Iron Ore Concentrate for Purifying Water from Oil

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Abstract

With the use of X-ray diffraction, SEM, XFA, IR spectroscopy, and a Cryogenic High Field Measurement System we studied the composition, structure, properties of powders of iron ore concentrate from the Mikhailovskiy OMPE with a view to its use as a magnetic adsorbent for removing oil from the surface of water. It was demonstrated that the specific surface of the concentrate is equal to 1.5 m^2/cm^3, the concentrate exhibiting hydrophobic properties due to the formation of carbon on the surface thereof after the pyrolysis of the flotation reagent and starch resulting from drying at 800 °C. The specific magnetic saturability of the concentrate is 2.3 times higher than the specific magnetic saturability of pure magnetite, which could be caused by the penetration of iron atoms from the equipment into the interior of the concentrate particles (1 μm from the surface) as a result of the procedures of extraction, grinding, of dry and wet magnetic separation and flotation in the course of obtaining the concentrate. It was noted that the oil exhibits weak magnetic properties due to the presence of natural and man-made magnetic substances therein. After adding 1–5 % of the concentrate the specific magnetic saturability of hydrocarbons reaches 0.6–3 A · m^2/kg. Ways to use the concentrate are under discussion.

Key words: powder, iron ore concentrate, the specific surface area, specific magnetic saturability, Verwey phase transition, oil, water purification

INTRODUCTION

The problem of water purification from oil is becoming increasingly important due to the increasing incidence of oil spills from tankers and oil blowout from boreholes. So, April 20, 2010 there was a major accident at the oil platform belonging to the British Petroleum Company, which resulted in the fact that the Gulf of Mexico was contaminated by hundreds tons of oil. A considerable damage was caused both to the environment and to the company; the latter has invested huge amounts of money to clean up the bay and the coast, to compensate the damages from pollution.

There are various methods known concerning water purification from oil pollution [1], including the use of wetting agents, dispersants, organic absorbents, *etc*. With the help of dispersants the oil can be moistened with water, to break into small slicks and to form sediment in the lower layers of water. Absorbents are able to absorb oil in amounts those are an order of magnitude greater than the mass thereof, but in this case it is required to solve the problems of collecting the swollen absorbent and its regeneration.

One of the promising methods for purifying water from oil is based on the use of a magnetic powder. The magnetic powder sprayed

over oil on can adsorb active oil components on the surface. Owing to the magnetic powder, the oil itself can obtain magnetic properties, because of this one could gather it from water area by means of magnetic devices. The oil is adhered to the magnet due to the action of electromagnetic field. Further, the oil is separated from the magnetic powder using magnetic separators. The recovered magnetic powder is calcined and used again for purifying oil from water.

Thus the oil itself exhibits weak magnetic properties; depending on the oilfield the oil can contain up to 150 g/t of paramagnetic vanadium and 50 g/t of ferromagnetic iron. Furthermore, on thee course of production, storage and transfer of oil as well as owing to the erosion and corrosion of the processing equipment, iron and iron oxides can appear therein.

A powdered sorbent is known [2], with a particle size of 0.015−0.5 µm and the value of specific saturation magnetization ranging within 30−70 A · m^2/kg that contains 60−90 % of ferromagnetics and a hydrocarbon-based oil-wetting agent (8.8−38.8 mass % of carbon, 0.2−1.2 mass % of hydrogen). The powder is prepared by means of plasma-chemical method. In the course of dispersing of a ferromagnetic material in the plasma arc the zone of spraying is fed with hydrocarbons, thereby a hydrophobic spherical magnetic powder composite is formed.

In this paper we studied the structure and properties of the magnetic powder made of iron ore concentrate, a potential magnetic adsorbent for oil and petroleum products. The concentrate is obtained at iron ore mining and processing enterprises. The technology of its preparation involves sequentially the processes of iron ore grinding, magnetic separation, reverse flotation with cationic amphiphiles, filtration and drying. In the course of the reverse flotation, the ore is purified from impurities (quartz) rather than from iron oxides. The flotation of quartz is performed in an alkaline medium using acetate salts of the esters of primary mono- and diamines with the depression of iron minerals by means of alkaline starch [3]. The remaining pulp is enriched with iron minerals. The pulp is filtered and the resulting slurry is dried to form a dry concentrate.

EXPERIMENTAL

As the objects of investigation we chose ore powder and "dried concentrate" from the Mikhailovsky GOK JSC. For modelling the oil we used a mixture of paraffin and Vaseline (mass fraction 10 %), the latter was added to the paraffin to provide the hydrocarbon mixture with plasticity. The identification of phases in the powders of the ore and concentrate was carried out by means of a DRON-3M X-ray diffractometer. The X-ray diffraction studies were performed with CuK$_\alpha$ radiation at a temperature of about 300 K, in a point-by-point registration mode. Signal accumulation time at a point $\Delta\tau = 3$ s, angle scanning increment $\Delta 2\theta = 0.03°$. The particle sizes of the ore and concentrate powder as well as the elemental composition of the powders were determined with a LEO 1455 VP SEM (Carl Zeiss, Jena, Germany).

In the analyzer, a narrow beam (electron probe) of 1 µm in diameter scans the surface of the powder. Falling into the sample, the electrons of the beam knock electrons out of the atomic shells of the substance under investigation to cause X-ray emission. The identification of chemical elements was performed basing on a characteristic set of frequencies, the concentration thereof was determined from the radiation intensity. For obtaining the IR spectra of the flotation reagent PA-14 (manufactured by Tomah) it was extracted from the sample powder after filtration by ethanol. The extract was filtered through track membrane filters. The flotation reagent IR spectra were registered using a Spectrum One spectrophotometer. The magnetic studies were carried out using a Cryogenic High Field Measurement System universal measuring system [4]. In addition to the usual measurements of the magnetic moment as a function of magnetic field and temperature we used a technique of measuring the magnetic susceptibility after cooling in zero-level (ZFC) and low-level (FC) magnetic fields.

RESULTS AND DISCUSSION

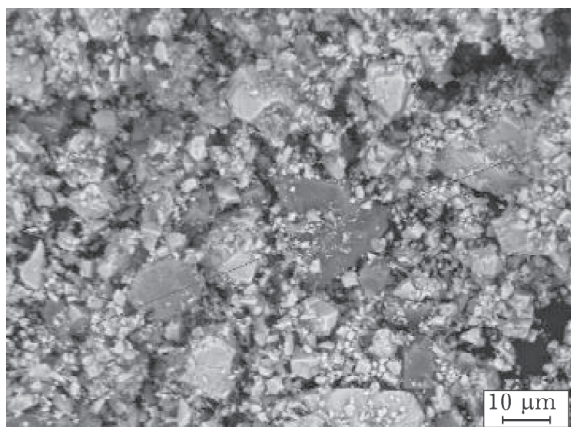The image of the powder concentrate (Fig. 1) demonstrates that the particle size of the pow-

Fig. 1. SEM image of the powder of iron ore concentrate.

der ranges within 0.5−50 μm. Provided that all the particles have a cubic shape and the mentioned size of the cube edges, the calculated specific surface area of the powder ranges from 0.12 to 1200 m^2/cm^3. The optimum concentration of hexylamine in the course of reverse flotation is equal to 250 g/t of the powder [3]. Hexylamine is adsorbed onto the powder surface as a dense layer with an area of 0.2 nm^2 per molecule [5]. With a uniform distribution of the amine in the powder of the pulp as a monomolecular layer at the powder concentrate density equal to 5000 kg/m^3 [3], the calculated value of the powder surface area should be of about 1.5 m^2/cm^3 that is comparable with the data obtained from the experimental values of the concentrate particle size (0.12−1200 m^2/cm^3). This indicates that the content of very fine fraction in the powder is insignificant, which is also confirmed by the results of SEM investigation.

The concentrate powder contains a small amount of the amine flotation reagent remaining after filtering. This is indicated by the IR spectra of a film of concentrate powder extract after filtration, where one could observe typical amine absorption bands ranging within 3200−3400, 3000−2800, 1700−1400, 1200−1400, 1000−700 cm^{-1}. These bands, in particular, coincide with the absorption bands of hexylamine IR spectrum according to the U.S. National Bureau of Standards [6]. After drying at 800 °C the flotation reagent and starch adsorbed on the powder particles are converted
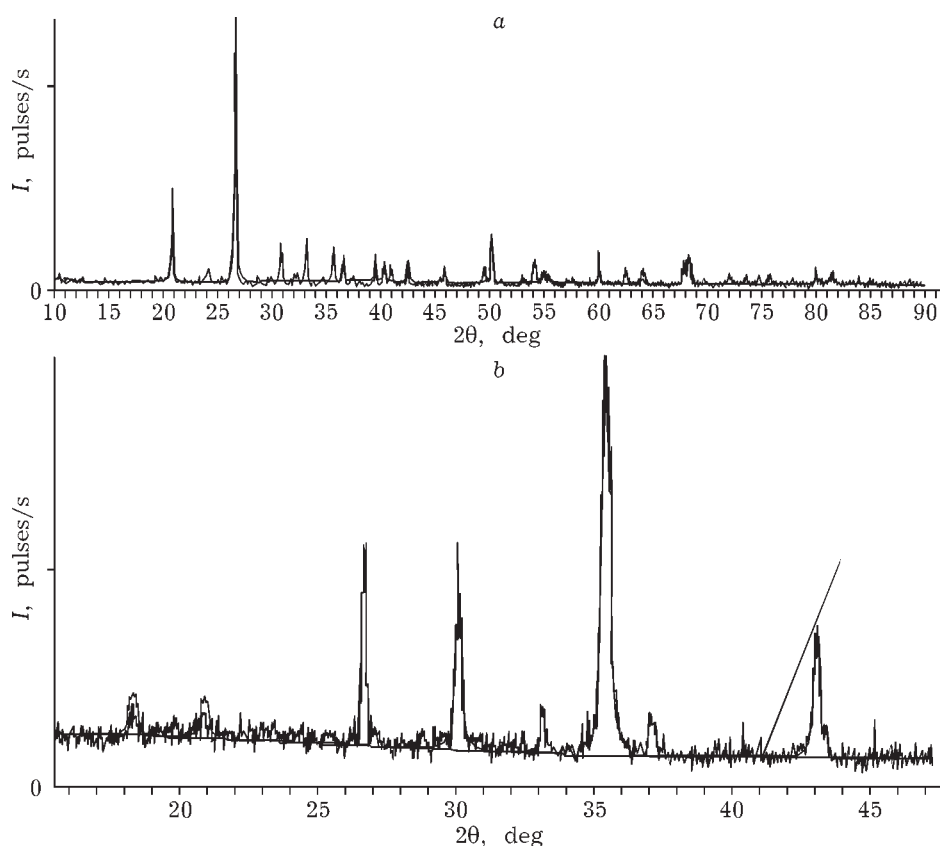

Fig. 2. X-ray diffraction profile of ore powder (a) and ore concentrate (b).

into carbon, which imparts hydrophobicity to the powder concentrate.

According to XRD phase analysis, the ore powder contains 13.5 mass % of Fe_2O_3 and 86.5 mass % of SiO_2. The concentrate has the following composition (mass %): Fe_3O_4 63.7, Fe_2O_3 3.9, SiO_2 32.4 (Fig. 2, *a*, *b*). The peaks indicated for Fe_2O_3, correspond to rhombohedral α-Fe_2O_3 (JCPDS card No. 33-0664). The XRD profiles of ore powder exhibit neither peaks corresponding to γ-Fe_2O_3 (JCPDS card No. 391346) nor Fe_3O_4 (JCPDS card No. 89-4319) with a cubic spinel structure. For the concentrate powder, the peak (311) at 36 deg coincides with the peak (311) for Fe_3O_4 standard (JCPDS card No. 89-4319) at the same angle, but no other peaks were revealed inherent in this standard.

In order to identify magnetite Fe_3O_4 in the ore powder we investigated the Verwey phase transition. It has been found that the metal-to-dielectric transition in the case of magnetite occurs at a temperature approximately 120 K (Verwey temperature), therewith changing the resistance amounting to two orders of magnitude is observed. Magnetite belongs to compounds with mixed-valence iron; it crystallizes at a room temperature to give an inverted cubic spinel structure with tetrahedral A type lattice points occupied by Fe^{+3}, and octahedral B type lattice points with equal number of randomly distributed Fe^{+3} and Fe^{+2} cations. Electron spins in A type lattice points are arranged in an antiparallel manner with respect to electron spins in the B type lattice points. Below the Verwey temperature, ordering the Fe^{+3} and Fe^{+3} ions occurs in the $(001)_c$ plane with respect the octahedral angles, whereas the cubic structure becomes monoclinic one that consists of four rhombohedral distorted cubic cells [7]. From the data presented in Fig. 3, *a* one can see that for the ore powder the Verwey transition occurs at 125 K. Figure 3, *b* demonstrates the reversion of the temperature of the powder concentrate, whose Verwey temperature is also equal to 125 K. The jump in the specific magnetization at the phase transition for the ore powder is equal to 0.08 A · m^2/kg, whereas for the concentrate this value is 120 times greater to be equal to 9.5 A · m^2/kg.

Interesting results were obtained in studying the field dependence of ore powders and ore concentrate magnetization (Fig. 4). The specific saturation magnetization of the concentrate was found to be 150 A · m^2/kg, which is significantly higher as compared to that for pure magnetite. Thus, the specific saturation magnetization of pure magnetite at 0 K is equal to 98 A · m^2/kg, whereas at a room temperature this value is equal to 92 A · m^2/kg [8]; for ore powder this value is equal to 7.5 A · m^2/kg. Thus, the specific saturation magnetization of the powder concentrate is 20 times greater than the specific magnetization of the ore powder and 1.6 times greater than that for pure magnetite. Let us try to find an explanation for this interesting phenomenon.

The theory of magnetic bodies is based on their domain structure. In the case of a bulk ferromagnetic the domain structure arises a the result of minimizing the total energy, which includes the exchange energy equal to the minimum value for parallel electron spins, and the energy of crystallographic anisotropy caused
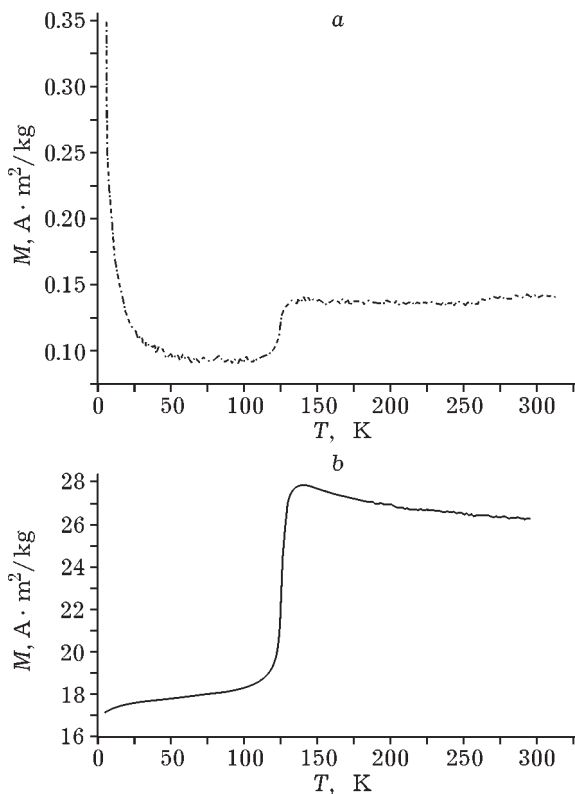

Fig. 3. Verwey phase transition on the curves of specific magnetization (*M*) depending on temperature inherent in ore powder (*a*) and concentrate (*b*).
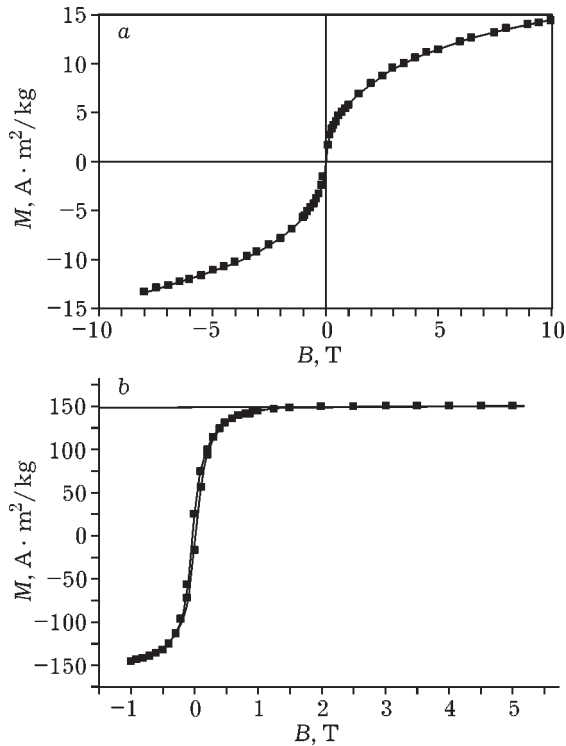
Fig. 4. Specific magnetization (M) depending applied field (B) inherent in ore powder (a) and concentrate (b).

by the presence of the axes of "easy" and "difficult" magnetization in the crystal. The minimization occurs with respect to the magnetostatic energy associated with the presence of magnetic poles inside and on the surface of the sample. The closure of magnetic flux from the domains reduces the number of poles in the sample and the associated magnetostatic energy. The domains those represent regions of ferromagnetic spontaneously magnetized up to saturation, are located mainly along the lines of «easy» magnetization. The domain size in magnetic materials is proportional to factor $A^{1/2}/M_s$, where $A^{1/2}$ is a constant caused by the types of energy listed; M_s is the theoretical maximum magnetization [9], which could be identified as a specific saturation magnetization of powders.

According to data concerning the specific magnetization of samples one can judge on the mass fraction of the magnetic component in the composition: $\varphi_m = \sigma/\sigma_s$, where φ_m is the mass fraction of a magnetic material (in this case magnetite); σ is the specific saturation magnetization of the sample; σ_s is the specific saturation magnetization of magnetite. From the

results of measuring the specific magnetization of the concentrate it follows that a substance is present in the samples which substance exhibits a higher specific magnetization value than that of magnetite. To all appearance, the ore and concentrate powders contain a small amount of pure iron, whose specific saturation magnetization, according to different authors, ranges within $225-245$ A $\cdot$ m^2/kg [10]. In the course of grinding, dry and wet magnetic separation procedures the iron parts of grinders and separators, to all appearance, can be abraded in contact with the ore to become a part of the ore powder and concentrate. The XRD profiles of iron standards (JCPDS card 87-0721) exhibit reflexes (110), (200) at the angles equal to 44.78° and 65.03°. Just these reflexes such as (110) 35.1°, (200) 42° are observed for ore powder (see Fig. 2, a). In the case of powder concentrate the reflex (110) 36° is reduced to a considerable extent, whereas the reflex of (200) disappears with appearing the reflex of (400) corresponding to Fe$_3$O$_4$ instead the former. The phase of pure iron in the concentrate, according to XRD phase analysis, was not explicitly detected.

Figure 5, a, b demonstrates changing the elemental content in the powders along the scanning line of 112.95 μm in size performed by X-ray analyzer. Such elements as Fe, Si, O, Mg, Al, K were determined in 200 points at a distance of 0.568 μm apart from each other. It is seen that the X-ray profile of ore powder exhibits six areas with a predominant content of silicon and only two areas mainly containing iron. In the case of the concentrate powder (see Fig. 5, b), on the contrary, there are five regions with a predominant content of iron, and only two with predominantly contained silicon.

We determined the average mass ratio between the content of iron and the content of oxygen $m(\text{Fe})/m(\text{O})$ for the powder concentrate on the scanning line (Table 1). For Fe$_3$O$_4$, this value is equal to 2.62. For pure oxide phases the $m(\text{Fe})/m(\text{O})$ ratio is equal to 2.3 (Fe$_2$O$_3$), 2.6 (Fe$_3$O$_4$), 3.5 (FeO). From Table 1 one can see that for all the five areas of scanning the $m(\text{Fe})/m(\text{O})$ ratio is greater than that inherent in Fe$_3$O$_4$ and other iron oxides. In other words, at 60 %
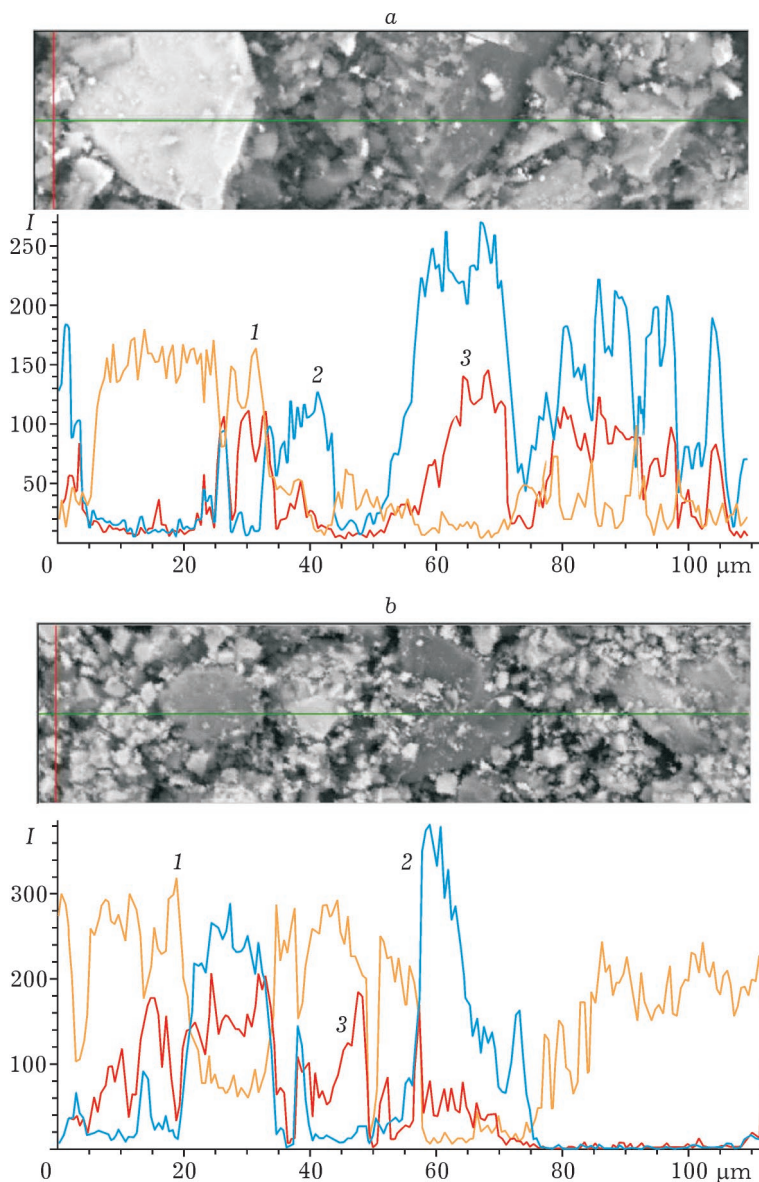
Fig. 5. Concentration of iron (*1*), Si (*2*) and oxygen (*3*) along scanning lines for ore powder (*a*) and concentrate (*b*).

TABLE 1

Level of concentrate powder enrichment with iron as compared to iron content in Fe_3O_4 along the scanning line by the electron beam of 1 μm in diameter (see Fig. 5, *b*). The scanning range equal to 0.568 μm, total 200 points

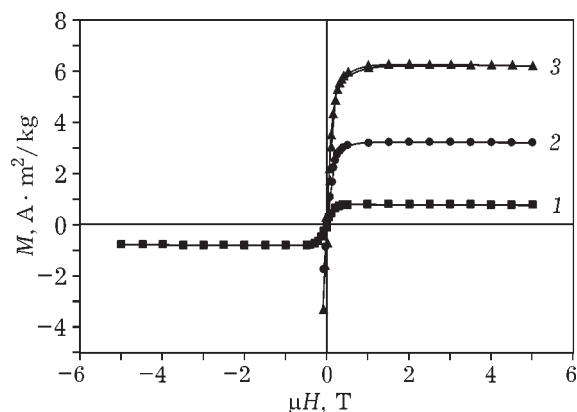| Scanning area, μm	$\varphi_{Fe_xO_y} = m(Fe)/m(O)$	$\varphi_{Fe_xO_y}/\varphi_{Fe_3O_4}$	Enrichment with iron along the scanning line, %
0−12.49	4.95	2.0	11.0
34.62−44.26	3.92	1.5	8.5
51.08−56.19	4.66	1.8	4.5
70.95−77.76	4.10	1.6	6.0
77.76−111.24	47.3	18.0	30.0

Fig 6. Specific magnetization (M) depending on applied field (μH) for the composite consisting of paraffin, Vaseline and concentrate. The content of concentrate (%): 1 (*1*), 5 (*2*), 10 (*3*).

of the scanning line the powder concentrate is enriched with iron to a significant extent within the area of 1 µm. For example, in the range of 77.76−111.24 µm the iron content in the powder concentrate is on average 18 times greater a compared to pure Fe_3O_4. The calculated values would be even greater if we consider that oxygen in these scanning areas is included in the structure of the quartz. Such a saturation of the surface of the concentrate particles with iron significantly improves the magnetic properties thereof, as it is observed in the experiment concerning the determination of the specific saturation magnetization.

The specific saturation magnetization of the composite consisting of the concentrate, paraffin and Vaseline demonstrates an increase in proportion to increasing the concentration of magnetic powder. Thus, at the 1 % content of the concentrate the specific magnetization of the composite is equal to 0.6 $A \cdot m^2/kg$ (Fig. 6), whereas at the 5 % content this value is already equal to 3 $A \cdot m^2/kg$. In the case when the concentrate content in the hydrocarbons amounts to 10 % the specific saturation magnetization of the composite would reach 7.5 $A \cdot m^2/kg$.

CONCLUSION

The "dried concentrate" produced by ore mining and processing enterprises (90 USD/t) could be used to gather oil and petroleum prod-

ucts from the surface of water. The particles of the powder concentrate have a size ranging within 0.5−50 µm; the average specific surface area is equal to 1.5 m^2/cm^3. The concentrate according to this indicator belongs to adsorbents with an average efficiency. The concentrate can be combined with oil due to the hydrophobicity thereof. Its surface is covered with carbon that is formed from the flotation reagent and starch at the technological stage of drying. Our investigations demonstrated that the specific saturation magnetization of the concentrate is equal to150 $A \cdot m^2/kg$, which is 2.3 times higher than the specific magnetization of magnetite. The anomaly of the magnetic properties of the concentrate compared with the powder of the ore is manifested also in the in an abrupt jump of the specific magnetization under the Verwey phase transition that appeared 120 times higher for the concentrate.

To all appearance, this could be connected with the penetration of the iron atoms into the interior of the concentrate surface. Enriching with iron occurs at the technological stages of extraction, grinding, dry and wet magnetic separation as well as flotation. By means of X-ray diffractometry, X-ray analysis and magnetometry it was demonstrated that the surface of the powder particles in the concentrate is from 2 to 18 times enriched with iron at a depth of 1 µm as to compare to the iron content in magnetite. Such forced modifying the "dried concentrate" in the course of the technological process, which had not been known to technologists up till now, could cause improving the products of the Mikhailovsky GOK with respect to obtaining alloys and using them as magnetic adsorbents.

Adding 1−5 % of the concentrate to the paraffin and Vaseline mixture results in forming a composite with the value of specific saturation magnetization ranging within 0.6−3 $A \cdot m^2/kg$. Oil exhibits weak magnetic properties due to a naturally occurring content of iron, vanadium, as well as man-caused iron and iron oxides therein those appear in the composition as a result of oil production and transportation. The magnetic concentrate sprayed over the oil adsorbs active oil components on the surface. Furthermore, *via* using the magnetic concentrate, the oil obtains additional

magnetic properties, which allows one to gather it from water area by means of magnetic devices. Oil can stick to the magnet of an oil collector at a distance due to the action of electromagnetic field. Further, the oil should be separated from the magnetic powder using magnetic separators. The recovered magnetic powder should then be calcined to remove the oil to further use the powder for purifying water from oil. In addition to purifying the surface of water from oil, the concentrate could be used in order to clean the coasts, beaches, to lift heavy oil from the bottom of reservoirs, to purify different processing solutions (cooling mixtures).

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