

Peculiarities of the Segregation Roasting Process of Gold-Bearing Copper Ores and their Processing Residues

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(Presented by Academy Member Grigor Tatishvili)

Abstract. This study investigates the potential of the segregation method for extracting copper, gold, and silver from deposits in the Bolnisi region of South Georgia. The materials examined included: oxide copper ores from the Dark Ravine deposit, secondary quartzites from the oxidation zone and iron cakes, which are residues of the joint autoclave leaching of chalcopyrite concentrate and low-grade manganese flotation concentrate of Chiatura. These ores were first subjected to pre-oxidative roasting, followed by segregation roasting. The metal extraction rates in the flotation concentrates of the segregation products was 86-93% for the copper oxide ore, within 80% for secondary quartzites, and 91-93% for iron cakes. As a result of the segregation of copper oxide ore, metallic copper accumulates around the coal, but during the segregation roasting of iron cakes, an additional process occurs – the sulfidation of metallic copper with the formation of chalcocite (Cu_2S) at the expense of the sulfur, contained in the cakes in sufficient quantities in the form of calcium sulfate. Phase transformations during the segregation of iron cakes were studied. To confirm the role of CaSO_4 in the copper sulphidation process, a separate experiment was conducted involving three solid substances – copper, calcium sulfate and coal – within a temperature range of 750-900°C. Micro-X-ray spectral analysis of the samples was performed using the MS-46 “Kameka” microanalyzer, and electron-raster microphotographs, taken on it, confirmed the mechanism of the formation of metallic copper around coal as a result of the segregation of iron cakes and its transformate into chalcocite (Cu_2S). The findings highlight the advantages of this process for improving the flotation enrichment of the segregation products and its subsequent metallurgical processing. © 2026 *Bull. Natl. Acad. Sci. Georg.*

Keywords: copper oxide ore, segregation roasting, copper, sulfidation, chalcocite

Introduction

In Bolnisi District of Georgia, the main products of the Mining Enrichment Factory of Kazreti are concentrates of sulphide ores, including chalcopyrite concentrate containing copper and noble metals.

The company “RMG” currently operates in this area, which extracts basic ores, enriches them and further processes them in order to extract non-ferrous and precious metals. In the Bolnisi area and its surrounding areas, together with the main sulphide ores, are low-quality hard-to-enrich gold-

bearing copper oxide ores, mixed ores and ores processing residues are mined. As the metal prices rise, the interest in them increases steadily. The enrichment of these ores by traditional methods is not always effective – the quality of metals in the concentrate is low. In this case, it is promising to use a segregation method for their processing, which can provide effective complex processing of these ores and their processing residues with maximum extraction of useful components.

Materials and Methods

Several years ago, a semi-industrial enterprise operated on the territory of the mining enrichment factory, where the chalcopyrite concentrate was processed using the hydrometallurgical method, which provided for joint autoclave extraction with the low-quality manganese flotation concentrate of Chiatura. The products of the enterprise were autoclaved copper powder and active electrolytic manganese dioxide. Production residues consisted of iron cakes containing significant amounts of copper (1-2%), iron (30-50%) and noble metals (10-40 g/t silver and 2-6 g/t gold).

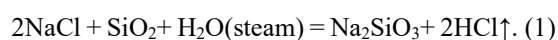
After testing various methods for processing cakes containing such valuable components and obtaining unsatisfactory results, the segregation roasting method was chosen, which was used for processing difficult-to-enrich copper ores.

The segregation method was discovered in the 1920s and found practical use three decades later by the Anglo-American group "TORCO" (Treatment of Refractory Copper Ores). The segregation roasting process has been introduced in several countries: the USA, Canada, Mauritania, South Africa, Zambia and Kazakhstan. Japan built a semi-industrial plant (150 t/day) in Katanga (Peru). This method ensures high quality and ecological safety of the extraction of non-ferrous and noble metals.

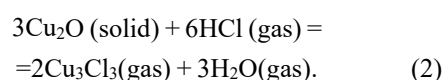
The segregation method on the first stage implies high temperature (750-900°C) burning of ores in neutral or weak-reduced area in the presence

of coal and sodium chloride. Chlorides copper and noble metals, obtained after the roasting, are reduced on the surface of carbon with hydrogen, which is formed by the interaction of water vapor with carbon. Metallic copper and noble metal particles are collected around the carbon. The second stage of processing is carried out by flotation enrichment of the segregation product. As a result of flotation, copper and noble metals are extracted together with coal in a concentrate, the content of which is much higher than that of conventional flotation concentrate. As for the chemistry of the segregation process for copper oxidized ores, there are several theories, but the generally accepted view (Rey, 1967; Pinknei & Plint, 1967; Brittan & Liebenberg, 1971; Ivasaki et al., 1973) is that the segregation process consists of three sequential stages:

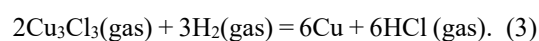
Stage I – Hydrolysis of metal chloride in the presence of ore components (silica, aluminosilicates, iron oxide, etc.) to form hydrogen chloride:



Stage II – Interaction of oxidized compounds of copper with hydrogen chloride to form volatile monovalent copper chloride. This process is accompanied by the release of water vapor involved in the hydrolysis of metal chloride:



Stage III – Recovery of copper chloride on the surface of a carbon regenerator by hydrogen, generated by the interaction of water vapor with carbon. Metallic copper is obtained, the particles of which accumulate around the carbon reducer:



The hydrogen chloride produced by this reaction re-participates in the chlorination of copper oxidized minerals, so the cost of sodium chloride is several times less than is required in the stoichiometric ratio.

The gold and silver chlorides are reduced by the same mechanism and, together with the copper,

surround the carbon reducer. As a result of flotation of the segregation product, these metals are extracted together with the coal in a concentrate, where their content is much higher than the initial one.

The process of segregation roasting has attracted the attention of many researchers around the world and it has been introduced in several enterprises. However, this method has not been used and studied for raw materials containing iron oxide and calcium sulfate in increased quantities. Such raw materials are the residues of the joint autoclave leaching of chalcopyrite copper concentrate of Madneuli and low-grade manganese flotation concentrate of Chiatura – iron cakes, which chemical composition is as follows: Cu – 1.3%, Fe – 32.5%, S – 6.33%, Ag – 38g/t, Au – 3.8g/t, CaO – 4.5%.

Iron cakes mainly contain finely dispersed grains of hematite, fragments of quartz and feldspar and residues of sulfides: such as chalcopyrite, pyrite and covellite, calcium sulfate in increased amounts and magnetite grains. Segregation roasting of the iron cakes was carried out in a rotating reactor placed in an electric furnace, in a neutral or weakly reducing area. The description of the equipment and operating conditions, as well as experimental results are given in earlier works (Chagelishvili et al., 2023; Chagelishvili et al., 2022).

Through experiments, it was established that before carrying out segregation roasting, iron cakes need oxidizing roasting at 850°C for one hour. After this stage, the burnt ash mainly contains hematite (Fe₂O₃), silicon dioxide (SiO₂), small amount of feldspar, calcium sulfate and copper oxide. The total sulfur content is 3.29%, of which 3.25% is present as sulfated sulfur.

To determine the optimal conditions for the process of segregation of residues, a series of experiments was conducted in order to study the influence of the main factors: temperature (750-900°C), consumption of sodium chloride (0.25-2% of cake mass), coal consumption (0.5-3%) and duration of segregation roasting (5-120 min) on the process. Anthracite – 250 µm in size was used for

the experiments, which contained: C – 91.12%, H – 2.16% and sodium chloride with the mark “pure for analysis” – size – 100 µm. The optimal conditions for cake segregation processing were determined: temperature – 850°C, coal consumption 1.5% of the cake mass, and sodium chloride consumption – 1%, and roasting duration – 30-60 min.

The flotation enrichment of the segregation roasting product was carried out in the following mode: pulp pH 8-11, consumption of potassium butyl xanthate – 100 g/t, and consumption of pine oil – 50 g/t, duration of main and control flotation 15 and 10 min.

Results

The degree of metals extraction in the flotation concentrate of the segregation product, carried out under these conditions, is: Cu – 91.6%, Ag – 85.8%, Au – 93.3%. Copper content in flotation tailings is 0.16% (Chagelishvili et al., 2022; Chagelishvili et al., 2023). Completely satisfactory results have been obtained.

In order to increase the quality of the flotation concentrate and reduce its yield, the flotation of a large amount of iron cake segregation roasting product was carried out with purification of the concentrates on a larger scale. The total amount of concentrates (470 g) was enriched on a 3 dm³ laboratory floatation machine, and the obtained concentrates were purified on a 0.3 dm³ floatation machine. As a result of the extended experiments, the flotation data was fundamentally improved. Copper content in purified concentrate was 42.7%, silver content – 1380 g/t, gold – 40-50 g/t. The flotation tails yield was 93% of the segregation product and contained 0.16% copper. The degree of removal of metals varied within 80%.

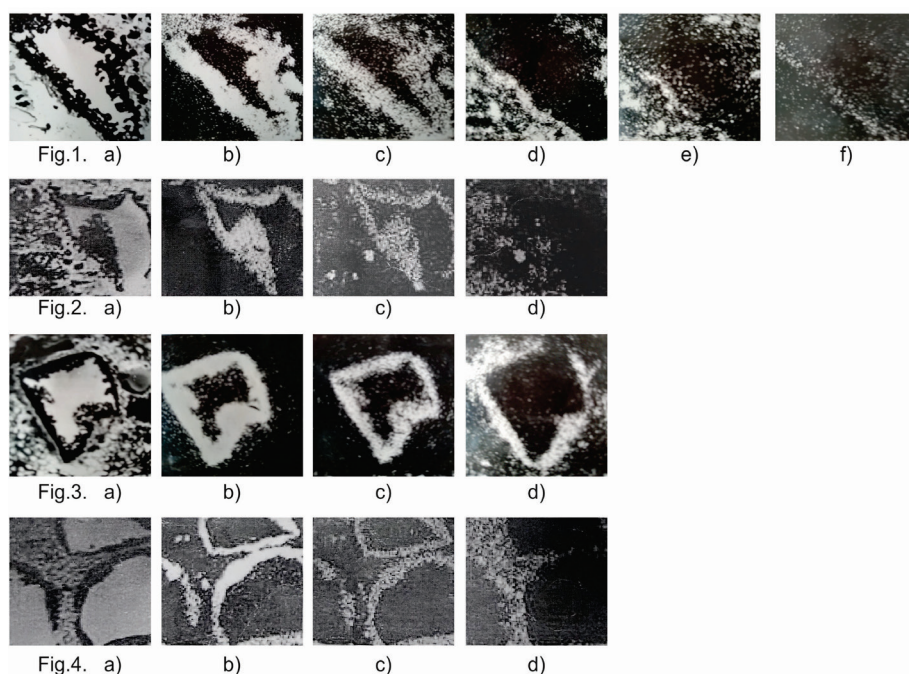
The X-ray, microscopic and micro-X-ray spectroscopic analyzes of the segregation roasting product on microanalyzer MS-46 “Kameka” show, that its main mass is represented by finely dispersed hematite, along with magnetite, copper and iron sulfides of the chalcopyrite series, coal, chalcosite

(Cu_2S) and non-mineral compounds. Chalcosite is observed mainly around coal particles (Figs. 1-4). The rich flotation concentrate is characterized by an increased amount of coal and a layer of chalcosite around it (Fig. 4). Metallic copper and white metallic deposits are found (Fig. 1).

As a result of the segregation of copper oxide ore, metallic copper gathers around the coal, which was also mentioned in the theoretical part above, and during the segregation roasting of iron cakes, an additional stage takes place – sulfidization of the free copper formed. The analyses of the products also show that copper is mainly present in them in the form of secondary sulfides – chalcosite (Cu_2S) and digenite (a high-temperature modification of chalcosite), which are formed as a result of re-sulfidization of separated metallic copper, probably, due to the sulfur, which is contained in a sufficient amount in cakes in the form of calcium sulfate. The content of copper in the form of sulphide makes easier the flotation process and further metallurgical processing of the concentrate to obtain final products.

Due to the relatively low content of gold and silver in the initial raw materials, attempts to determine the form of their existence and the combination with other elements did not yield results. Only on “Kameka” polished section (Fig. 1, f) weak silver impulses were observed, according to which it can be concluded that silver follows the segregated copper and, probably, gold as well, because the degree of their recovery in the flotation concentrate is at the level of the degree of copper recovery.

The experiment was conducted to study the sequence of phase transformations during the segregation roasting process of cakes. The samples were collected at 700° , 800° and 850°C , followed by further sampling every 10 min for one hour of the isothermal process. The collected samples were examined using the X-ray diffractometer “Drone-05”, studied under a microscope and on the X-ray microanalyzer MS-46 “Kameka”, where microphotographs of specially prepared sample slides were taken.



Figs. 1-4. Electron-raster microphotographs of polished section from iron cake segregation products (Figs. 1, 2, 3) and concentrate (Fig. 4) with absorbed electrons (a) and characteristic X-ray radiation: copper b), sulfur c), calcium d), iron e) and silver f).

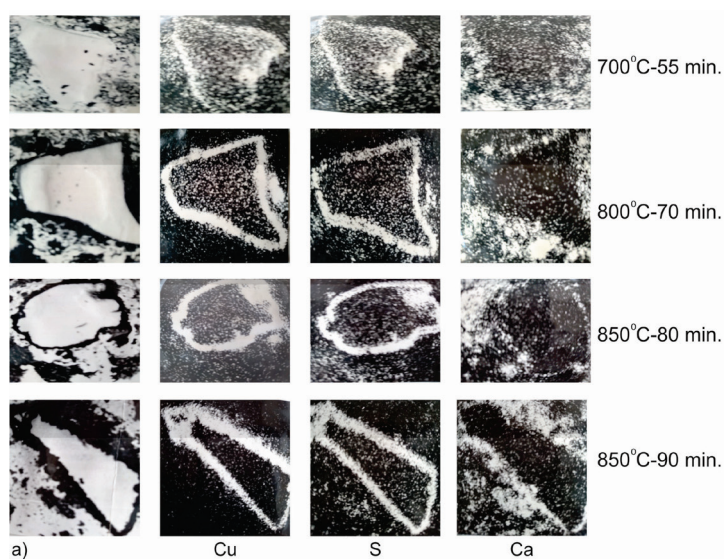


Fig. 5. Electron-raster microphotographs on the microanalyzer "Kameka" of the polished section of samples, taken every 10 minutes during the process of segregation of iron cakes – a) absorbed electrons and characteristic X-ray radiation of copper, sulfur and calcium.

The results obtained on X-ray diffractometer "Drone-05", where the sizes of individual particles of the segregation product are presented in detail in Table (Chagelishvili et al., 2022), clearly show how a thin layer of metallic copper is formed around coal particles from copper oxide at 700°C. In some areas, separate formations of chalcocite and digenite are also observed in the sample taken at 800°. The size of the layer of copper particles increases slightly at 850°, which is the optimal temperature for segregation roasting, Cu_2S (1-5 μm) form a thin chain around the coal particles. It can be concluded that the copper is completely transferred to chalcocite. After 10 min of isothermal process, hematite (Fe_2O_3) partially transforms into magnetite (Fe_3O_4). Around the coal the thickness of the chalcocite-digenite particles increases to 10 μm , after 20 min – to 50 μm , and accordingly, the thickness of the chain of particles also increases. These results are also clearly visible on the microphotographs of the slides taken on the X-ray microanalyzer MS-46 "Kameka" (Fig. 5).

Near the segregated copper the calcium content is higher than in the remaining mass, while the iron is evenly distributed throughout the mass. As a result of observing the phase and structural trans-

formations of product during the segregation roasting process of cakes, it can be concluded that in the presence of calcium sulfate, the free copper, formed during the process, is transformed into secondary sulfide – chalcocite.

There are no data on the kinetics and process mechanism of copper sulfidation with sulfur of calcium sulfate during segregation roasting. Therefore, the sulphiding process was studied separately with the participation of three solid substances – copper, calcium sulfate and coal in the same temperature range (750-900°C), which was required for segregation roasting.

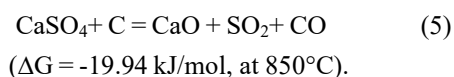
Discussion

A preliminary thermodynamic assessment of the main reactions that can take place in the system $\text{Cu-CaSO}_4\text{-C}$ in the same temperature interval was carried out. The method of Tiomkin-Schwartzman (Ruzinov & Gulyanitskii, 1975) was used for thermodynamic calculations. Isobaric-isothermal potentials were calculated using the following equation:

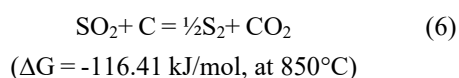
$$\Delta G_T = \Delta H_{298^\circ} - T\Delta S_{298^\circ}. \quad (4)$$

From the 25 possible reactions in this system, according to the reactions with negative values of

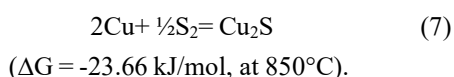
isobaric-isothermal potentials (Kireev, 1975; Kubaschewski et al., 1967), it can be assumed that copper sulphidation proceeds according to the following scheme: thermal decomposition of calcium sulfate with the participation of carbon with the formation of sulfur dioxide:



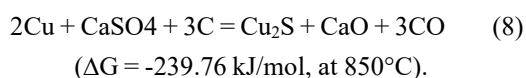
Reduction of sulfur dioxide with coal to elemental sulfur:



and sulphidizing of copper with elemental sulphur:



As a result, chalcocite Cu_2S is obtained. The total reaction for the sulphiding of metallic copper with calcium sulphate in the presence of coal is probably expressed as follows:



The results of micro-X-ray spectral analysis of the samples taken during the experiments on microprobe MS-46 "Kameka" are presented in (Fig. 6).

Observation of the phase and structural transformations of the samples confirmed our assumption of copper sulphidation with calcium sulfate in the presence of coal.

The advantage of obtaining a segregation product containing copper sulfide is that its flotation enrichment is more successful, the duration of melting of such a concentrate on the stein decreases, and the extraction of copper in the melt increases.

Studies using the segregation method were also carried out on the copper oxide ore of the Dark Ravine deposit in the Bolnisi region (Cu – 3.6%, Au – 0.5 g/t, Ag – 2 g/t) and on secondary quartzites of the oxidation zone (Cu – 0.02%, Au – 2.0 g/t, Ag – 1.5 g/t). Initially, flotation enrichment of these ores was carried out, but due to the low degree of metal recovery (50-60%), they were also subjected to segregation roasting after preliminary oxidizing roasting. The experiments were conducted under the optimal conditions selected for iron cakes: temperature – 850°C, coal consumption 1.5% of the mass of cakes, and sodium chloride consumption – 1%, roasting duration – 60 min. Under these conditions, the metals extraction in the flotation concentrate of copper oxide ore's segregation product was

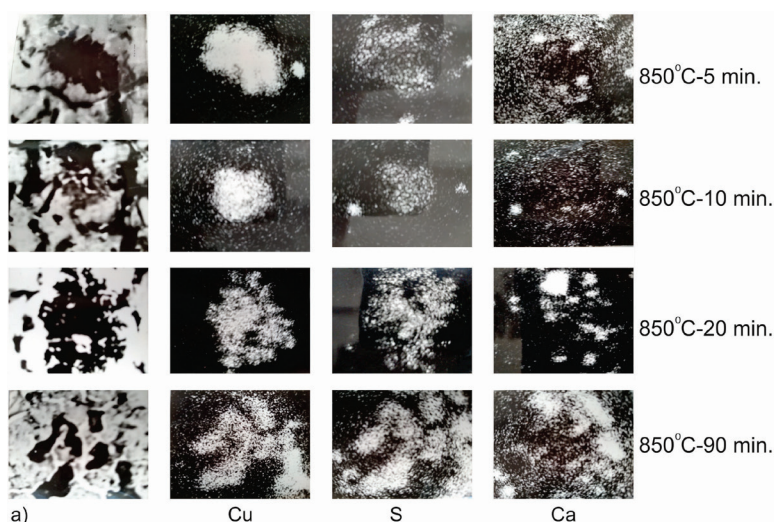


Fig. 6. Electron-raster microphotographs of the slides taken on the microanalyzer "Kameka" of the samples taken with calcium sulfate and coal during the study of the copper sulphiding process: a) absorbed electrons and characteristic X-rays Cu, S, Ca.

86-93%, and in the case of secondary quartzite it was within 80%, which was probably due to the low content of copper in quartzites (0.02%), which plays the main role in the process of segregation.

Conclusion

As discussed above in the mechanism of the segregation process, metallic copper initially

accumulates around the coal, and in the case of iron cakes, the recovered metallic copper first accumulates around the coal, then it gradually passes into chalcocite (Cu_2S) of calcium sulfate's sulfur in the cakes. Therefore, when the processing copper oxide and mixed ores using the segregation method, we consider it expedient to add a certain amount of calcium sulfate to the ore, if it does not contain it.

ქიმიური ტექნოლოგია

ოქროშემცველი სპილენძის მადნებისა და მათი გადამუშავების შედეგად მიღებული ნარჩენების სეგრეგაციული გამოწვის პროცესის თავისებურებანი

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(წარმოდგენილია აკადემიის წევრის გ. ტატიშვილის მიერ)

კვლევები ჩატარდა სამხრეთ საქართველოს ბოლნისის რაიონის საზადოს ბნელი ხევის სპილენძის ოქსიდური მადნებიდან, ჟანგვის ზონის მეორადი კვარციტებიდან და ქალკოპირიტული სპილენძის კონცენტრატისა და ჭიათურის მანგანუმის დაბალხარისხიანი ფლოტოკონცენტრატის ერთობლივი ავტოკლავური გამოტუტვის ნარჩენებიდან – რკინის კეკებიდან სპილენძის, ოქროსა და ვერცხლის ამოსაღებად სეგრეგაციის მეთოდის გამოყენების შესაძლებლობის დასადგენად. ეს მადნები ჯერ დაექვემდებარა წინასწარ დამჟანგველ გამოწვას, შემდეგ სეგრეგაციულ გამოწვას. სპილენძის ოქსიდური მადნის სეგრეგაციის პროდუქტის ფლოტაციურ კონცენტრატში მეტალების ამოღების ხარისხი 86-93%-ს შეადგენდა, მეორადი კვარციტების – 80%-ის ფარგლებში იყო, ხოლო კეკების – 91-93%. სპილენძის ოქსიდური მადნის სეგრეგაციის შედეგად ნახშირის ირგვლივ თავს იყრის მეტალური სპილენძი, ხოლო რკინის კეკების სეგრეგაციული გამოწვის დროს ადგილი აქვს დამატებით სტადიას – მეტალური სპილენძის სულფიდირებას ქალკოზინის (Cu_2S) მიღებით იმ გოგირდის ხარჯზე, რომელსაც საკმაო რაოდენობით შეიცავს კეკები კალციუმის სულფატის სახით. შესწავლილია

რკინის კვების სეგრეგაციის პროცესში მიმდინარე ფაზური გარდაქმნები. აგრეთვე, სპილენძის სულფიდირების პროცესში CaSO_4 -ის მონაწილეობის დასადასტურებლად, ცალკე შესწავლილ იქნა სულფიდირების პროცესი სამი მყარი ნივთიერების – სპილენძის, კალციუმის სულფატის და ნახშირის მონაწილეობით იმავე ტემპერატურულ ინტერვალში (750-900°C). ჩატარდა სინჯების მიკრორენტგენოსპექტრალური ანალიზები მიკროზონდ „კამეკაზე“ და მასზე გადაღებული ელექტრონულ-რასტრული მიკროფოტოგრაფიებით დადასტურებულ იქნა რკინის კვების სეგრეგაციის შედეგად ნახშირის ირგვლივ მეტალური სპილენძის წარმოქმნის და მისი ქალკოზინში (Cu_2S) გარდაქმნის მექანიზმი და ამ პროცესის უპირატესობა სეგრეგაციის პროდუქტის ფლოტაციური გამდიდრებისა და მისი შემდგომი მეტალურგიული გადამუშავებისთვის.

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