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BENEFICIATION AND PROCESSING OF NATURAL AND TECHNOGENIC RAW MATERIALS

Research paper

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Material composition of magnetic fractions of copper-smelting slag flotation tailings

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Abstract

Finely ground tailings from flotation processing of waste copper reverberatory smelting slags of the Sredneuralsky Copper Smelter (“SUMZ technical sands”) was accumulated in significant amounts and may pose a threat to the environment as a potential source of heavy metals. At the same time, the waste can be considered as a promising source of useful components due to relatively high contents of zinc (3.3–3.9%) and copper (0.4–0.5%). Development of technologies for recycling the “technical sands” is a promising task of nonferrous metallurgy and requires their comprehensive study. The purpose of this research was to study the material composition of magnetic fractions of the “SUMZ technical sands” and assess the prospects of extraction of useful components (zinc and copper) from their flotation tailings using wet magnetic separation. Chemical analyses of the obtained fractions were carried out at the Center for Collective Use “Geoanalitik” of the Institute of Geology and Geochemistry, UB RAS by inductively coupled plasma mass spectrometry method using an Elan-9000 quadrupole mass spectrometer. Phase analyses were carried out at the Ural-M Collective Use Center of the Institute of Metallurgy, UB RAS by X-ray phase analysis using a Bruker D8 Advance diffractometer. The magnetic properties of the magnetic separation fractions were studied by thermomagnetic analysis. After treating the tailings by wet magnetic separation, the yield of the magnetic fraction (48 kA/m) was approximately 83%, that of the weakly magnetic fraction (200 kA/m) was 11%, and that of the non-magnetic fraction, 6%. The data on the phase and chemical composition of the tailings magnetic separation fractions were obtained. It was found that zinc and copper were distributed relatively uniformly among the fractions with a slightly higher content of copper in the non-magnetic fraction and that of zinc in the weakly magnetic fraction. The dependence of magnetic susceptibility of the “technical sands” minerals on the presence of isomorphic impurities in them was confirmed. The joint evaluation of the data of X-ray phase and thermomagnetic analyses showed that at practically identical X-ray diffraction patterns the thermomagnetic curves in the range of 20-700°C demonstrate significant differences between the magnetic separation fractions. All the obtained thermomagnetic curves are irreversible. At the used parameters of wet magnetic separation, this method proved inefficient for the “technical sands” separation, and additional research is required to find optimal methods of the tailings pretreatment and magnetic intensity modes. The research findings contribute to the study of magnetic properties of copper-smelting slag processing tailings and are of interest for the development of new flow schemes for their utilization and recycling.

Keywords

copper smelting production, mineral waste, copper smelting slag, flotation processing tailings, recycling, magnetic separation, thermomagnetic analysis, magnetic fractions, magnetic properties, fayalite (Fe_2SiO_4), forsterite ($(MgMn)SiO_4$), diopside ($CaZn(Si_2O_6)$), magnetite (Fe_3O_4), sphalerite (ZnS), zincite (ZnO)

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ОБОГАЩЕНИЕ, ПЕРЕРАБОТКА МИНЕРАЛЬНОГО И ТЕХНОГЕННОГО СЫРЬЯ

Научная статья

Вещественный состав магнитных фракций хвостов флотации медеплавильных шлаков

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Аннотация
Тонкоизмельченные отходы флотационной переработки отвальных медеплавильных шлаков отражательной плавки Среднеуральского медеплавильного завода («технические пески СУМЗ») накоплены в значительных объемах и могут представлять опасность для окружающей среды как потенциальный источник тяжелых металлов. В то же время они могут рассматриваться как перспективный источник полезных компонентов вследствие относительно высокого содержания цинка (3,3–3,9%) и меди (0,4–0,5%). Разработка технологий по утилизации «технических песков» является перспективной задачей цветной металлургии и невозможна без их всестороннего исследования. Целью наших исследований являлись изучение вещественного состава магнитных фракций «технических песков СУМЗ» и оценка перспектив извлечения полезных компонентов (цинка и меди) из хвостов флотации с использованием мокрой магнитной сепарации. Химический анализ полученных фракций выполнен в Центре коллективного пользования «Геоаналитик» Института геологии и геохимии УрО РАН методом масс-спектрометрии с индуктивно связанной плазмой на квадрупольном масс-спектрометре Elan-9000. Фазовый анализ выполнен в центре коллективного пользования «Урал–М» Института металлургии УрО РАН методом рентгенофазового анализа на дифрактометре Bruker D8 Advance. Магнитные свойства фракций магнитной сепарации изучены методом термомагнитного анализа. После обработки отхода методом мокрой магнитной сепарации выход магнитной фракции (48 кА/м) составил приблизительно 83%, слабомагнитной (200 кА/м) – 11%, немагнитной – 6%. Получены данные о фазовом и химическом составе фракций магнитной сепарации отхода. Отмечено, что цинк и медь распределяются по фракциям относительно равномерно с несколько повышенным содержанием меди в немагнитной, а цинка – в слабомагнитной фракции. Подтверждена зависимость магнитной восприимчивости минералов «технических песков» от наличия в них изоморфных примесей. Совместная оценка данных рентгенофазового и термомагнитного анализов показала, что при практически идентичных рентгенограммах термомагнитные кривые в интервале 20–700 °С демонстрируют существенные различия фракций магнитной сепарации. Все полученные термомагнитные кривые необратимые. При использованных параметрах мокрой магнитной сепарации для разделения «технических песков» данный метод малоэффективен, необходимы дополнительные исследования по поиску оптимальных способов предподготовки отходов и режимов напряженности магнитного поля. Результаты исследований вносят вклад в изучение магнитных свойств отходов переработки медеплавильных шлаков, представляют интерес для разработки новых схем их утилизации и повторной переработки.

Ключевые слова
медеплавильное производство, минеральные отходы, медеплавильные шлаки, хвосты флотационной переработки, утилизация, магнитная сепарация, термомагнитный анализ, магнитные фракции, магнитные свойства, фаялит (Fe_2SiO_4), форстерит ($(MgMn)SiO_4$), диопсид ($CaZn(Si_2O_6)$), магнетит (Fe_3O_4), сфалерит (ZnS), цинкит (ZnO)

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Introduction

Mining and metallurgical wastes occupy vast areas around the world and cause significant environmental damage [1–3]. Nonferrous metallurgy wastes are particularly dangerous for the environment due to high content of heavy metals [4–6].

At present time, flotation method is most often used for slag processing at copper smelters [7–9]. As a result, a concentrate of copper-containing components is obtained and the processing tailings, "technical sands", which are a finely dispersed and mechanically activated materials, are produced. These tailings find limited application in construction [10] and for reclamation of disturbed territories [11, 12]; there are ongoing developments in the application of copper-smelting slag flotation tailings for industrial wastewater treatment [13]. However, for the most part the tailings are buried and, to date, have been accumulated in significant volumes in the areas where smelters operate. The "technical sands" can cause contamination of groundwater, surface water, soil, and plants [14, 15].

Copper-smelting slag flotation tailings can be considered as a potential source of useful components [16, 17]. The development and implementation of technologies involving processing and recycling of technogenic waste is an extremely urgent task for current industries, sustainable nature management, and environmental conservation [18–20]. The solution of the problem of multipurpose utilization of copper-smelting slag flotation tailings requires their comprehensive study.

The Ural and Siberian regions are among the main production centers of nonferrous metallurgy in Russia. In 1994–1995, Sredneuralsky Copper Smelter (OJSC SUMZ) and Kirovograd Copper Smelter began processing of waste cast slag as a source of copper-zinc concentrate. The material composition of the OJSC SUMZ flotation tailings [21–23] accumulated in the amount of more than 10 mln t, has been studied in detail. According to preliminary estimates, this amount may contain about 340 kt of zinc, 43 kt of copper, 43 kt of lead, as well as 3.5 mln t of iron. The "technical sands" of SUMZ contain up to 4% zinc and up to 0.5% copper. Acid leaching method is applicable for their extraction. Maximum recovery of zinc (up to 77 %) and copper (up to 64 %) was achieved using sulfuric acid (in concentration of 300 g/dm^3) [24]. For increasing zinc and copper recovery it is necessary to take into account the "technical sands" phase composition, their distribution among mineral phases, as well as grinding fineness [25] and magnetic properties of the waste.

The studies on the extraction of valuable components from copper-smelting slags by magnetic separation are known in literature [25, 26]. It was established by the example of JSC Svyatogor converter copper-smelting slag flotation tailings that the change in magnetic field strength (1,200, 800, 400 E) in wet magnetic separation, grinding size, and the method of slag cooling practically does not affect the iron content in the resulting iron concentrate [25]. Chinese scientists proposed a combined process of direct reduction and magnetic separation of copper-smelting slag flotation tailings using limestone [26]. However, not enough attention has been paid to the mineral composition of the resulting magnetic fractions.

The purpose of our research was to study the material composition of Sredneuralsky copper smelter waste cast slag processing tailing magnetic fractions and to assess the prospects for the extraction of useful components (zinc and copper) from the flotation tailings using wet magnetic separation. In this connection the following problems were solved: fractionation of SUMZ copper-smelting slag processing tailings by wet magnetic separation; determination of chemical and phase composition of the obtained magnetic fractions; characterization of their magnetic properties using thermomagnetic analysis; evaluation of the efficiency of the flotation tailings separation by wet magnetic separation methods.

Research Subjects and Methods

Waste cast slag from reverberatory smelting at the Sredneuralsky copper smelter is subjected to grinding first at cone crushers to a fraction of 10 mm, then at ball mills to 0.05 mm. The subsequent extraction of copper concentrate is carried out by flotation. The liquid concentrate and tailings ("technical sands") are separately thickened in radial thickeners and filtered. Vacuum filters were used to dewater the tailings.

«"SUMZ technical sands" is a finely dispersed material of the following grain size: (–0.21 + 0.10) mm, 1.1–4.1%; (–0.1 + 0.05) mm, 21–30%; < 0.05 mm, 69–75%. Their chemical composition is as follows, wt.%: FeO – 32.3; SiO_2 – 31; Fe_2O_3 – 14.29; Al_2O_3 – 7.05; CaO – 4.53; Zn – 3.28; MgO – 1.64; S – 1.32; K_2O – 0.74; Na2O – 0.64; As – 0.53; Cu – 0.44; Ba – 0.43; TiO_2 – 0.26; Pb – 0.2; P_2O_5 – 0.1; MnO – 0.09 [23].

The separation of the SUMZ copper-smelting slag flotation tailings into magnetic fractions was performed at the Department of Mineral Processing, Faculty of Mining and Mechanical Engineering, Ural State Mining University. For the separation of magnetic fractions the method of wet magnetic separation was used[1], characterized by the continuity of

[1] Svertkov A.A., Chekmenev A.N., Bratus S.V., Sharkhov V.V. Patent No. RU 2013109184 A, Russian Federation, IPC B03C1/00. Method of wet magnetic separation of magnetite ores and devices for its implementation: appl. 2013109184/03, 28.02.2013: publ. 10.09.2014.

the separation process, which was provided by creation (in the working chamber) of the magnetic field with the intensity decreasing in the direction of pulp movement.

The chemical and phase compositions of the obtained fractions were determined at the Center for Collective Use "Geoanalitik" of the Institute of Geology and Geochemistry, UB RAS by inductively coupled plasma mass spectrometry (ICP-MS) using an Elan-9000 quadrupole mass spectrometer (Perkin-Elmer, Canada). The phase analyses were carried out at the Ural-M Collective Use Center of the Institute of Metallurgy, UB RAS by X-ray phase analysis using a Bruker D8 Advance diffractometer (Bruker AXS GmbH, Germany).

The study of magnetic properties of the "technical sands" was carried out at the Institute of Geophysics, UB RAS. The thermomagnetic analysis method was used to determine the total magnetization of the magnetic separation fractions. The scheme of the installation is presented in the monograph [27]. The samples magnetic susceptibility was measured using a commercially available KT-3 kappometer.

Research Findings and Discussion

The "SUMZ technical sands" are finely dispersed materials (particle size <0.05 mm) consisting of a mixture of fayalite, pyroxene, iron-containing glassy phase of acidic and basic compositions, magnetite, hematite, wustite, spinelides, sulfides, and intermetallics. Magnetite and sulfides are confined to the glass phase. A characteristic feature of the "sands" is the increased content of zinc (about 3.3–3.9%) and copper (0.4–0.5%) at Zn/Cu ratio of 7.5. Zinc is present in all the phases. Silicate zinc is contained in the fayalite and the glass phase. Other heavy metals including copper are predominantly concentrated in the sulfides and intermetallics. According to the literature data [25] primary copper minerals are represented by chalcopyrite, cubanite, and cuprite, which are usually accompanied by secondary copper minerals, covellite and bornite. The total mass fraction of the copper-bearing minerals is 1.5%. About 50% of iron is contained in the fayalite. The bulk of alkali and alkaline-earth elements, as well as aluminum and silicon, are encapsulated in the glass phase [23].

Magnetic properties of the SUMZ copper-smelting slag processing tailings are governed by the magnetic properties of its constituent minerals. Almost all mineral phases of the "technical sands" are magnetics, capable of magnetizing in a magnetic field. This is due to the fact that they usually include atoms with their own magnetic moment due to the presence of unpaired electrons, such as Fe^{2+}, Fe^{3+}.

Therefore, the application of magnetic field could not provide desirable separation of the "SUMZ technical sands". The yield of magnetic fraction was 83.27%, that of weakly magnetic fraction, 10.85%, and that of non-magnetic fraction, 5.88% (Table 1).

In addition, the presence of glass (up to 30 wt.% in the SUMZ slags) has a significant effect on the separation of the copper-smelting slag flotation tailings using wet magnetic separation. It was found for copper-smelting slags of Karabashmed that crushing in centrifugal-impact apparatuses (disintegration) occurs with a low degree of selectivity due to their glassy structure [28].

The cooling conditions of the copper-smelting cast slag, which serves as a source material for the investigated "technical sands", are markedly different from natural ones. As a consequence, homogenized mineral individuums represent a smaller part of the volume. The predominant part of the waste is represented by to varying extent crystallized glass [23, 29]. In the clastic material of the "SUMZ technical sands", fine clastic glass representing fragments of forming minerals at different stages of homogenization of their composition quantitatively dominates. The glass fills interstitials between olivine, magnetite, and sulfide mineral individuums. The glass composition (according to microanalyzer data) is as follows: 30–50% silica, 7 to 20% alumina, up to 10% alkaline metals, 1.5–10% zinc, up to 1% copper, and up to 30% iron oxides [30]. The presence of complex cryptocrystalline structures, solid solution decomposition structures, the structures of elements substitution in the crystalline lattice of minerals in the form of hems on the periphery of grains reduces the degree of the slag disintegration selectivity when crushed.

The chemical analysis of the obtained magnetic fractions of the "SUMZ technical sands" (Table 2) showed that zinc and copper are distributed relatively evenly among the fractions. Some increase of copper content in the non-magnetic fraction and that of zinc content in the weakly magnetic fraction was found.

Table 1

Results of separation of copper-smelting slag flotation tailings by wet magnetic separation

Fraction	Magnetic field strength, kA/m	Weight, g	Yield, %
Magnetic	48	119.52	83.27
Weakly magnetic	200	15.57	10.85
Non-magnetic	–	8.44	5.88
Total	–	143.53	100.00

According to the historical studies, zinc-bearing magnetite phase is observed in copper-smelting slag processing tailings [21, 23]. This fact can be regarded as one of the manifestations of incomplete homogenization of the mineral. It can be assumed that the increase of zinc content in the weakly magnetic fraction is connected with this fact. The presence of zinc was also determined in wustite, which is inferior in quantity to magnetite in the "technical sands", but also contains a certain amount of zinc.

Copper remains predominant in the non-magnetic fraction, most likely due to the presence of emulsion impregnation of matte [23] and copper-bearing minerals in the glass [25].

The mineral basis of the "technical sands" are silicates (about 84%) represented by olivines, pyroxenes, and glass phase. The secondary phases are oxides of iron and nonferrous metals (about 14%), sulfides (about 2%) (Table 3). Intermetallics are present in small amounts.

The indicated mineral phases (see Table 3) have the corresponding crystal lattices. However, it should be noted that most of the minerals of the "technical sands" have not yet reached full homogenization. The peculiarity of the majority of the mineral fragments in the clastic material of the tailings is noticeable deviations from stoichiometric compositions.

According to the data of X-ray phase analysis the olivines in the "SUMZ technical sands" have predominantly fayalite composition $(Fe_{1.64}, Ca_{0.04}, Zn_{0.15})(Si_{0.85}, Al_{0.27})O_4$. The studies of the magnetic properties of olivines [31, 32] have shown that at low temperatures antiferromagnetic ordering occurs in them, with the magnetic cell coinciding with the crystallographic one.

Pyroxenes in the "SUMZ technical sands" are ferrosilicates of the following composition: $(Fe, Mg, Ca, Zn)_{2.0}Si_{1.9}O_{6.0}$ with Al impurities. It was noted earlier that augite $(Ca, Fe, Mg)[SiO_3]_2$ individuums are sometimes found in waste slags [33]. Trivalent iron and copper cations are often found in the crystal lattice of pyroxenes.

The main segregations of magnetite, sulfides, nonferrous metal oxides and intermetallics are concentrated in the glassy phase of the "technical sands". The grains of these minerals are well bounded, of various sizes, including nanocrystalline ones. Magnetite also forms complex intergrowths with fayalite. Pure magnetite in flotation tailings is rare; its composition can be represented by the following structural formula: $(Fe_{2,8}, Al_{0,5}, Si_{0,1}, Zn_{0,1})O_4$. It often includes copper, while Cr, Ti, Cd, Sn cations are occasionally found. Magnetite is a typical ferromagnet [34]. Magnetite crystals and grains are themselves natural permanent magnets, having the strength and polarity of a true magnet. But the presence of isomorphic impurities in magnetite composition will reduce the magnetic susceptibility.

Table 2

Data of chemical analysis of magnetic fractions of copper-smelting slag flotation tailings, wt. %

Fraction	SiO_2	Al_2O_3	MnO	CaO	MgO	P_2O_5	Cu	Zn	Pb	As	Fe_{tot}
Initial "sands"	32.4	2.9	0.04	4.39	0.98	0.05	0.18	1.17	0.06	0.07	35.5
Magnetic	32.4	3.1	0.04	4.54	1.01	0.05	0.19	1.20	0.07	0.07	37.8
Weakly magnetic	35.2	3.3	0.04	5.15	1.28	0.06	0.15	1.36	0.07	0.06	34.8
Non-magnetic	37.2	3.9	0.05	5.01	1.71	0.07	0.24	1.20	0.07	0.05	33.1

Table 3

Mineral composition of magnetic fractions of copper-smelting slag flotation tailings according to X-ray phase analysis, wt.%

Mineral	Initial "SUMZ technical sands"	Magnetic fraction	Weakly magnetic fraction	Non-magnetic fraction
Fayalite Fe_2SiO_4	48.2	51.3	64.6	64.5
Forsterite $(MgMn)SiO_4$	15.4	10.0	9.0	10.0
Diopside $CaZn(Si_2O_6)$	20.4	19.9	19.3	19.6
Magnetite Fe_3O_4	13.7	15.7	4.1	1.4
Sphalerite ZnS	1.8	1.8	1.9	1.3
Zincite ZnO	0.5	1.3	1.1	3.2

Wustite ($Fe_{0,9}$, $Al_{0,02}$, $Si_{0,01}$, $Zn_{0,04}$)O and hematite (Fe, Al, $Si_{0,4})_2O_3$, sometimes with admixtures of Zn and Sn, were found in the "SUMZ technical sands". They are antiferromagnetic minerals whose magnetic susceptibility is small but positive [35]. When a magnetic field is applied, isomorphic impurities will have a significant effect on the magnetic susceptibility of these minerals.

Pyrrhotite-like sulfides in the "technical sands" have the following compositions (Pb, Fe, Cu, Zn, $Si_{0,08}$, $Sn_{0,07}$)S, $FeS \cdot Cu_2S$, $(Pb, Fe, Cu)_{1,06}S$, (Pb, Fe, $Si_{0,44}$, $Ca_{0,18})_{1,1}S$. Pure pyrrhotite is a ferromagnetic [36]. Just like magnetite, it has its own magnetic moment and is capable of creating a magnetic field around it.

Diamagnetics in the "SUMZ technical sands" are represented by copper metal, antimony-bearing intermetallics, sulfides (chalcosine and sphalerite), cuprite and zincite, anhydrite of ($Ca_{0,74}$Ca, Na, Al, Mg) SO_4, composition, aluminum and silicon hydroxides.

96% of magnetite, more than 80% of silicate and sulfide phases belong to the magnetic fraction (Table 4). Such distribution of the substances can be connected with thin impregnation of magnetic minerals in the glass phase and the formation of intergrowths with silicates, as well as with the change in the magnetic structure of mineral phases, arising in the presence of isomorphic impurities in the crystal structure of minerals when magnetic field is applied.

Isomorphous impurities (in the crystal lattice of the "technical sands" silicates) of cations possessing their own magnetic moment due to the presence of unpaired electrons, for example, Fe^{2+}, Mn^{2+}, Fe^{3+}, Mn^{3+}, Mn^{4+}, Ni^{2+}, Cu^{2+}, as well as magnetite and pyrrhotite inclusions lead to the appearance of areas of increased magnetization inside silicate grains and thin aggregates of silicate minerals and glass, preserved after crushing of the copper-smelting slag. Therefore, more than 80% of the silicates are concentrated in the magnetic fraction.

The concentration of diamagnetics in the magnetic fraction (see Table 4) can be explained both by electrostatic capture of small grains of diamagnetic minerals and the presence of dusty particles of magnetite and/or pyrrhotite dispersed in them.

The distribution of magnetite in the magnetic fractions depends on its chemical composition, as well as on the degree of disintegration (disclosing) intergrowths with fayalite and glass phase. The more impurities in the crystal lattice of magnetite, the lower the magnetic susceptibility. Magnetite was detected even in the non-magnetic fraction.

According to the XRD data, copper is predominantly concentrated in the pyrrhotite-like sulfides. The distribution of zinc by mineral phases is as follows: 15–20% of the total zinc content belong to magnetite, 30–35% to silicates (olivine), 20–25% to zincite, and up to 20% to sphalerite.

The joint evaluation of the data of X-ray phase and thermomagnetic analyses of the copper-smelting cast slag flotation tailings showed that at practically identical X-ray diffraction patterns thermomagnetic curves in the range of 20–700 °C demonstrate significant differences of the magnetic separation fractions (Fig. 1).

All the obtained thermomagnetic curves are irreversible. The magnetic properties of the "sands" magnetic separation fractions are determined by the presence of magnetite and pyrrhotite-like sulfides.

The magnetic fraction reaches Curie temperatures between 470 and 520 °C upon heating, indicating the presence of an isomorphous series of ferromagnetic minerals.

When the weakly magnetic fraction is heated, an increase in magnetic susceptibility after cooling by about 20% is observed (Curie temperature ranges 420 to 570 °C). Two inflections are noticeable on the cooling curve; one probably corresponds to the magnetite formed during cooling, the other corresponds to the admixture of initial ferromagnetic

Table 4

Distribution of minerals in magnetic fractions of copper-smelting slag flotation tailings taking into account weight yield of fractions, wt. %

Mineral	Magnetic fraction	Weakly magnetic fraction	Non-magnetic fraction
Fayalite Fe_2SiO_4	79.81	13.09	7.09
Forsterite $(MgMn)SiO_4$	84.17	9.87	5.94
Diopside $CaZn(Si_2O_6)$	83.63	10.57	5.82
Magnetite Fe_3O_4	96.13	3.27	0.61
Sphalerite ZnS	84.04	11.56	4.29
Zincite ZnO	77.69	8.56	13.50

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minerals with the same Curie temperature as that of the strongly magnetic fraction.

When heating the non-magnetic fraction, the Curie temperature was 550 °C, which indicates some presence of ferromagnetic minerals, while cooling resulted in the formation of magnetite, due to which the magnetic susceptibility increased about 3 times.

The precursors of magnetite formed during cooling of weakly magnetic and non-magnetic fractions are probably iron hydroxides and isomorphously substituted ferromagnetic minerals: magnetite and pyrrhotite.

The thermograms analysis showed that the magnetic separation fractions contain quite a large amount of impurities that significantly reduce their magnetic susceptibility and, correspondingly, magnetic strength. Therefore, a more complete separation of the “technical sands” requires an increase in magnetic field strength, possibly rather considerable, using superconducting magnetic systems [37].

Thus, the copper-smelting slag flotation tailing phase composition, mineral magnetic properties and structural features determine the low efficiency of the “technical sands” separation by generally accepted methods of wet magnetic separation. For their successful separation, the material preparation is necessary prior to magnetic separation.

As is known, the existing flowsheets of iron ore beneficiation based on magnetic separation and developed on the principle of staged separation of waste tailings with obtaining finished concentrate, only in the last operation are applicable and efficient for rich ores. In the beneficiation of finely impregnated lean ores, there are problems associated with reducing the coarseness of the material fed to magnetic separation. The maximum complete disclosing (releasing) of minerals is achieved only when grinding to the size of the extracted mineral grains that entails an increase in both energy costs and overgrinding of the ore components, including already disclosed minerals [38].

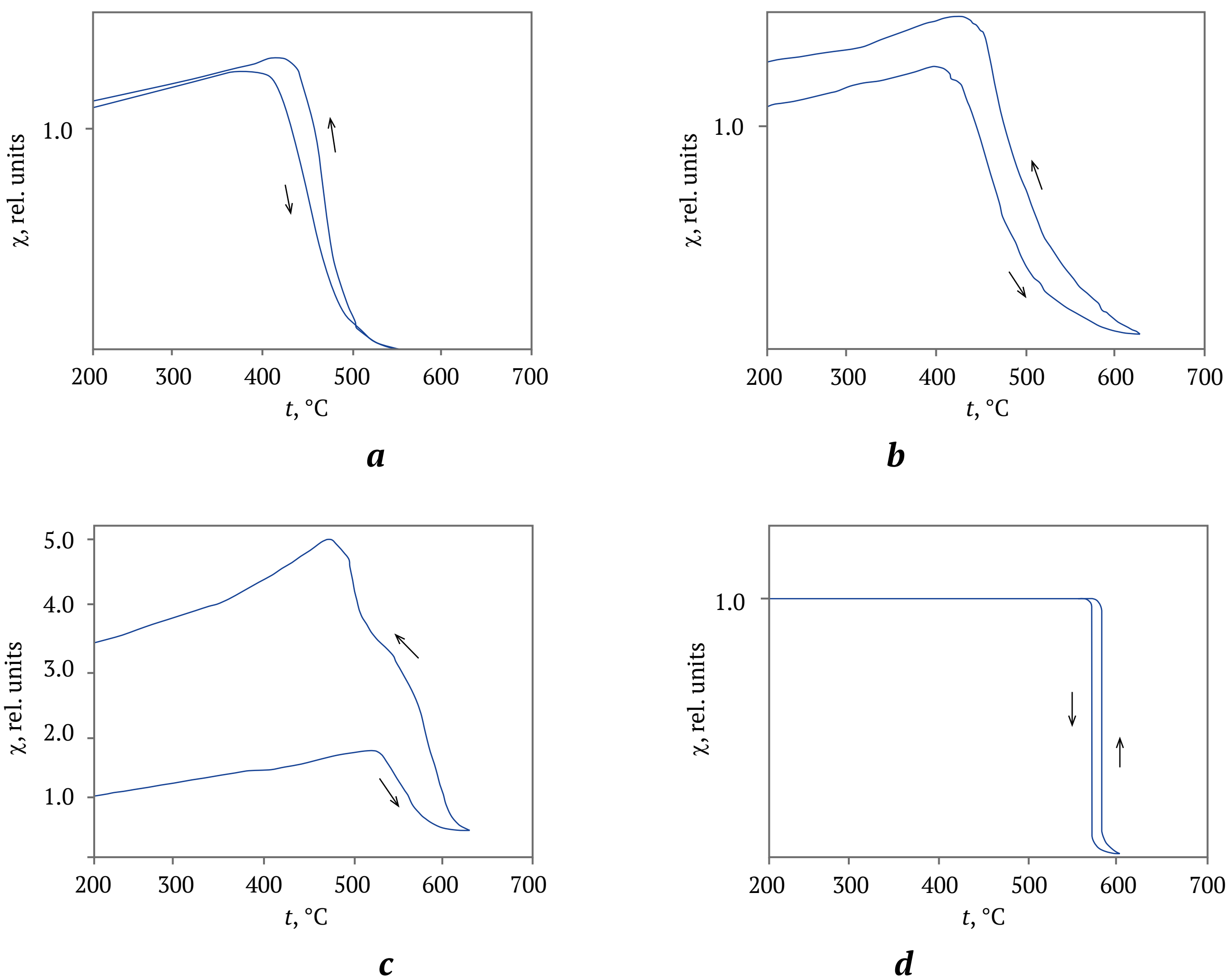

Fig. 1. Thermomagnetograms: *a* – magnetic fraction of “SUMZ technical sands” (measurement limit of 10 mV); *b* – weakly magnetic fraction (measurement limit of 3 mV); *c* – non-magnetic fraction (measurement limit of 0.3 mV); *d* – natural magnetite from Abakan deposit (measurement limit of 10 mV)

Ultrafine grinding of minerals [25] using ball and bead mills leads to the destruction of crystal integrity and defect formation with the appearance of X-ray- amorphous layers, as well as increasing their hydration and solubility. It was found that sulfide minerals undergo such structural and chemical changes as sulfatization and amorphization under mechanical impacts [39].

In the process of magnetite grinding to 0.04–0.02 mm its primary domain structure is broken that first of all causes the growth of coercive force of the particles. This contributes to increased flocculation and entrapment of significant amounts of non-metallic particles into the floccules that reduces the efficiency of separation of magnetite and non-metallic minerals. At the same time, the specific magnetic susceptibility of magnetic particles finer than 0.02 mm sharply decreases that contributes to the loss of overground magnetite with tailings. It was also revealed that during mechanical processing (crushing, grinding) the defectivity of magnetite structure increases, which leads to magnetite transformation towards magnetite-martite-hematite [40].

The processes of slurry and defect formation reduce the separation selectivity. To reduce the negative effects of these processes, the introduction of surfactants into the grinding process was proposed [39].

The disadvantages of mechanical disclosure can be avoided by applying a high-voltage pulse method of disclosure of solids, including glass [41], which demonstrates high selectivity and efficiency, as well as allows the process regulating and automating.

The separation selectivity can be also improved by using a spiral separator, which makes it possible to remove grains of iron-bearing minerals of different densities from inter-cycle operations as they are disclosed to avoid overgrinding [42].

Conclusion

For the first time for the Sredneuralsky copper smelter copper-smelting slag flotation tailings (“SUMZ technical sands”) the material composition of magnetic fractions was studied and thermomagnetic curves were obtained. The “technical sands” have pronounced magnetic properties, as they contain ferromagnetic minerals and isomorphic impurities – cations with their own magnetic moment in the crystal lattices of minerals. Magnetite is concentrated in the magnetic fraction (about 97 %). The increase of copper and zinc contents in the non-magnetic fraction is probably due to non-stoichiometry of olivine, as well as the presence of microinclusions.

The joint evaluation of the data of X-ray phase and thermomagnetic analyses showed that at practically identical X-ray diffraction patterns the thermomagnetic curves in the range of 20–700 °C demonstrate significant differences of the fractions of the copper-smelting slag flotation tailings magnetic separation. All the obtained thermomagnetic curves are irreversible. Therefore, a more complete separation of the “technical sands” requires an increase in the magnetic field strength. We believe that the use of thermomagnetic analysis to assess the magnetic susceptibility of the fractions will be useful for quality control of the produced concentrates at all stages of the separation.

Phase composition, magnetic properties of minerals of the “technical sands” and their structural features: the presence of cryptocrystalline structures, complex mineral intergrowths, solid solution decomposition structures, the structures of elements substitution in the mineral crystals in the form of hems on the periphery of grains – all of this reduces the efficiency of the “technical sands” separation by conventional methods of wet magnetic separation. For their successful separation an additional research to find optimal methods of the tailings pretreatment and modes of magnetic field strength is required.

The “technical sands” pretreatment should include up-to-date methods of disintegration and separation of hard-dressable finely impregnated lean ores, such as ultrafine grinding using high-voltage pulses, spiral separation with withdrawal of iron-bearing minerals of different densities (as they are disclosed) from inter-cycle operations to avoid overgrinding, use of surfactants to reduce slurry and defect formation. For magnetic separation, the application of high-gradient wet magnetic separation with superconducting magnetic system would be promising.

The research findings contribute to the study of magnetic properties of copper-smelting slag processing tailings and are of interest for the development of new flow schemes for their utilization and recycling.

References

1. Bexeitova R., Veselova L., Kassymkanova K.K. et al. The problem of environmental safety of the fields of mining industrial production of arid zone of Kazakhstan. *Geodesy and Cartography*. 2018;44(4):146–155. https://doi.org/10.3846/gac.2018.4314
2. Worlanyo A.S., Jiangfeng L. Evaluating the environmental and economic impact of mining for post-mined land restoration and land-use: A review. *Journal of Environmental Management*. 2021;279:111623. https://doi.org/10.1016/j.jenvman.2020.111623
3. Covre W.P., Ramos S.J., da Silveira Pereira W.V. et al. Impact of copper mining wastes in the Amazon: Properties and risks to environment and human health. *Journal of Hazardous Materials*. 2022;421:126688. https://doi.org/10.1016/j.jhazmat.2021.126688
4. Izydorczyk G., Mikula K., Skrzypczak D. et al. Potential environmental pollution from copper metallurgy and methods of management. *Environmental Research*. 2021;197:111050. https://doi.org/10.1016/j.envres.2021.111050
5. Jia L., Liang H., Fan M. et al. Spatial distribution characteristics and source appointment of heavy metals in soil in the areas affected by non-ferrous metal slag field in the dry-hot valley. *Applied Sciences*. 2022;12(19):9475. https://doi.org/10.3390/app12199475
6. Men D., Yao J., Li H. et al. The potential environmental risk implications of two typical non-ferrous metal smelting slags: contrasting toxic metal(loid)s leaching behavior and geochemical characteristics. *Journal of Soils and Sediments.* 2023;23:1944–1959. https://doi.org/10.1007/s11368-023-03468-0
7. Mamonov S.V., Gazaleeva G.I., Dresvyankina T.P. et al. Improvement of technological indices of copper smelters slags processing on the basis of their slow cooling and ultra-fine grinding. *News of the Higher Institutions. Mining Journal.* 2018;(2):83–90. (In Russ.) https://doi.org/10.21440/0536-1028-2018-2-83-90
8. Sibanda V., Sipunga E., Danha G., Mamvura T.A. Enhancing the flotation recovery of copper minerals in smelter slags from Namibia prior to disposal. *Heliyon*. 2020;6(1):e03135. https://doi.org/10.1016/j.heliyon.2019.e03135
9. Zhou H., Liu G., Zhang L., Zhou C. Mineralogical and morphological factors affecting the separation of copper and arsenic in flash copper smelting slag flotation beneficiation process. *Journal of Hazardous Materials*. 2021;401:123293. https://doi.org/10.1016/j.jhazmat.2020.123293
10. Alp İ., Deveci H., Süngün H. Utilization of flotation wastes of copper slag as raw material in cement production. *Journal of hazardous materials*. 2008;159(2–3):390–395. https://doi.org/10.1016/j.jhazmat.2008.02.056
11. Guman O.M., Dolinina I.A., Makarov A.B., Rudoi A.G. The use of waste processing waste slag for land reclamation of the mining complex. *News of the Higher Institutions. Mining Journal.* 2010;(4):43–49 (In Russ.)
12. Guman O.M., Makarov A.B., Wegner-Kozlova E.O. Technogenic formations as a recultivation material. *Upravlenie Tekhnosferoi*. 2020;3(4):447–461 (In Russ.) https://doi.org/10.34828/UdSU.2020.35.32.004
13. Zhai Q., Liu R., Wang C. et al. A potential industrial waste–waste synchronous treatment scheme of utilizing copper slag flotation tailings to remediate Cr (VI)-containing wastewater. *Journal of Environmental Chemical Engineering*. 2022;10(3):107685. https://doi.org/10.1016/j.jece.2022.107685
14. Zolotova E.S., Ryabinin V.F., Kotelnikova A.L., Ivanova N.S. Assessment of element mobility from copper smelting waste slag into forest soils. *Lithosphere* (*Russia*). 2020;20(5):717–726. (In Russ.) https://doi.org/10.24930/1681-9004-2020-20-5-717-726
15. Zolotova E., Kotelnikova A., Ryabinin V. The content of toxic elements in soil-plant system based on ombrotrophic peat with the copper smelting slag recycling waste. *Pollution*. 2023;9(1):286–298. https://doi.org/10.22059/poll.2022.346474.1551
16. Kart E.U. Evaluation of sulphation baking and autogenous leaching behaviour of Turkish metallurgical slag flotation tailings. *Physicochemical Problems of Mineral Processing*. 2021;57(4):107–116. https://doi.org/10.37190/ppmp/138839
17. Gümüşsoy A., Başyiğit M., Kart E.U. Economic potential and environmental impact of metal recovery from copper slag flotation tailings. *Resources Policy*. 2023;80:103232. https://doi.org/10.1016/j.resourpol.2022.103232
18. Svetlov A.V. Development of enrichment methods for low-grade non-ferrous metallurgy objects in the Murmansk region. *Mineralogy of Technogenesis*. 2018;(19):205–216. (In Russ.)
19. Tian H., Guo Z., Pan J. et al. Comprehensive review on metallurgical recycling and cleaning of copper slag. *Resources, Conservation and Recycling*. 2021;168:105366. https://doi.org/10.1016/j.resconrec.2020.105366

20. Araujo F.S., Taborda-Llano I., Nunes E.B., Santos R.M. Recycling and reuse of mine tailings: A review of advancements and their implications. *Geosciences*. 2022;12(9):319. https://doi.org/10.3390/geosciences12090319
21. Makarov A.B., Guman O.M., Dolinina I.A. Mineral composition of waste slag processing from the Sredneuralsk copper smelter and assessment of their potential environmental hazard. *Bulletin of the Ural Branch of the Russian Mineralogical Society*. 2010;(7):80–86. (In Russ.)
22. Grudinsky P.I., Dyubanov V.G. Research of the process of sulphating roasting of zinc-containing tailings in copper production using iron sulfates. *International Research Journal*. 2018;(12–1):83–87. (In Russ.) https://doi.org/10.23670/IRJ.2018.78.12.014
23. Kotelnikova A.L., Ryabinin V.F. The composition features and perspective of use for the copper slag recycling waste. *Lithosphere* (*Russia*). 2018;18(1):133–139. (In Russ.). https://doi.org/10.24930/1681-9004-2018-18-1-133-139
24. Reutov D.S., Khalezov B.D. The search for optimal conditions for sulfuric acid leaching to recover copper and zinc from flotation tailings copper slag. *Butlerov Communications*. 2015;44(12):199–203. (In Russ.)
25. Bulatova K.V., Gazaleeva G.I. (sci. ed.) *Modern technologies for processing technogenic raw materials*. Monograph. Yekaterinburg: JSC "IPP "Ural Worker"; 2019. 200 p. (In Russ.)
26. Li S., Guo Z., Pan J. et al. Stepwise utilization process to recover valuable components from copper slag. *Minerals*. 2021;11(2):211. https://doi.org/10.3390/min11020211
27. Filatov V.V., Ivanchenko V.S., Glukhikh I.I. *Petromagnetism in ore geophysics*. Ekaterinburg: UGGU; 2011. 414 p. (In Russ.)
28. Gorlova O.E., Orekhova N.N., Kolodezhnaya E.V. et al. Providing a rationale for an integrative criterion to predict the potential selective disintegration of technology-related, complex structured raw materials. *Vestnik of Nosov Magnitogorsk State Technical University*. 2023;21(3):15–26. https://doi.org/10.18503/1995-2732-2023-21-3-15-26
29. Sanakulov K.S., Khasanov A.S. *Processing of slag in copper production*. Tashkent: Fan Publ. House; 2007. 206 p. (In Russ.)
30. Erokhin Yu.V., Kozlov P.S. Fayalite from slags of the Sredneuralsk copper smeltery (Revda city). *Mineralogy of Technogenesis*. 2010;(11):32–40. (In Russ.)
31. Belley F., Ferré E.C., Martín-Hernández F. et al. The magnetic properties of natural and synthetic $(Fe_x, Mg_{1-x})_2SiO_4$ olivines. *Earth and Planetary Science Letters*. 2009;284(3–4):516–526. https://doi.org/10.1016/j.epsl.2009.05.016
32. Geiger C.A., Vielreicher N.M., Dachs E. Are the thermodynamic properties of natural and synthetic Mg_2SiO_4–Fe_2SiO_4 olivines the same? *American Mineralogist: Journal of Earth and Planetary Materials*. 2021;106(2):317–321. https://doi.org/10.2138/am-2021-7764CCBY
33. Erokhin Yu.V., Kozlov P.S. Magnetite slags from the Sredneuralsk cooper smeltery. *Mineralogy of Technogenesis*. 2013;(14):29–37. (In Russ.)
34. Ziese M., Esquinazi P.D., Pantel D. et al. Magnetite (Fe_3O_4): a new variant of relaxor multiferroic. *Journal of Physics: Condensed Matter*. 2012;24(8):086007–086015. https://doi.org/10.1088/0953-8984/24/8/086007
35. Pelevin A.E. Magnetic susceptibility of weakly magnetic rock minerals. In: *Scientific foundations and practice of processing ores and technogenic raw materials: materials of the XXIV International Scientific and Technical Conference held as part of the XVII Ural Mining Decade*. Yekaterinburg, April 09–12, 2019. Ekaterinburg: Publ. House "Fort Dialog-Iset"; 2019. Pp. 314–316. (In Russ.)
36. Pisakin B.N. Identification features of pyrrhotite as a cation-deficient magnetic mineral. *Vestnik of Saint Petersburg University. Earth Sciences*. 2004;1(7):3–12. (In Russ.)
37. Karmazin V.I., Karmazin V.V. *Magnetic methods of enrichment*. Moscow: Nedra Publ. House; 1984. 416 p. (In Russ.)
38. Gzogyan T.N., Golovin Yu.I., Tyurin A.I., Gzogyan S.R. Effect of intergrowth boundaries between mineral species of ferruginous quartzite on ore pretreatment. *Journal of Mining Sciences*. 2017;(3):154–162. (In Russ.)
39. Yusupov T.S., Urakaev F.Kh., Isupov V.P. Prediction of structural-chemical change in minerals under mechanical impact during grinding. *Journal of Mining Sciences*. 2015;(5):161–168. (In Russ.)
40. Gzogyan T.N. On the issue of genetic defectiveness of magnetite from the Mikhailovskoye KMA deposit. *Obogashchenie Rud*. 2002;(3):29–33. (In Russ.)
41. Kharlov A.V. Generators for electric-discharge technologies and their technical applications (review). Instruments and Experimental Techniques. 2022;65(1):1–28. https://doi.org/10.1134/S0020441221060154

42. Prokopyev S.A., Prokopyev E.S., Emelyanova K.K., Napolskikh S.A. High-quality magnetite–hematite concentrate production by spiral separation. *Gornyi Zhurnal*. 2021;(6):86–90. (In Russ.) https://doi.org/10.17580/gzh.2021.06.07

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