraction and one reextraction (1+1) at a CR60LT dosage of 10 ml/m³, then the circuit was rearranged as one in three parallel extractions and one reextraction for a period of 148 hours at a CR60LT dosage of 15 ml/m³.

The difference in the formation of stain was evident between the two circuits (starting with reagent dosing); the control circuit (without dosing) recorded a greater amount of interfacial stain, whereas the test circuit (with dosing) showed much less stain formation. In the paper, the figures relating to the formation and comparison of the stain are given in cm³.

In order to determine the selectivity values of each type of organics, and as a sample to compare phase separation times, a prepared model solution was used in addition to the productive solution from the field. Extraction was carried out on laboratory extractors.



Figure 13 – laboratory extraction plant

The target concentration of copper in the model solution was 1 g/l, total iron was 2.4 g/l ($\text{Fe}^{2+} : \text{Fe}^{3+} \approx 1:1$), the pH was adjusted to 1.7 by sulfuric acid (in accordance with pH = 1.7 in the productive solution). Copper sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was used to prepare the model solution by recalculating the molecular proportion of copper (25 %) – 4 g/l of copper sulfate to achieve 1 g/l of Cu^{2+} ions. Similarly, iron salts were dissolved to achieve a given concentration of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions = 2.4 g/l.

The selectivity tests were carried out with Acorga series extractants (5747, 5910, 5640) and Lix 984. The diluent used was KO-30 paraffin.

During the initial selectivity tests a longer separation time of aqueous and organic phases was observed during extraction of copper from the productive solution. Complete separation of aqueous and organic phases was observed only after more than 5 – 7 minutes, while in the model solution complete separation was achieved in 20 seconds. The recommended separation time for hydrometallurgical SX-EW cathode production should not exceed 30 seconds. This test, under production conditions, is performed by taking a sample of the organic and aqueous phase mixture from the mixer chamber, followed by fixing the moment of complete separation.

In addition to the long phase separation, there was also an indistinct interfacial separation – visible traces of organics were present in the upper layer of the aqueous phase, similar to the "beard" interfacial suspension described earlier. A clear separation of the phases in the extraction process is shown in figure 14.



productive solution



model solution

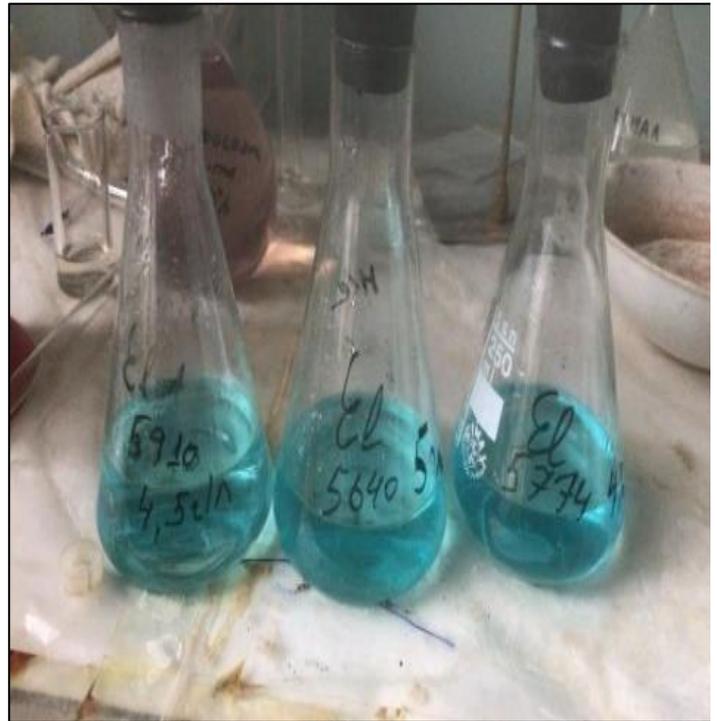
Figure 14 – Separation of organic and aqueous phases, product and model solution in the separating funnel

At the subsequent re-extraction and electrolyte generation, by washing the organics with 20 % sulphuric acid solution, the separation of the phases took place within the required duration of not more than 30 seconds. At the same time the electrolyte obtained by washing the organics after the extraction of the productive solution had a markedly different colour shade from the electrolytes obtained during the processing of the model solutions. The green colouring indicated possible transfer of a significant amount of iron ions into the electrolyte, the electrolyte in the model solutions was more dominated by the blue colour characteristic of copper sulphate in figure 15.

In practice, the freshly prepared organic phase is translucent with a slight yellowish tinge, the colour changes to light brown when it is first run in the liquid-extraction cycles. From the start up in the organic phase, after the reextraction stage, a certain amount of copper from 0.2 to 0.5 g/l will be continuously present. This amount of copper is quite acceptable and there should be no tendency for the concentration of copper present to increase at all times.



after productive solution



after model solutions

Figure 15 – Electrolytes after washing of the organic phase in the reextraction step

3.3 Extraction results for copper recovery using different extractants

The data in the table shows the highest efficiency when using 5 % Acorga 5640 extractant the final copper transfer from the pregnant solution to the electrolyte is 87.5 %, at the extraction stage the copper recovery into the organic phase is 94 %. For the productive solution with 1 g/l copper concentration, the Acorga 5640 extractant concentration of 5 % is the best compared to 10 % due to the transfer mechanism.

Table 7 – Extraction of copper with different extractants in the model solution

Test	Solvent extraction							
	Cu in PLS, g/l	V PLS, l	Cu B Raf, g/l	V Raf, ml	O:W	Stages	E Cu, %	PH
Acorga 5910 – 10 %	1,0	0,6	0,15	0,6	1:1	3	85,0	1,7
Acorga 5640 – 10 %	1,0	0,6	0,09	0,6	1:1	3	91,0	1,7
Acorga 5640 – 5 %	1,0	0,6	0,06	0,6	1:1	3	94,0	1,7
Lix984 – 10 %	1,0	0,6	0,07	0,6	1:1	3	93,0	1,7

Continuation of table 7

	Re – extraction							
	Cu in org., g/l	V org., l	Cu B Elect., g/l	V Elect., l	O:W	Stages	E Cu, % (from org.)	E Cu, % (final)
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
Acorga 5640 – 5 %	2,82	0,2	5,25	0,1	2:1	3	93,1	87,5
Lix984 – 10 %	2,79	0,2	5,14	0,1	2:1	3	92,1	85,7
Residual Cu in the org. phase g/l	Acorga 5910 – 10 %	Acorga 5747 – 10 %		Acorga 5640 – 10 %		Acorga 5640 – 5 %		Lix984 – 10 %
	0,3	0,25		0,23		0,195		0,22

To assess the selectivity of the organic phases the transport of iron ions during extraction and re-extraction of model solutions was analysed. The balance was calculated using the same parameters as in the copper extraction calculations. The initial $\text{Fe}^{2+}/\text{Fe}^{3+}$ ion content in the model solution was 2.4 g/l. Final balance of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions is shown in table 8.

Table 8 – Selectivity of extractants by $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions (on the model solution)

Test	Solvent extraction							
	$\text{Fe}^{3+}/\text{Fe}^{2+}$ in PLS, g/l	V PLS, l	$\text{Fe}^{3+}/\text{Fe}^{2+}$ B Raf, g/l	V Raf, ml	O:W	Stages	E $\text{Fe}^{3+}/\text{Fe}^{2+}$, %	PH
Acorga 5910 – 10 %	2,4	0,6	2,2	0,6	1:1	3	8,3	1,7
Acorga 5747 – 10 %	2,4	0,6	2,0	0,6	1:1	3	16,7	1,7
Acorga 5640 – 10 %	2,4	0,6	2,2	0,6	1:1	3	8,3	1,7
Acorga 5640 – 5 %	2,4	0,6	2,38	0,6	1:1	3	0,8	1,7
	Re – extraction							
	$\text{Fe}^{3+}/\text{Fe}^{2+}$ in the org., g/l	V org., l	$\text{Fe}^{3+}/\text{Fe}^{2+}$ in Elect., g/l	V Elect., l	O:W	Stages	E $\text{Fe}^{3+}/\text{Fe}^{2+}$, % (in org.)	E $\text{Fe}^{3+}/\text{Fe}^{2+}$, % (final)

Continuation of table 8

	Fe ³⁺ /Fe ²⁺ in the org., g/l	V org., l	Fe ³⁺ /Fe ²⁺ in Elect., g/l	V Elect., l	O:W	Stages	E Fe ³⁺ /Fe ²⁺ , % (in org.)	E Fe ³⁺ /F ²⁺ , % (final)
Acorga 5910 – 10 %	0,6	0,2	0,17	0,1	2:1	3	14,2	1,2
Acorga 5747 – 10 %	1,2	0,2	0,18	0,1	2:1	3	7,5	1,3
Acorga 5640 – 10 %	0,6	0,2	0,1	0,1	2:1	3	8,3	0,7
Acorga 5640 – 5 %	0,06	0,2	0,1	0,1	2:1	3	83,3	0,7
Lix984 – 10 %	0,33	0,2	0,1	0,1	2:1	3	15,2	0,7
Residual Cu in the org. phase g/l	Acorga 5910 10 %	Acorga 5747 – 10 %		Acorga 5640 – 10 %		Acorga 5640 – 5 %		Lix984 – 10 %
	0,515	1,11		0,55		0,01		0,28

According to the results shown in table 8, the best Fe²⁺/Fe³⁺ ion selectivity is shown by the Lix984 and Acorga 5640 series (5 % and 10 %).

3.4 Testing the Acorga CR60 mottling suppressant

A CR60 additive developed by Solvay was tested to suppress mottling. For carrying out studies on copper extraction we used extractant Acorga 5640 – 5 % with the addition of additive CR60 from the productive solution, g/dm³: copper 2.3; iron 21.55; SiO₂ – 0,34. pH of solutions – 1,7. The study of the influence of impurities was carried out in a separating funnel, the ratio between organic and aqueous phases – 1:1, temperature - 20 °C, stirring intensity – 750 rpm, phase contact time – 60 sec, retention time – 60 sec. Re-extraction was carried out with sulphuric acid solution of concentration 200 g/dm³. In parallel, as a comparative sample, extraction test was carried out using Lix 984 extractant on the studied productive solution. The results are shown in tables 9 – 10.

Table 9 – Extraction of copper from productive solution of Almala with extractant Acorga 5640 - 5 % + RC60

Test	Solvent extraction							
	PLS, g/l	V PLS, l	Cu B Raf, g/l	V Raf, ml	O:W	Stages	E Cu, %	P _H
Cu	2,350	1,6	1,21	1,6	1:1	3	48,5	1,7

Continuation of table 9

Test	Solvent extraction							
Fe	PLS, g/l	V PLS, l	Cu B Raf, g/l	V Raf, ml	O:W	Stages	E Cu, %	P _H
SiO ₂	0,34	1,6	0,21	1,6	1:1	3	38,2	1,7
Re – extraction								
	Cu B org., g/l	V org., l	Cu B Elect., g/l	V Elect., l	O:W	Stages	E Cu, % (from org.)	E Cu, % (final)
Cu	9,12	0,2	11,55	0,15	2:1,5	3	95,0	46,1
Fe	12	0,2	10,25	0,15	2:1,5	3	64,1	4,5
SiO ₂	1,04	0,2	0,16	0,15	2:1,5	3	11,5	4,4
Residual Cu in the org. phase g/l	Cu		Fe		SiO ₂			
	0,4575		4,3125		0,92			

Table 10 – Extraction of copper from productive solution of Almala with extractant Lix 984 – 10 %

Test	Solvent extraction							
	PLS, g/l	V PLS, l	Cu B Raf, g/l	V Raf, ml	O:W	Stages	E Cu, %	P _H
Cu	2,350	0,6	0,35	0,6	1:1	3	85,1	1,7
Fe	21,55	0,6	20,8	0,6	1:1	3	3,5	1,7
SiO ₂	0,34	0,6	0,21	0,6	1:1	3	38,2	1,7
Re – extraction								
	Cu B org., g/l	V org., l	Cu B Elect., g/l	V Elect., l	O:W	Stages	E Cu, % (from org.)	E Cu, % (final)
Cu	6,0	0,2	7,0	0,15	2:1,5	3	87,5	74,5
Fe	2,25	0,2	2,6	0,15	2:1,5	3	86,7	3,0
SiO ₂	0,39	0,2	0,24	0,15	2:1,5	3	46,2	17,6
Residual Cu in the org. phase g/l	Cu		Fe		SiO ₂			
	0,75		0,3		0,21			

3.5 Investigation of the interfacial suspension (crud) formed

The intensity of interfacial sedimentation of crud in plants depends on the quality of the liquor, the processing conditions, the type of organics, and other factors. Usually formation of stable crud layer is observed within 10 –15 days in the amount from 0.2 to 1.0 % of total mass of organic phase.

In the studied productive solution, accumulation of crud has been observed already at the 3rd stage of extraction at optimum stirrer speed of 350 rpm, and after 10 stages its quantity has exceeded 1.0 %. The filtration of an organic phase weighing 100 g after 10 extraction stages resulted in a crude weight of 2.55 g, as shown in figure 16.



Figure 16 – Crud

It was found that CR-60 additive, contributes to some reduction of crud formation, but high concentrations of iron salts (18 – 20 g/l) and other salts do not allow to avoid fully contamination of the organic phase. Evaporation of the productive solution showed that the total concentration of salts reaches 35 %.

3.6 Mathematical model of copper extraction of productive solutions of Almaly deposit

Using the program “Solvay Extraction”, calculations of extraction schemes have been made according to the composition of productive solutions obtained during leaching of ores from Almaly deposit, which contain copper – from 1 g/dm³ to 3.2 g/dm³ with pH equal to 1 (figures 17 and 18). Based on calculations the extraction isotherm was constructed and extraction processes of copper were simulated (figures 17, 18) with the scheme 3E+1P, allowing to reach a through extraction of copper 84.1 %.

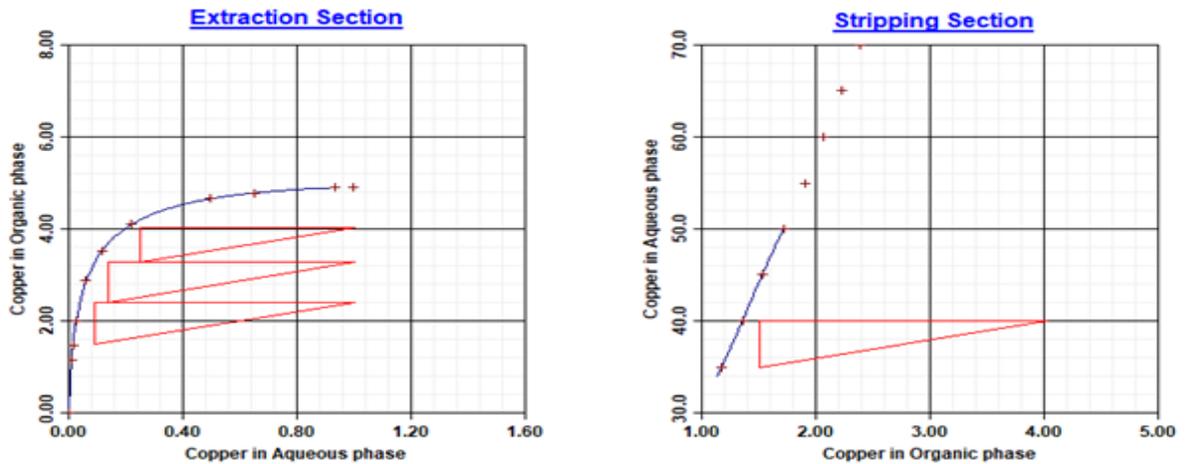


Figure 17 – Extraction (a) and re-extraction (b) isotherms of copper from the Almay deposit PLS

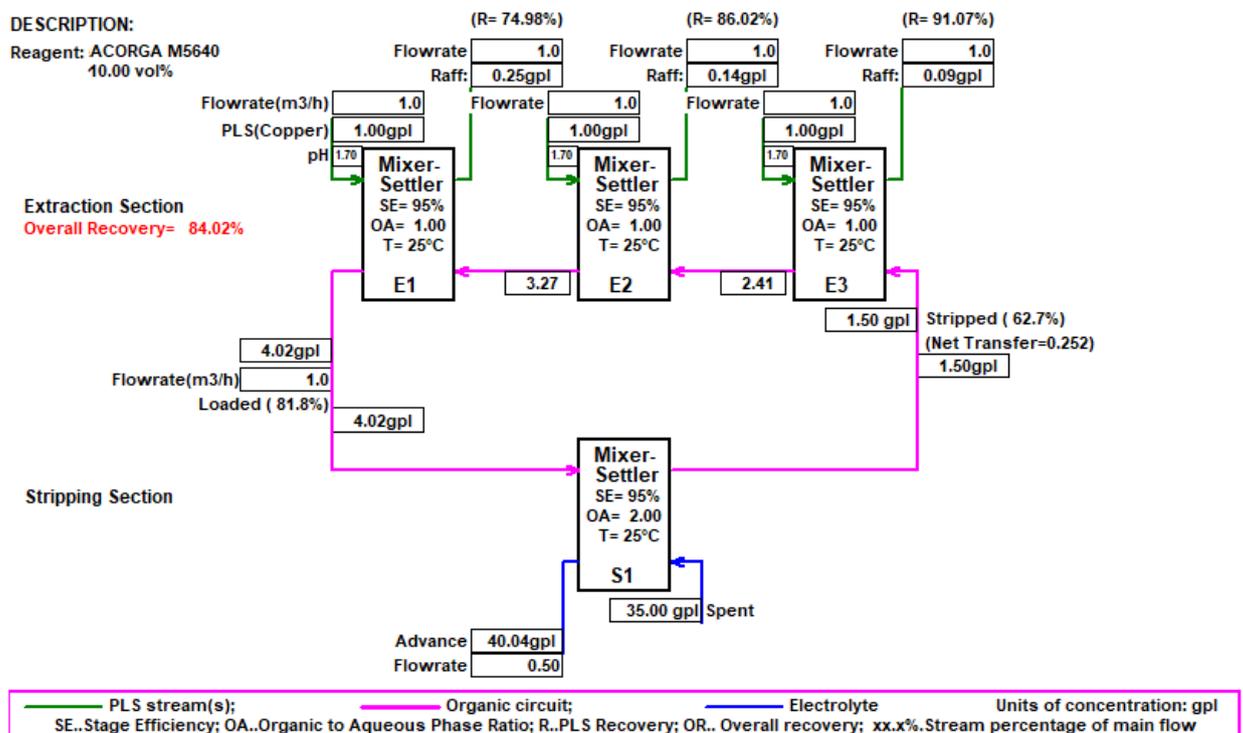


Figure 18 – Schematic of the liquid copper extraction process from the Almay deposit PLS

Based on the data obtained, a mathematical model of liquid copper extraction was calculated. The main factors that affect the process of copper extraction are Cu concentration ($1 - 2.35 \text{ g/dm}^3$) (X1), pH of the medium (X2), extraction duration, min (X3).

Mathematical model of copper extraction was built by full-factor experiment. Constant values for planning the experiment and building a mathematical model taken stirring speed equal to 350 rpm.

Variable technological factors at construction of mathematical model were the following:

- concentration of copper in the initial solution, g/l (X1);
- pH of the initial aqueous phase (X2);
- duration of extraction, min (X3).

Boundary conditions of copper extraction realization by «Acorga 5640» extractant are shown in table 11.

Table 11 – Boundary conditions for copper extraction with extractant «Acorga 5640»

Level of variation	X ₁ , (C, g/dm ³)	X ₂ , pH of the medium	X ₃ , extraction time, min
Lower level	1,0	1,6	10
Upper level	2,35	1,7	60

The number of experiments N to be performed is determined as follows [43]:

$$N = n^k \quad (5)$$

where n is the number of levels;

k is the number factors.

Therefore, for 2 levels and 3 factors N = 8. The matrix planning matrix for 8 experiments looks like that shown in table 12.

Table 12 – Experiment planning matrix for copper extraction with extractant based on «Acorga 5640» for the three varying factors

Test	X ₁	X ₂	X ₃	X ₁ X ₂	X ₁ X ₃	X ₂ X ₃	X ₁ X ₂ X ₃
1	+	+	+	+	+	+	+
2	–	+	+	–	–	+	–
3	+	–	+	–	+	–	–
4	+	+	–	+	–	–	–
5	+	–	–	–	–	+	+
6	–	+	–	–	+	–	+
7	–	–	+	+	–	–	+
8	–	–	–	+	+	+	–

Let's write down the form of the regression equation according to according to the planning matrix

$$Y = Y_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 + b_{123} X_1 X_2 X_3 \quad (6)$$

Where \bar{Y}_0 is a free term of the regression equation;

b_i is coefficients

Of the regression equation \bar{Y}_0 . The free term of the regression equation can be calculated as follows:

$$\bar{Y}_0 = \frac{\sum_{i=1}^N \bar{Y}_i}{N} \quad (7)$$

Where N – the number of extraction experiments;

\bar{Y}_0 – the average value of the degree of copper extraction into the extract during extraction with the extractant “Acorga 5640”.

The data obtained in accordance with the plan of experiment (table 12) for copper extraction with the extractant «Acorga 5640» are presented in table13.

Table 13 – Results of copper extraction experiments by the extractant «Acorga 5640» obtained in accordance with the plan of experiment

Test	Y_1	Y_2	\bar{Y}
1	87,5	87,7	87,6
2	81,4	81,6	81,5
3	72,6	72,2	72,4
4	68,4	68,8	68,6
5	63,1	62,5	62,8
6	55,6	56	55,8
7	51,4	52,4	51,9
8	48,5	47,9	48,2
			$\bar{Y}=66,1$

Calculation of parameters of the mathematical model were calculated in accordance with the following algorithm for calculating the coefficients, variance, and Student’s t-test and Fisher criteria [43], [44]. which performed using the capabilities of an office program Microsoft Excel:

Of the regression equation were determined by equation:

$$b_j = \frac{\sum X_{ij} Y_i}{N} \quad (8)$$

The variance of the coefficients (S_{bj}) and reproducibility (S_{vosp}) were calculated

by expressions, where N – number of experiments

$$S_{bj} = \frac{S_{\text{BOCII}}}{\sqrt{N}}, \quad (9)$$

$$S_{\text{BOCII}} = \sqrt{\frac{\sum_{i=1}^N S_i^2}{N}} \quad (10)$$

Where S_j^2 is the variance of the unit measurement, determined by the formula:

$$S_j^2 = (Y_1 - \bar{Y})^2 + (Y_{11} - \bar{Y})^2 \quad (11)$$

The significance of the coefficients was evaluated by the Student's test

$$t_j = \frac{b_j}{S_{bj}} \quad (12)$$

comparing with the reference table its value $t_{\text{cr.tab.}} = 2.78$ for the level $p = 0.05$ and the number of degrees of free

$$f = N(m - 1) \quad (13)$$

where $m = 2$ is the number of parallel experiments ($m = 2$ and $f = 4(2 - 1) = 4$). If t_j is greater than $t_{\text{cr.tab.}}$, then this coefficient is significant.

Checking adequacy of the obtained equation was performed according to Fisher's criterion [44]:

$$F = S_{\text{OCT.}}^2 / S_{\text{BOCII.}}^2, \quad (14)$$

$$S_{\text{OCT.}}^2 = \frac{\sum_{i=1}^N (Y_i - \bar{Y})^2}{N - L} \quad (15)$$

Where L is the number of significant coefficients: $L = 2$. Regression coefficients and values of the unit variances of the experiments, which were obtained from the experimental data, are presented in table 14.

Complete regression equation for copper extraction with extractant «Acorga 5640»

$$Y = 66,1 + 6,7x_1 - 7,31x_2 - 7,28x_3 + 3,88x_2x_3 \quad (16)$$

In the course of calculating dispersion of reproducibility and regression coefficients, the following values were obtained: $S_{\text{vosp}} = 0.377$; $S_{bj} = 0.133$.

The reference table value of the criterion Student $t_{cr.tab.} = 2.12$ for significance level $p = 0.05$ and number of degrees of freedom F , calculated according to formulas (11) and (12) [43], [44].

Table 14 – Regression coefficients and unit variance for the construction of the mathematical model of copper extraction with the extractant «Acorga 5640»

Regression coefficient	Value	Unit variance	Value
b_1	6,7	S_1^2	0,02
b_2	7,31	S_2^2	0,02
b_3	7,28	S_3^2	0,08
b_{12}	-1,98	S_4^2	0,08
b_{13}	-0,0612	S_5^2	0,18
b_{23}	3,88	S_6^2	0,08
b_{123}	-1,61	S_7^2	0,5
		S_8^2	0,18

Significance of the calculated coefficients regression coefficients were determined by comparing them with the table value Student's criterion. Regression coefficient is significant if Student's t-test for coefficient (t_j) is greater than the table Student's criterion $t_{cr.tab.}$

Based on from the data obtained, it follows that only four coefficients of the equation of the regression equation are significant, that is why $L = 4$ and the final form of the regression equation has not changed (Eq.(16)).

The residual variance at $L = 4$ is $S_{ost}^2 = 0.1425$, and the variance value of the Fisher's criterion:

$$F_{расч} = 0,1425 / 0,1421 = 1,002. \quad (17)$$

Tabulated value of Fisher's criterion at $F_2 = 8$ and $F_1 = 4$ is $F_{table} = 3.84$. The obtained mathematical model of copper extraction with the extractant «Acorga 5640» is adequate to the experiment, as the condition:

$$F_{settl} < F_{tabul}, 1,002 < 3,84 \quad (18)$$

Thus, by method of full-factor experiment the mathematical model adequately describing the process of extraction of copper extraction with extractant «Acorga 5640».

3.7 Feasibility study on copper extraction

3.7.1 Process comparisons

Elements of penalties. All processes provide acceptable rejection of major deleterious elements such as arsenic and antimony, provided the Fe: As + Sb ratios are acceptably high.

Copper cathode quality. The Placer and CESL processes use modest versions of the commercially proven SX-EW technology, which when operated well should guarantee an acceptable cathode product. In the absence of documentation, the Dynatec/Direct REB solution cleaning technology should be regarded as unproven.

Copper recovery. High leaching efficiencies and copper recovery with SX-EW are practical for CESL and alluvial processes. Based on very limited published information, it is difficult to see how copper would be effectively recovered from Dynatec bleed solution without at least some use of SX technology.

Grinding. It is believed that the differences in technical characteristics of concentrate regrind are not a significant cost difference between the processes.

Pressure oxidation. The principle difference in pressure oxidation costs between the high and low refining processes is due to the higher oxygen consumption during general oxidation. The complete oxidation of chalcopyrite requires 2.14 kg of oxygen per kg of copper compared with about 1 kg/kg for low grade (20 % S → SO₄). For a concentrate containing pyrite and chalcopyrite in a 1:1 molar ratio (21 % copper sulphide only), the total oxygen consumption under pressure increases to 4 kg/kg, whereas for low gravity pressures the oxygen consumption increases slightly to 1.3 kg/kg at 20 % S → SO₄. Assuming a low energy scenario with a correspondingly low oxygen cost of US \$33/tonne, moving to the traditional mode of comparing the cost of copper in USD/lb indicates the following.

Clearly, in a scenario with relatively high electricity and oxygen costs (say \$66 per tonne of oxygen), the cost for oxygen under total pressure of pyrite concentrate (\$0.12 per lb cu m or \$52.80 per tonne of concentrate) becomes the dominant operating cost see "Operating Cost Comparison" and negates much of the cost associated with in situ processing.

Table 15 – Operating costs of the O₂ pressurised process

Product	Oxygen cost, USD/lbc	
	oxygen under selective pressure	oxygen under selective pressure
Chalcopyrite	0,032	0,010
1:1 Chalcopyrite:Pyrite	0,06	0,013

The high gold content in pyrite would be necessary to justify the total oxygen pressure in this scenario. Placer recently reported 98 % copper recovery from a

continuous pilot campaign at 30 minutes storage. [45] CESL reports (very limited) batch testing data for 1 hour of storage, while Dynatec reports 4 hours of batch storage. Even taking into account the higher tank pressure and pumping requirements for total pressure oxygen, these data show a significant but difficult to quantify capital cost advantage for pressurised oxygen compared to CESL or, especially, Dynatec.

SX-EW copper. Due to the necessary dilution of free acid in the total POx PLS, it is estimated that the hydraulic load on the SX will be approximately double that for low gravity processes. As settling tank mixers are inexpensive per unit volume, the capital cost disadvantage compared to total POx is not severe. However, the loss of organics will be roughly proportional to the aqueous PLS consumption, resulting in an operating cost penalty of \$0.005 per pound of Cu for total POx.

Waste Disposal/Decontamination. Placer publications clearly take neutralisation costs into account; whereas, in the authors' view, these costs are neglected in documenting low severity processes. In an era when acid drainage is almost universally recognised as a potential problem for mining waste, disposal of sulphur and unreacted pyrite without equivalent, effective calcium alkalinity would only be allowed in the context of carefully considered containment (i.e. hazardous waste) and retention of owner responsibility, probably in the form of a large closure bond. Thus, neutralisation is not necessarily a significant cost driver. In the case of an acid-consuming heap or tailings leach, a total POx company could get an acid credit of up to \$40 per tonne or \$0.09 per pound of copper if the alternative acid source is, for example, market acid delivered by truck over long distances. In such a situation, sulphur credits would also be applicable to low-treatment processes, but would be reduced to take into account the cost of converting sulphur and pyrite into usable acid.

Construction materials. The Placer and Dynatec processes use sulphate solutions, which outside the autoclave allow extensive use of stainless steel for wetted metal processing. The chloride content in CESL of (approximately) 12 g/l would require more exotic alloys and/or lined or coated equipment, with correspondingly higher (but difficult to quantify in general comparison) capital and maintenance costs.

Confirmed process status. Based on published data and the relationship of unit operations to commercial practice, a subjective ranking of the authors of the 'proven status' of the technologies is as follows

Placer>> CESL>>> Dynatec

The placer mining process has required much less time for continuous experimental demonstration, but this is considered to be more than compensated by the extensive commercial operation of the high-toxicity refractory gold ore and concentrate treatment processes. This provides reliable assurance of precious metal recovery (and cost estimates), while the recovery of PM from CESL process residues is not yet documented in the technical literature. The very small amount of published

information is the main reason for the relatively low "proof of concept" rate of the Dynatec process.

Capital cost comparison. A recent presentation by Placer included a preliminary capital cost estimate of US\$248 million for a plant to produce 100,000 tonnes per year of copper cathode from 20 % copper concentrate at an unspecified mine [45]. At a capacity of (about) US\$2,500/year tonne, this meets the published CESL "target" of US\$2,000-2,500/year tonne and is comparable to Noranda [46] capital costs by an order of magnitude (US\$2,500 – 3,000/year tonne) at a minimum cost. ((200 000 tons/year) is considered acceptable for a new greenfield smelter. No capital cost data is available for Dynatec technology, but the additional plant operation (sulphur melt filtration) and longer autoclave residence time do not give much hope for cost reduction.

Comparison of operating costs. Using the recently presented Placer estimate of operating costs [45] as a basis, it is possible to sing the recently presented Placer estimate of operating costs [45] as a basis, the operating costs of the high and low severity POx-SX-EW processes can be compared as follows.

Table 16 – Comparison of operating costs for POx-SX technology \$US/lb copper

\$US/lb copper			
	high severity	low severity	
	total POx	Pox*	
Oxygen	0,041	0,012	
Neutralisation (mill tailings)	0,006	0,006	
Autoclave grinding and agitation	0,018	0,018	Less mass transfer, but more agitators
Maintenance consumables	0,013	0,019	Scaled up
Salary / Labour Force	0,006	0,006	
Total leaching	0,084	0,061	
Total SX-EW	0,109	0,103	Less reagent loss and mixing
Waste handling	0,02	0,02	
Cathode transportation and marketing	0,03	0,03	
Total	0,243	0,214	
*Based on CESL, Dynatec estimate 10-20 % higher			

Thus, with an additional operating cost of \$0.03 per pound of copper or \$13.20 per tonne of 20 % concentrate (a difference that is within the likely range of these preliminary estimates), the potential operator of the whole POx process could benefit from a more proven technology and guaranteed gold and silver recovery.

Extraction of an additional 1.3 grams of gold from fully reacted pyrite could also have made up for the difference in costs. Conversely, the significantly higher total cost or oxygen consumption of smallpox could skew the comparison in favour

of smallpox. In this regard, it may be interesting to note that the total oxidation study, resulted in total costs for POx, SX-EW, neutralisation and disposal of US\$0.42/lb cc. This was expected to be mitigated by the relatively high energy and oxygen consumption costs of the project. This was expected to be mitigated by significant gold recovery, avoidance of port costs for trans-shipment and improved socio-economic (i.e. political) impacts of additional employment. Judging by the lack of follow-up, the high operating costs were unacceptable.

Overall economic viability. Again, drawing on Placer's recent presentation, their summarised venture analysis of 20 % copper concentrate shows [45].

Table 17 - Overall economic viability

Capital expenditure	\$248 million
Difference between transportation and smelting costs and total production costs Pox	0.175 per pound of copper or \$US 38.6 million/year
Payback period at 6 % interest rate of	8 years

Given the protection from additional smelter costs due to (hopefully) copper prices above the base level of \$0.80/lb and increased freight rates, these figures indicate a potentially viable venture.

Conclusions. The potential viability of hydrometallurgical technology (POx) versus toll smelting for new copper projects still depends on transport cost savings and the availability of relatively cheap electricity at the mine. However, the use of a combination of industrially proven processes (such as alluvial technology) clearly indicates that suitably qualified new mines may have a viable, cost-effective alternative to contract smelting of their products. Subject to further cost validation, low-cleaning processes can provide equivalent or greater savings in the associated concentrates.

CONCLUSION

Geotechnological methods are the most promising for processing of off balance and waste ores. They allow to expand the raw material base of deposits by extracting metals directly from ore.

The key factors influencing the quality of productive leaching solutions are the presence of silicate minerals, carbonate minerals, clay, feldspar, iron oxides, highly porous copper minerals and/or slurries.

Interfacial slurry/scalding is recommended to manage not only the continuous removal of this phase from the system, but also to pay attention to factors that lead to interfacial slurry formation such as leaching regime, settling time of the product solutions, agitator rates, organic levels in the settling chutes and acidity of the solutions to avoid formation of a silica gel.

Experiments show that the use of ACORGA CR60 with a dosage of 10 ml/m³ in the PLS line before feeding it into the liquid extraction, results in a significant reduction of interfacial crusting in the circuit. The phase separation time in the test chain extraction step increased by an average of 8 seconds, which is explained by the reduced amount of solids in the organic phase. The increase in WRF was due to less interaction of solids with the organic phase caused by the addition of the reagent. The recovery of copper was similar in both circuits, confirming that the reagent does not affect the metallurgical characteristics of the process and does not carry any risk to the overall process. At the time of this comparison test, the main advantage was the reduction of mole formation in the test circuit and a positive effect was observed in the difference of organics entrainment.

ACORGA CR60LT is used on an industrial scale in many plants in North America, Latin America and also in the DR Congo. The main advantage of CR60 is the reduction of stain build-up in settling tanks, thus increasing the capacity of the PLS and organics flows which directly leads to an increase in the productivity of the plants. In addition, the liquid extraction process is known to be difficult in the presence of silica in PLS solutions, but with the addition of ACORGA CR60LT a stable process is observed.

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Annex A

Prints of publications on the topic of research



**"СӘТБАЕВ ОҚУЛАРЫ-2022. ҚАЗІРГІ ҒЫЛЫМИ ЗЕРТТЕУЛЕРДІҢ
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КОНФЕРЕНЦИЯ ЕҢБЕКТЕРІ**

12 сәуір 2022 ж.

III Том

**ТРУДЫ МЕЖДУНАРОДНОЙ НАУЧНО-ПРАКТИЧЕСКОЙ
КОНФЕРЕНЦИИ «САТБАЕВСКИЕ ЧТЕНИЯ – 2022. ТРЕНДЫ
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12 апреля 2022 г.

Том III

**PROCEEDINGS OF THE INTERNATIONAL SCIENTIFIC AND PRACTICAL
CONFERENCE "SATBAYEV CONFERENCE - 2022. TRENDS IN MODERN
SCIENTIFIC RESEARCH"**

12 April 2022

Volume III

Алматы 2022

Труды Международной научно-практической конференции «САТПАЕВСКИЕ ЧТЕНИЯ – 2022. ТРЕНДЫ СОВРЕМЕННЫХ НАУЧНЫХ ИССЛЕДОВАНИЙ».

- Шокпаров А.Ж.** – Член Правления - Проректор по науке и международному сотрудничеству, **председатель**
- Бактыгали Ж.К.** – Директор Департамента науки, **ответственный исполнитель**
- Сыздыков А.Х.** – Директор Института геологии и нефтегазового дела
- Рысбеков К.Б.** – Директор Горно-металлургического института
- Ускенбаева Р.К.** – Директор Института автоматизации и информационных технологий
- Елемесов К.К.** – Директор Института энергетики и машиностроения
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- Удербаяев А.Ж.** – И.о. директора Института базового образования
- Узбаева Б.Ж.** – Директор Научной библиотеки

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В сборнике рассматриваются тренды современных научных исследований следующих направлений: Науки о Земле; Актуальные вопросы биотехнологии, химической технологии и защиты окружающей среды; Энергетика и машиностроение; Инновационные технологии в геопространственной инженерии и горном деле; Прогрессивные технологии в ИКТ; Проблемы и перспективы развития архитектуры и строительной инженерии в современных условиях; Управление развитием бизнеса, проектный менеджмент и логистика; Современные тенденции преподавания базовых дисциплин в эпоху цифровой трансформации.

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ВЛИЯНИЕ КРАДООБРАЗОВАНИЯ НА ПРОЦЕСС ЖИДКОСТНОЙ ЭКСТРАКЦИИ МЕДИ КАЗАХСТАНСКИХ ПРЕДПРИЯТИЙ

М.И. Есиркегенов¹, А.Ө. Мұқанғалиева¹, Алтмышбаева А.Ж.,
Чепуштанова Т.А.¹, Nikoloski A.²

¹Satbayev University, Казахстан, Алматы

²Murdoch University, Australia
1603sh_mukangalieva@mail.ru

Аннотация. Накопление твердых частиц в контурах экстракции растворителем (SX) может вызвать проблемы с физическими и экономическими показателями операции. Эти твердые вещества ответственны за образование твердой стабилизированной эмульсии, содержащей органические, водные, воздушные и мелкие твердые частицы. Накопление крада в отстойниках SX может ограничить производительность операции SX, потребовать простоя установки, привести к более высоким органическим потерям или привести к более высокому уносу воды в органические вещества (все это может иметь значительные негативные экономические последствия). Существующие методы управления крадом обычно носят реактивный характер. Крад физически удаляется после того, как подается чрезмерное количество в контуре, и обрабатывается механически с использованием центрифуг или фильтрации. Было разработано новое упреждающее решение для предотвращения образования и накопления межфазных взвесей. В статье представлены результаты технических решений, которые были осуществлены на заводах SX-EW в Казахстане.

Ключевые слова. экстракция, крад, экстрагент, выщелачивания.

Образование и накопление крада в контурах экстракции растворителем (SX) давно обсуждается и считается критически важным для всего гидрометаллургического процесса [1]. Образование крада присутствует во всех системах SX, будь то медь, уран, цинк и т. д. В работах Ритчи, 1980 были определены крады - как стабилизированные эмульсии, содержащие органические, водные и мелкие твердые частицы. Тип руды и состав сырья являются основным определяющим фактором образования руды и обычно содержат Si, Al, Fe, P и сульфаты [2]. Обычно крад образуется на границе раздела между органической и водной средами, но его также можно наблюдать в виде плавающей взвеси на поверхности отстойника или донной фракции, которая часто встречается в контурах, обрабатывающих взбалтываемое выщелачивающее сырье. Поскольку образование крада практически неизбежно, многие современные методы управления крадом являются реактивными, что позволяет краду образовываться и встраиваться в контуры SX. Как только это происходит, его удаляют и обрабатывают с помощью различных механических методов, обычно с помощью фильтрации или трехфазной центрифуги, для удаления твердых частиц и извлечения органической фазы, захваченной в эмульсии [3]. Также разрабатываются автоматизированные насосные системы, которые часто используются на предприятиях во всем мире, в том числе и на предприятиях Казахстана: Казминералс Актогай, на месторождении Алмалы. Время и финансовые затраты, необходимые для управления образованием крада, могут быть решающим аспектом работы SX-EW завода.

Во многих заводах по производству катодной меди в Казахстане, применяющие технологии кучного выщелачивания, жидкостной экстракции и электролиза являются более высокая концентрация диоксида кремния, присутствующего либо в растворенном, либо в коллоидном виде. Растворимость диоксида кремния будет зависеть от температуры и pH среди других факторов, при этом более низкие температуры и более высокая кислотность приводят к усиленному осаждению и образованию коллоидного кремния [4].

Было замечено, что коллоидный диоксид кремния в PLS влияет на разделение фаз в жидкостной Экстракции, и работа в непрерывном органическом режиме является известной практикой, помогающей преодолеть проблемы разделения фаз, связанные с диоксидом кремния [5]. В непрерывной водной среде коллоидный диоксид кремния может привести к увеличению времени разделения фаз, что приведет к увеличению уноса воды и тем самым увеличит физический трансфер примесей примесей в электролит. В экстремальных условиях

могут образовываться стабильные эмульсии, что значительно влияет на производительность предприятия [6]. Коллоидные частицы не оседают и их трудно удалить из выщелачивающего раствора [7]. Когда эти частицы объединяются, может образоваться силикагель, который оседает на успокоителях экстракторов, что создает дополнительные проблемы для поддержания заданных скоростей потока и производительности.

Объект исследования. Объектом исследования был раствор кучного выщелачивания (PLS) месторождения Алмалы, в котором функционирует металлургический комплекс по производству катодной меди мощностью 10 тыс. тонн катодной меди в год. На данном месторождении наблюдаются специфические условия PLS (диоксид кремния, высокая концентрация растворенных веществ, высокая вязкость), которые благоприятны образованию крада в отстойниках, что приводит к движению крада и нестабильности завода, отчасти и повышенному уносу органической фазы с водной. Несмотря на такие специфические условия, комплекс по производству катодной меди функционирует согласно проектным значениям и имеет потенциал для наращивания производства.

Цель данной работы состояла в том, чтобы определить совместимость и эффективность новой химической добавки для уменьшения образования крада и ее влияния на физические и металлургические характеристики процесса, а также уноса органической с водной фазой как основной приоритет

Концентрация основных элементов в растворе составила: Cu – 2,35г/дм³, Fe – 21,55г/дм³, SiO₂ – 0,34г/дм³.

Для определения элементного состава продуктивного раствора, была произведена выпарка с получением твердого осадка. Выпарка продуктивного раствора (PLS) показала, что общая концентрация солей достигает 35 %.

Подготовка образца крада к анализам включала в себя предварительную сушку пробы до полного обоживания и последующее истирание до крупности не более 0,1 мм. С целью определения основных минеральных форм присутствующих в краде выполнялся рентгенофазовый анализ, результаты которого представлены в таблице 1.

Таблица 1 – Результаты рентгенофазового анализа крада(образование межфазного отхода)

Наименование	Формула	%
Кварц	SiO ₂	63,98
Англезит	Pb(SO ₄)	14,94
Магнетит	Fe ₃ O ₄	13,73
Гематит	Fe ₂ O ₃	7,35

Основные моменты испытаний на пилотной установке с применением реагента.

Пилотная установка была расположена в самом здании завода жидкостной Экстракции. Цепи Тест (с дозировкой реагента ACORGA CR60LT в PLS) и Контроль (без дозировки – контрольная) были настроены с конфигурацией 1E+1S (1 стадия экстракции и 1 стадия реэкстракции), рафинаты и богатые электролиты сливались в дренажную систему завода.

Дозировка реагента (ACORGA CR60LT) была выбрана равной 10 ч/млн или мл/м³ раствора, и увеличена до 15 мл/м³ по ходу проведения тестов.

Первые 72 часа испытания проводились в параллельных двух цепях как одна экстракция и одна реэкстракция (1+1) при дозировке CR60LT 10 мл/м³, далее цепь была перестроена как одна в три параллельной экстракции и одной реэкстракции на период 148 часов при дозировке CR60LT 15 мл/м³.

Различие в формировании крада было очевидным между двумя цепями (начиная с дозирования реагента); в цепи Контроль (без дозировки) зафиксирован больший объем межфазного крада, тогда как цепь Тест (с дозировкой) показала образование крада намного меньше. В этом отчете цифры, связанные с образованием и сравнением крада, приведены в см³.

Результаты металлургических параметров по тестам на пилотной установке

Пробы PLS, рафинатов, бедного электролита и двух богатых электролитов отбирались каждые 4 часа, в основном для анализа на содержание меди. Содержание меди в PLS, рафинатах и в электролитах показаны в Таблице 2.

Таблица 2. Результаты металлургических параметров.

Условия	Медь в PLS	Медь в рафинате	Медь в богатом Электролите	Медь в бедном Электролите
Тест, г/л	1,8 – 2,36	0,11 – 0,24	36 - 41	34 - 36
Контроль, г/л	-	0,13 – 0,22	36,4 – 41,2	-

Результаты физических параметров по испытания на пилотной установке

В течении испытательного периода в обеих цепях не было зарегистрировано крада на дне сетлеров. Разница в объемах межфазной массы между цепями Тест и Контроль была значительной на стадиях экстракции, крад в цепи Контроль образовывался интенсивно. Время разделения фаз для цепи Тест и Контроль было немного различным в стадиях экстракции. Наблюдается увеличение ВРФ в цепи Тест в среднем на 10 секунд, как показано в таблице 3. Это ожидалось и наблюдалось во время испытаний на других заводах. Увеличение вызвано меньшим взаимодействием твердых веществ с органической фазой, чему способствует дозировка реагента для уменьшения образования крада. Увеличение ВРФ, не повлияло на физические характеристики процесса в отношении увеличения уноса органики с водной фазой.

Таблица 3. Результаты определения времени расслоения фаз.

Стадии	Контроль			Тест		
	ВРФ(сек.)	Глубина орг. (см)	Межфазный крад (см)	ВРФ(сек.) орг. (см)	Глубина	Межфазный крад (см)
E1	130,00	9,40	7,10	138,00	9,10	4,70
S1	83,00	8,60	0,50	81,00	8,45	0,50

Заключение. Геотехнологические способы наиболее перспективны для переработки забалансовых, отвальных и потерянных руд. Они позволяют расширить сырьевую базу месторождений, извлекая металлы непосредственно из руды.

Ключевыми факторами влияющие на качество продуктивных растворов выщелачивания являются наличие силикатных минералов, карбонатных минералов, глина, полевой шпат, оксиды железа, высокопористые медные минералы и/или шламы образующие минералы.

Образование межфазовой взвеси/крада рекомендуется управлять не только постоянным удалением из системы этой фазы, но и уделять внимание на факторы которые приводят к образованию межфазовой взвеси, такие как режим выщелачивания, время отстаивания продуктивных растворов, скорости мешалок, уровень органики в желобах отстойника и кислотность растворов чтобы избежать образование кремниевого геля.

Эксперименты показывают, что использование реагента для уменьшения образования крада ACORGA CR60 с дозировкой 10 мл/м³ в линию PLS перед его подачей в Жидкостную экстракцию, приводит к значительному уменьшению образования межфазного крада в цепи.

Время разделения фаз увеличилось на стадии экстракции в цепи Тест в среднем на 8 секунд, что объясняется снижением количества твердых веществ в органической фазе. Увеличение ВРФ связано меньшим взаимодействием твердых веществ с органической фазой, вызванным добавкой реагента. Извлечение меди было одинаковым в обеих цепях, подтверждая, что реагент не влияет на металлургические характеристики процесса, и не несет никакие риски для всего процесса. Во время проведения данного сравнительного испытания, основное преимущество зафиксировано в уменьшении образования крада в цепи Тест, позитивный эффект был отмечен и в разнице уноса органики, но зависимости, что это действительно влияние реагента CR60, заключить сложно, так как при отключении дозировки унос оставался на прежнем уровне без повышения. Как следствие, рассчитать экономический эффект именно по уносу органической фазы на данный момент не предоставляется возможным.

Реагент ACORGA CR60LT используется в промышленных масштабах на многих заводах Северной и Латинской Америки, а также на производствах в ДР Конго. Как показано в данной статье основное преимущество — это снижение образования крада в отстойниках, тем самым увеличение объема для потоков PLS и органики, что напрямую ведет к увеличению производительности заводов. В дополнении, как известно процесс жидкостной экстракции в присутствии диоксида кремния в растворах PLS затрудняется, но с добавкой реагента ACORGA CR60LT наблюдается стабильная работа процесса.

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Мысты сұйық экстракциялау процесіне сабақ түзілудің әсері

Есиркегенов М.И.¹, Мұқанғалиева А.Ө.¹, Алтмышбаева А.Ж.¹, Чепуштанова Т.А.¹,
Nikoloski A.²

Аңдатпа. Еріткішті алу тізбектерінде қатты бөлшектердің жиналуы (SX) операцияның физикалық және экономикалық көрсеткіштеріне қиындық тудыруы мүмкін. Бұл қатты заттар органикалық, су, ауа және ұсақ қатты заттардан тұратын қатты тұрақтандырылған эмульсияның түзілуіне жауап береді. SX тұндырғыштарындағы ұрлықтың жиналуы SX жұмысының жұмысын шектеуі, қондырғының тоқтап қалуын талап етуі, жоғары органикалық шығындарға әкелуі немесе органикалық заттарға судың көбірек түсуіне әкелуі мүмкін (мұның бәрі айтарлықтай теріс экономикалық салдарға әкелуі мүмкін). Қрадты басқарудың қолданыстағы әдістері әдетте реактивті. Қрад тізбекте шамадан тыс мөлшерде берілгеннен кейін физикалық түрде алынып тасталады және центрифугалар немесе сүзгілеу арқылы механикалық өңделеді. Фазалық суспензиялардың пайда болуы мен жиналуына жол бермеу үшін жаңа алдын-ала шешім жасалды. Мақалада Қазақстандағы SX-EW зауыттарында жүзеге асырылған техникалық шешімдердің нәтижелері ұсынылған.

Негізгі сөздер. экстракция, қрад, экстрагент, шаймалау.

Influence of stalk formation on the process of liquid extraction of copper

Yesirkegenov M.I.¹  Mukangalieva A. O.¹ Altmyshbaeva A. Zh.¹  Chepushtanova T.A.¹  Nikoloski A.²

Abstract. The accumulation of solids in solvent extraction (SX) circuits can cause problems with the physical and economic performance of the operation. These solids are responsible for the formation of crud, a solid stabilized emulsion containing organic, aqueous, air, and fine solid particles. The build-up of crud in SX settlers can limit SX operation throughput, require plant downtime, lead to higher organic losses, or result in higher aqueous in organic entrainment (all of which can have a significant, negative economic impact). Current practices for crud management are typically reactive. Crud is physically removed after it has been allowed to build to excessive levels in the circuit and processed mechanically using centrifuges or filtration. A new proactive solution has been developed to prevent crud formation and build-up. This paper will review results from operations in Kazakhstan covering heap leach, concentrate leach, and agitated leach feeds.

Keywords. extraction, theft, extractant, leaching.

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