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Research article
Научная статья

Obtaining copper concentrate during iron ore processing

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Abstract: The data on the complex processing of iron ore from one of the deposits of the Republic of Kazakhstan, which involves several operations of wet magnetic separation with re-grinding of raw products and their subsequent refining to produce a conditioned iron concentrate with 65–66 % iron containing 79–80 % Fe and 2.2–2.5 % Si, are presented. It was found that during the magnetic enrichment of the ore under study, the copper minerals concentrate in the magnetic separation tailings and the copper content in them increases from 0.093 to 0.2 %. A scheme and reagent system have been developed for the recovery of conditioned copper concentrate from magnetically enriched tailings. To obtain copper concentrate, magnetic separation tailings are subjected to regrinding in a lime medium to a fineness of 75 % of the –0.071 mm grade. After two operations of the main copper flotation with the use of water glass, butyl xanthate and frother MIBK, waste tailings are obtained. The froth product of the first basal flotation is cleaned twice. The result is a copper concentrate containing 15.2 % copper, 26.5 % iron, 17.5 % sulfur, 3.47 % silicon, 1.4 % aluminum and 8.5 % zinc, which corresponds to the KM-7 grade according to GOST R 52998-2008. Waste tailings contain: copper 0.08 %, iron 20.1 %, sulfur 0.25 %, silicon 16.2 %, aluminum 6.4 % and zinc 0.045 %. The influence of xanthates with different length and structure of hydrocarbon radical as well as hostaflots and amyl aeroflots on the process of copper flotation is studied. The high efficiency of butyl xanthate in the flotation of copper minerals has been confirmed.

Keywords: wet magnetic separation, iron ore, butyl xanthate, aeroflot, Hostaflots, copper concentrate

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Получение медного концентрата при обогащении железных руд

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Аннотация: Приведены данные по комплексной переработке железной руды одного из месторождений Республики Казахстан, которая предусматривает несколько операций мокрой магнитной сепарации с доизмельчением полученных черновых продуктов и последующую их перечистку с получением кондиционного железного концентрата, содержащего 65–66 % железа при извлечении 79–80 % Fe и 2,2–2,5 % Si. Установлено, что при магнитном обогащении исследуемой руды медные минералы концентрируются в хвостах магнитной сепарации и содержание меди в них повышается с 0,093 до 0,2 %. Разработана схема и реагентный режим получения кондиционного медного концентрата из хвостов магнитного обогащения. Для получения медного концентрата хвосты магнитной сепарации подвергаются доизмельчению в известковой среде до крупности 75 % класса –0,071 мм. После двух операций основной медной флотации с применением жидкого стекла, бутилового ксантогената и вспенивателя МИБК получают отвальные хвосты. Пенный продукт первой основной флотации дважды перечищается. В результате получается медный концентрат с содержанием, %: 15,2 Cu, 26,5 Fe, 17,5 S, 3,47 Si, 1,4 Al и 8,5 Zn, который соответствует марке КМ-7 (ГОСТ Р 52998-2008). Отвальные хвосты содержат, %: 0,08 Cu, 20,1 Fe, 0,25 S, 16,2 Si, 6,4 Al и 0,045 Zn. Рассмотрено влияние на процесс медной флотации ксантогенатов с различной длиной и строением углеводородного радикала, а также Хостафлотов и амилового аэрофлота. Подтверждена высокая эффективность бутилового ксантогената при флотации медных минералов.

Ключевые слова: мокрая магнитная сепарация, железная руда, бутиловый ксантогенат, аэрофлот, Хостафлоты, медный концентрат

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Introduction

The industry's increasing demand for nonferrous metals has made it increasingly important to involve poor ores and enrichment tailings in comprehensive processing of minerals. The practice of iron ore enrichment shows that the tailings of iron ore enrichment plants often contain significant amounts of nonferrous metal minerals. The content of these constituents is usually less than in the ores of the same name, and the usefulness of their extraction is not always apparent.

The processing of raw materials with an unbalanced content of valuable components is usually carried out according to combined schemes involving enrichment and metallurgical methods [1—3]. The preparation of mineral raw materials for enrichement plays an important role [4—6], and often requires finer grinding in comparison with the initial ore raw materials for breaking down the aggregates [7].

Development of rational enrichement schemes and effective choice of reagent regime in flotation of prepared (previously grinded) raw materials (enrichment tailings) makes it possible to include products with unbalanced content of valuable components in processing [8—12].

The objective of this work was to develop a technology to recover not only iron ore concentrate but also copper concentrate from current magnetic enrichment tailings.

Objects and research methods

Studies were conducted on an ore sample with a content of 44.6 % iron and 0.093 % copper. The composition of the main elements of the ore is given below, %:

Ag	1.36 g/t	K	0.25
Al	1.96	Na	0.31
Ca	1.51	Zn	0.087
Cu	0.093	S	3.46
Fe	44.60	Si	7.2

It can be seen that of the precious metals silver is present in the sample — about 1.4 g/t.

Using *X*-ray phase analysis on *X*-ray diffractometer X'Pert PRO MPD (PANanytical, Netherlands) the following mineral composition of the ore sample, wt.% was established:

Magnetite	56.19
Hematite	3.3
Chalcopyrite	0.62
Pyrite	6.19
Chlorite	0.95
Mica	0.14
Feldspar	4.9
Asbestos	0.71
Sphalerite	1.9
Amphibole	8.06
Pyroxene	4.74
Quartz	6.42
Carbonate	1.1
Epidote	2.77
Others: gypsum, talc, apatite, polymineral aggregates	2.01
Total	100

Optical and mineralogical analysis showed that the main ore mineral is magnetite, which is noted both in the form of grains and aggregates with rock-forming minerals (Fig. 1). Secondary minerals are hematite, pyrite, feldspar, quartz, pyroxene, amphibole, and epidote. The ore also contains sphalerite, carbonate, chlorite,

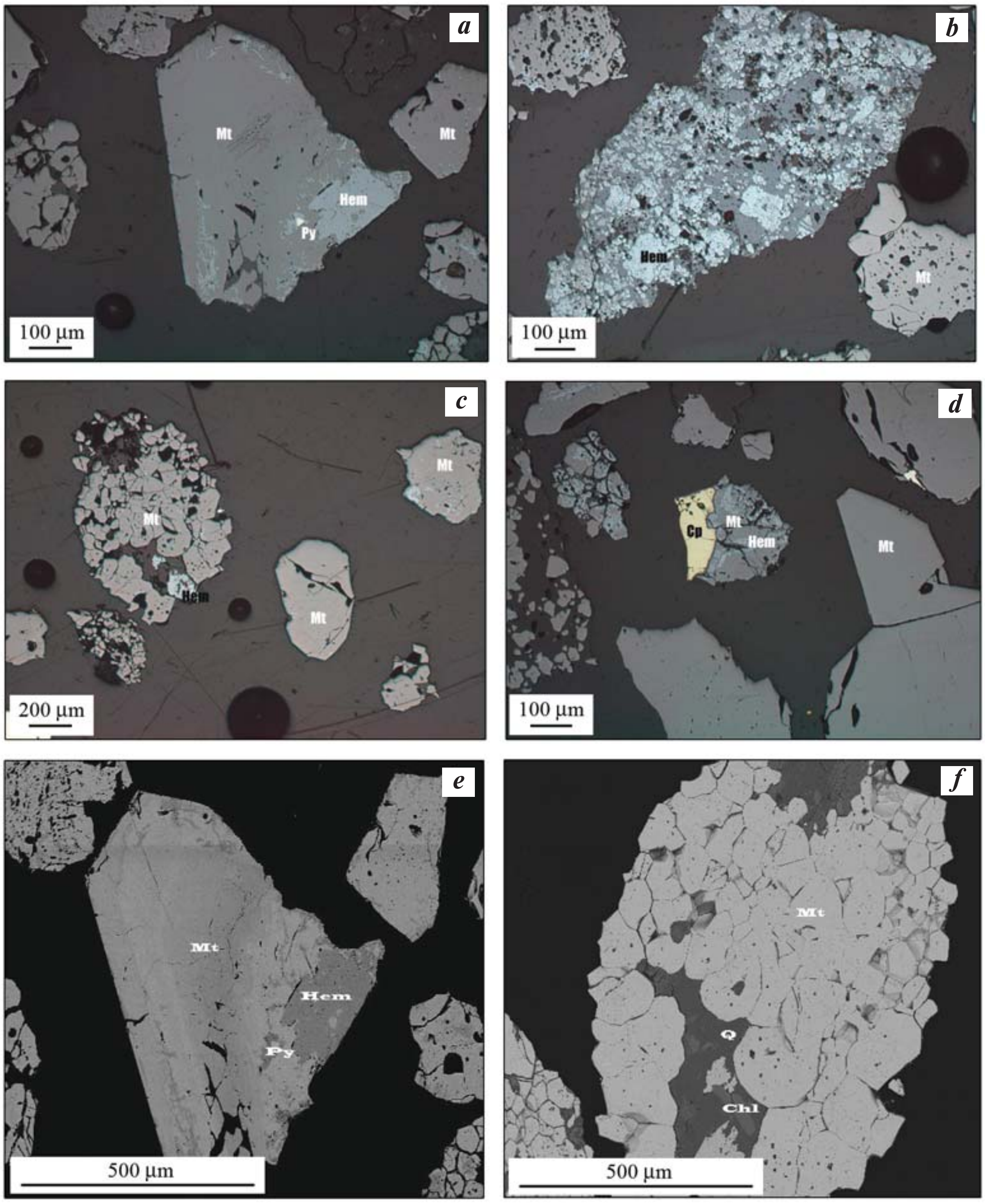

Fig. 1. Optical and mineralogical analysis results.

a – magnetite grains fragments, some grains are subject to hematization, reflected light, nicoli are parallel;
b – magnetite, hematized to various degrees, and hematite grains fragments, reflected light, nicoli are parallel; ***c*** – magnetite and hematite grains fragments, reflected light, nicoli are parallel; ***d*** – magnetite and chalcopyrite aggregation, reflected light, nicoli are parallel;
e – magnetite with hematite and pyrite aggregation, back-scattered electrons image; ***f*** – magnetite with quartz and clinochlorite aggregation, back-scattered electrons image

Рис. 1. Результаты оптико-минералогического анализа

a – фрагменты зерен магнетита, некоторые зерна подвержены гематитизации, отраженный свет, николи параллельны;
b – фрагменты зерен магнетита, в различной степени подверженные гематитизации, и гематита, отраженный свет, николи параллельны; ***c*** – фрагменты зерен магнетита и гематита, отраженный свет, николи параллельны;
d – сросток магнетита и халькопирита, отраженный свет, николи параллельны; ***e*** – сросток магнетита с гематитом и пиритом, изображение в обратно-рассеянных электронах; ***f*** – сросток магнетита с кварцем и клинохлором, изображение в обратно-рассеянных электронах

and asbestos. The rest of the minerals are represented in a landmark quantity.

The study of the composition of the sample material has shown that the basic processing of the ore is associated with the technology of extraction of ferrous minerals. Further it is useful to extract copper from the magnetically enriched tailings, which requires solving some schematic problems.

In the laboratory technological study, the ore was grinded in a jaw grinder SChKD 150×200, then the grinder KID-100 was used. Ore grinding was carried out in a roller ball mill with a volume of 1 L. The PBSZ-22 magnetic separator with two drums with variable rotational speed and constant magnetic induction of 0.15 and 0.25 T was used for dry magnetic separation at different magnetic field strengths.

To simulate a continuous process of wet magnetic separation, we used a system consisting of a wet magnetic separator MMS-0.1 PM and a pump. The magnetic induction of the drum separator is 0.15 T. The rotation speed of the magnetic system and the pump power are regulated. The flotation tests were performed in the FM2M laboratory flotation machine with a chamber volume of 150—500 cm^3. Various xanthates (butyl, isobutyl, amyl, isoamyl), Hostaflots, amyl aeroflot, lime, liquid glass, MIBK were used. Hostaflots contained major components such as LIB E, sodium salt of Dithiophosphoric acid O,O-diisobutyl; Hostaflot 3403, Sodium O,O-diisobutyl dithiophosphate; Hostaflot X-23, O-ethyl-N-isopropyl thionocarbamate; Hostaflot X 231, O-N-isopropyl thiocarbamate.

Operational determination of useful constituent content was performed using Olympus X-5000 *X*-ray fluorescence analyzer (USA) and balance determination was performed using ARL Advants *X*-ray fluorescence spectrometer (ThermoFisher Scientific, Switzerland).

Technological study

The main technological studies on the ore with the aim of developing an optimal scheme and technology of its enrichment were carried out in two directions: dry and wet magnetic separation and copper flotation from magnetically enriched tailings.

The scheme of laboratory tests for obtaining iron concentrate included: grinding of the initial ore to a size of –2+0 mm, two operations (base and control) of dry magnetic separation, the concentrates of which were combined. The coarseness of the combined concentrate was 8 % of the –0.071 mm grade. The grinding of the concentrate to a content of 63 % of the –0.071 mm grade and its dry magnetic separation make it possible to increase the quality of the iron concentrate from 52.8 % to 57.3 %, while the iron yield in the concentrate remains constantly high at 82—83 %.

Further investigations to improve the quality of the concentrate were carried out involving the wet magnetic enrichment process. As a result, an optimal technological scheme for the recovery of iron ore concentrate with wet magnetic separation of grinded combined concentrate was developed (Fig. 2).

Preparation of the studied ore with grinding of the combined dry concentrate to the content of 63 % of the –0.071 mm grade and subsequent wet magnetic separation according to the proposed scheme allows to obtain an iron ore concentrate containing in %: 65.4 Fe, 0.01 Cu, 0.42 S, 2.7 Si, 0.95 Al. Zinc was not detected in the iron concentrate.

For the elaboration of the final scheme of ore processing with the definition of enrichment regimes and parameters, studies have been carried out that allow defining the possibility and expediency of flotation processing of the tailings obtained after wet magnetic separation. Magnetic separation tailings have the following composition, %: 0.2 Cu, 0.14 Zn, 3.5 S, 21.0 Fe, 8.9 Al, 13.4 Si. Analysis has shown that the copper content in the magnetic separation effluents increas-

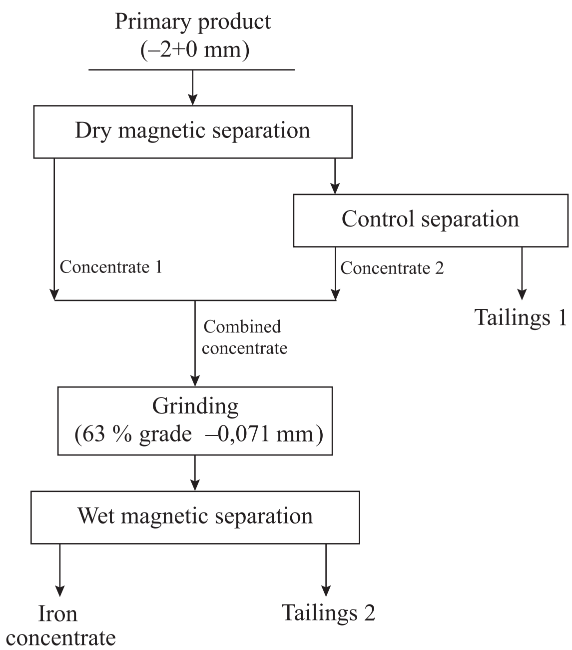

Fig. 2. Scheme of obtaining iron ore concentrate with wet magnetic separation

Рис. 2. Схема получения железорудного концентрата с мокрой магнитной сепарацией es by more than 2 times and may be of economic interest.

The flotation experiments to determine the flotation and reagent regimes basic scheme were carried out according to a scheme that included the following operations: re-grinding of the combined magnetic separation tailings (dry and wet); the first base copper flotation with addition of lime carbonate, liquid glass, collector and foaming agent. In the second base flotation, 40 % of the reagents were fed from their consumption in the first main flotation.

Previously, tailings flotation with magnetic separation without re-grinding (50 % grade –0.071 mm) was carried out using butyl xanthate as collector at a consumption rate of 40 g/t in the first and 16 g/t in the second basic operation and foaming agent MIBK at consumption rates of 40 and 16 g/t, respectively, with a copper recovery rate in the common concentrate of 77 %. Grinding to a particle size of 75 % grade –0.071 mm grade increased the copper recovery rate to 83.3 %. The further increase of the fineness degree up to 95 % grade –0.071 mm did not lead to significant changes in the technological parameters of flotation. Therefore, in further flotation studies, the grinding mode was adopted up to a size of 75 % grade –0.071 mm.

The effect of the collector consumption rate on the flotation results for a total process time of 6 min is shown in Fig. 3. From the data presented, when the butyl xanthate consumption rate is increased up to 40 g/t, the copper extraction into concentrate reaches 88.3 % with a concentrate recovery of about 31 %. A further increase in the collector consumption rate does not have a significant impact on the flotation performance. The low copper content in a concentrate is connected with a high pyrite yield caused by its flotation activity.

Lime carbonate $Ca(OH)_2$ was used for pyrite depression. The possibility of its delivery to different points of the technological process was studied. Introduction of the reagent in the flotation pulp did not lead to satisfactory results of flotation. The results of the study of the effect of lime in the grinding process on the results of flotation are shown in Fig. 4. Xanthates consumption rate during flotation was 40 g/t. MIBK was used as a foaming agent and its consumption rate was 40 g/t. From the data shown in Fig. 4, it can be seen that the addition of lime carbonate during grinding can increase the quality of the concentrate. The optimum consumption rate for lime carbonate was 9 kg/t ore — in this case, the copper content in the concentrate was 0.93 % and the extraction was 85 %. The increase in

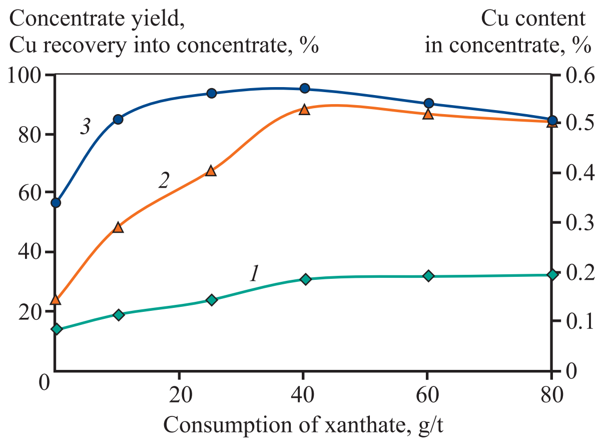

Fig. 3. Butyl xanthate consumption rate influence on concentrate yield (*1*), copper recovery (*2*) and its concentrate content (*3*) (τ_{fl} = 6 min)

Рис. 3. Влияние расхода бутилового ксантогената на выход концентрата (*1*), извлечение меди в концентрат (*2*) и ее содержание в нем (*3*) ($\tau_{фл}$ = 6 мин)

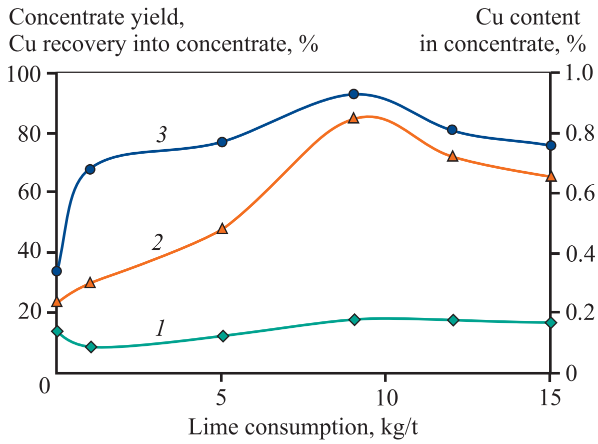

Fig. 4. $Ca(OH)_2$ at grinding consumption rate influence on yield concentrate (*1*), copper recovery rate (*2*) and its content in concentrate (*3*) at flotation with butyl xanthate

Рис. 4. Влияние расхода $Ca(OH)_2$ при измельчении на выход концентрата (*1*), извлечение меди в концентрат (*2*) и ее содержание в нем (*3*) при флотации бутиловым ксантогенатом

lime carbonate consumption leads to a decrease in copper extraction and its content in the concentrate. Thus, it can be seen that the alkaline environment created by the carbonate of lime further promotes the separation of the copper from the iron oxide [13].

The study of the influence of liquid glass on the depression of rock minerals was carried out with the consumption rates for xanthate — 40 g/t, lime — 800 g/t and MIBK — 40 g/t. The increase of liquid glass consumption rate to 800 g/t results in a 2 % decrease of a concentrate recovery rate (from 17.1 to 15.3 %), also a 2 % decrease of copper recovery rate (from 71.8 to 69.6 %), but its content in a concentrate remains almost the same. At the same time, aluminum extraction decreases by 5 %, silicon extraction — by 6—7 %.

Fig. 5 shows the kinetics of copper sulfide flotation. It can be seen that after the 1st minute of flotation, the copper content in the concentrate is 3.5 % and the recovery rate is 73 %. During the first 3 minutes of flotation, 83 % of the copper is extracted, but the copper content in the combined concentrate decreases significantly. Thus, the time of the first basal flotation — 1 min, the second basal flotation — 2 min was accepted.

The results of the tests carried out with the application of xanthates with different length of hydrocarbon radical and structure in flotation for 1 min are shown in Fig. 6. The comparison of butyl and amyl xanthate shows that amyl has a stronger collecting power, which can be explained by the large size of the hydrocarbon radical. But in this case the quality of the concentrate decreases. The authors [14] used quantum chemical calculations to show that amyl xanthate binds more strongly to a mineral surface containing copper ions compared to other xanthates.

When comparing butyl and isobutyl as well as amyl and isoamyl xanthates, it was found that the isomerization of the hydrocarbon radical leads to a deterioration of the collection properties. This is consistent with the data from the paper [15] that the authors applied to pyrite: "Radical isomerization of hydrocarbons reduces the flotation activity of pyrite due to

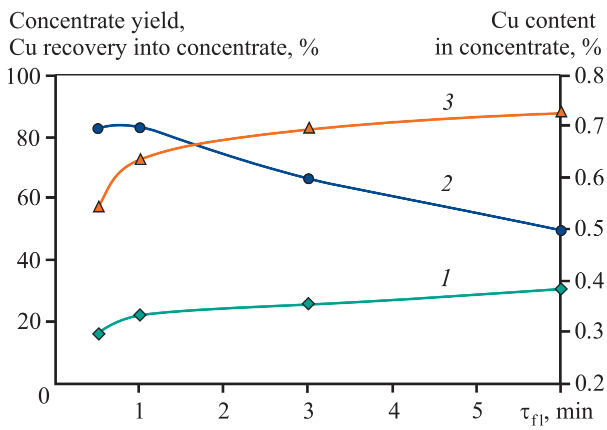

Fig. 5. Flotation with butyl xanthate kinetics

1 – concentrate yield, *2* – Cu content in concentrate,
3 – copper recovery in concentrate

Рис. 5. Кинетика флотации бутиловым ксантогенатом

1 – выход концентрата, *2* – содержание Cu в концентрате,
3 – извлечение меди в концентрат

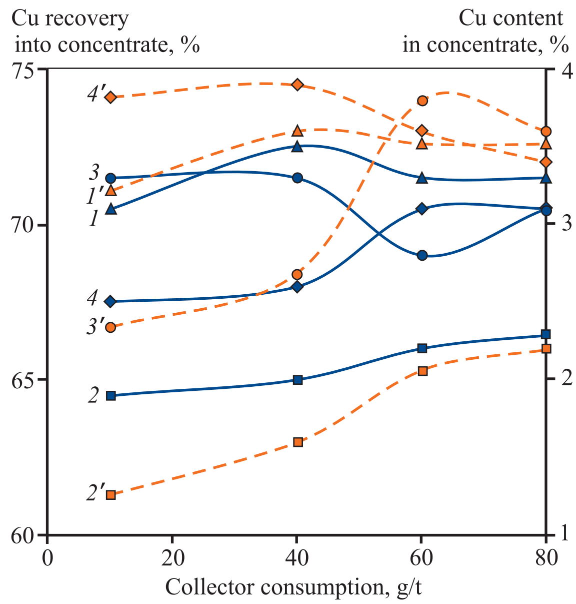

Fig. 6. Various xanthates and their consumption rate influence on copper extraction and its content in the concentrate

1, *1′* – butyl xanthate; *2*, *2′* – isobutyl xanthate;
3, *3′* – isoamyl xanthate; *4*, *4′* – amyl xanthate
Solid curves – content, dashed curves – extraction

Рис. 6. Влияние различных ксантогенатов и их расхода на извлечение меди в концентрат и ее содержание в нем

1, *1′* – бутиловый ксантогенат; *2*, *2′* – изобутиловый;
3, *3′* – изоамиловый; *4*, *4′* – амиловый
Сплошные кривые – содержание, штриховые – извлечение

the lower susceptibility of the collector to oxidation". Comparing straight and branched chain compounds, the authors [16] concluded that branched chain xanthates higher homologues are less effective. Fig. 6 data shows that the most effective collector is butyl xanthate at a consumption rate of 40 g/t. When using it, the highest copper content in the concentrate is achieved.

Thiophosphates, thiophosphinates, thiocarbamates etc. are widely used to increase the flotation efficiency. These reagents are used for various sulfides in combination with xanthates and independently [17—23]. Our flotation studies with different collectors (Fig. 7) have shown that amyl aeroflot and Hostaflots have weaker collection properties compared to xanthates. Of the Hostaflots used, Hostaflot X-231 showed the strongest collection characteristics — at a consumption rate of 40 g/t copper, the extraction rate in concentrate was 54 % with an increase in grade in concentrate up to 3.6 %. Stronger collecting properties in comparison with Hostaflot were revealed in amyl aeroflot. The maximum copper content of 3.3 % at

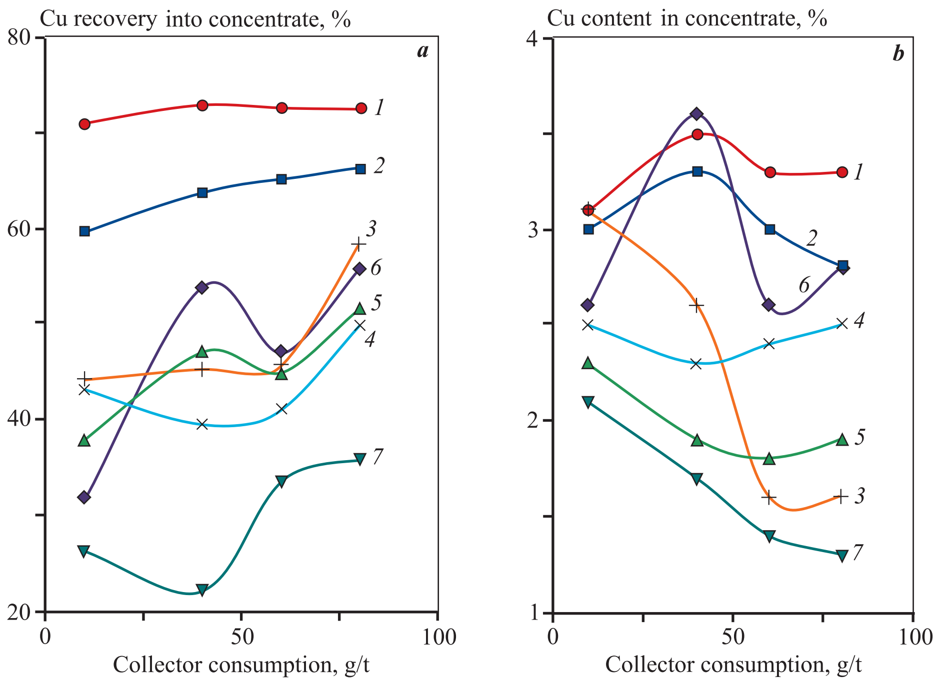

Fig. 7. Various collectors and their consumption rate influence on copper recovery (***a***) and its content (***b***) in a concentrate

1 – butyl xanthate, ***2*** – Aeroflot, ***3–7*** – Hostaflot: ***3*** – 3403, ***4*** – LIB, ***5*** – X-023, ***6*** – X-231, ***7*** – 10093

Рис. 7. Влияние различных собирателей и их расхода на извлечение меди в концентрат (***а***) и ее содержание в нем (***б***)

1 – бутиловый ксантогенат, ***2*** – Аэрофлот, ***3–7*** – Hostaflot: ***3*** – 3403, ***4*** – LIB, ***5*** – X-023, ***6*** – X-231, ***7*** – 10093

extraction rate of 63.8 % was reached at the aeroflot consumption rate of 40 g/t. By increasing the aeroflot consumption rate, the extraction can be increased, but the quality of the concentrate decreases. At a similar consumption rate (40 g/t) of butyl xanthate, the copper extraction in the concentrate was 73 % at a content of 3.5 %.

In order to improve the efficiency of copper flotation, studies were carried out using a combination of xanthates with amyl aeroflot, as these collectors demonstrated the strongest collecting properties (see Fig. 7). Using one aeroflot reduced the copper recovery by 9 % and its content by 0.2 % (Fig. 8). A comparison of the results of flotation with one xanthogenate, one aeroflot and their combination shows that flotation with only one xanthogenate is preferable. Therefore, the further ore studying was carried out with use of butyl xanthate as collector at its consumption rate of 40 g/t.

Based on the flotation results after determining the optimum reagent consumption, flotation studies were carried out to improve the quality of the copper concentrate using post-purification procedures according to the scheme shown in Fig. 9. At that, the following reagent regime parameters were chosen:

— the first basal flotation: liquid glass — 800 g/t, butyl xanthate and MIBK — 40 g/t each, pH before flotation — 11.7, CaO_{free} — 0.47 g/L, flotation time — 1 min;

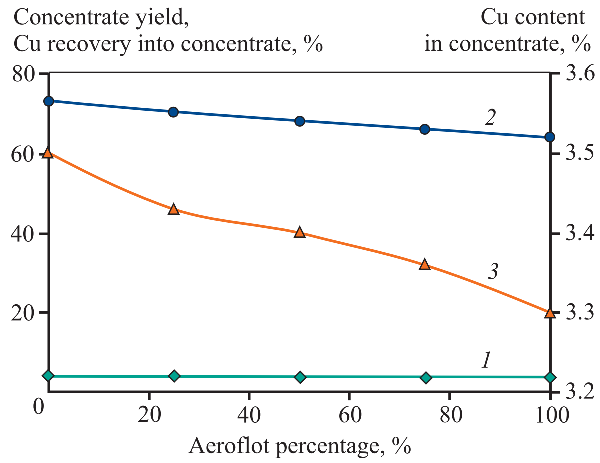

Fig. 8. Amyl aeroflot in a mixture with xanthate influence on concentrate yield (***1***), copper extraction (***2***) and its content in concentrate (***3***)

Рис. 8. Влияние амилового аэрофлота в смеси с ксантогенатом на выход концентрата (***1***), извлечение меди в концентрат (***2***) и ее содержание в нем (***3***)

Balance indicators of investigated ore enrichment

Балансовые показатели обогащения исследуемой руды

Product name	Output, %	Content, %		Extraction, %	
		Fe	Cu	Fe	Cu
Iron concentrate	54.60	65.4	0.01	80.0	5.9
Copper concentrate	0.33	26.5	15.2	0.2	54.0
Final tailings	45.07	20.0	0.08	19.8	40.1
Primary ore	100.00	44.7	0.093	100.0	100.0

— the second basal flotation: reagent consumption rate — 40 % of the consumption during the first basal flotation, pH before flotation — 11.5, CaO_{free} — 0.35 g/L, flotation time — 2 min;

— the recleaning flotation (1st and 2nd): lime carbonate — 330 g/t, CaO_{free} — 0.14 g/L, flotation time — 15 s.

The size of the magnetic separation tailings after regrinding with lime carbonate (9 kg/t) was 75 % grade –0.071 mm. The basal and control flotations resulted in final tailings. The froth product of the basal flotation was processed twice. The first recleaning tailings and the control flotation froth product were returned to the basal copper flotation and the chamber product of the second recleaning was fed to the first recleaning. The froth product of the second recleaning was copper concentrate with copper content of 15.2 % (KM-7 grade according to GOST R 52998-2008, group A32).

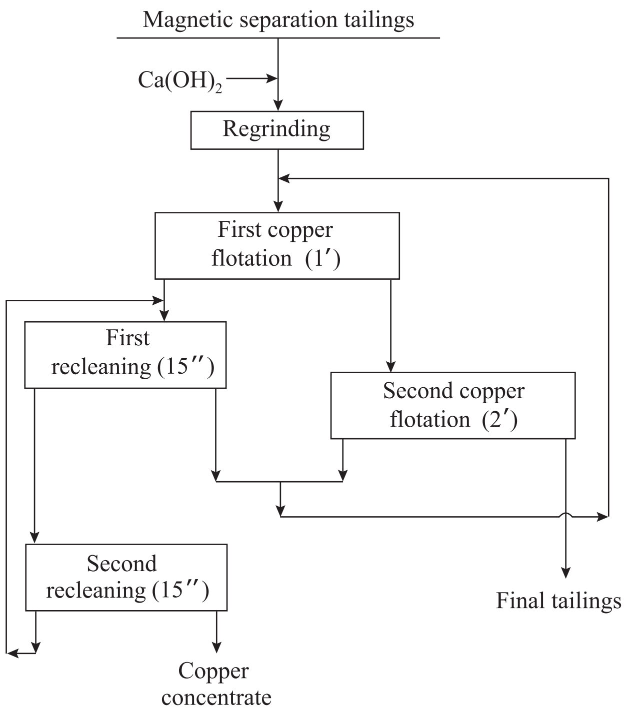

Fig. 9. Scheme of obtaining copper concentrate from magnetic separation tailings of iron ore

Рис. 9. Схема получения медного концентрата из хвостов магнитной сепарации железной руды

Thus, the scheme (Fig. 9) and the reagent regime of the flotation cycle for obtaining copper concentrate and tailings were developed according to the results of flotation of magnetic separation tailings of iron-containing ore. Copper concentrate contains %: 15.2 Cu, 26.5 Fe, 17.5 S, 3.47 Si, 1.4 Al and 8.5 Zn, which corresponds to KM-7 grade (GOST R 52998-2008, group A32). The final tailings have the following content of main components %: 0.08 Cu, 20.1 Fe, 0.25 S, 16.2 Si, 6.4 Al and 0.045 Zn.

Balance indicators of investigated ore enrichment are shown in the table.

Conclusion

1. The use of wet magnetic separation in deep grinding of iron ore allows obtaining iron ore concentrates with iron content of 65—66 % with its extraction of 79—80 %. Thus, the Si content does not exceed 2.2—2.5 %.

2. During magnetic enrichment of the ore under study, copper minerals concentrate in the tailings and the copper content in them increases from 0.093 to 0.2 %.

3. The application of the flotation method for the enrichment of magnetically separated tailings with their pre-grinding and the use of butyl xanthate makes it possible to obtain a conditioned copper concentrate of the quality KM-7 with a copper content of 15.2 %. The high efficiency of butyl xanthate in flotation of copper minerals is confirmed.

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