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OBTAINING MAGNETITE BY REDUCING IRON-CONTAINING WASTE

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Based on the analysis of the literature data, it is determined that as a result of the expanding directions of application of the magnetic fluid, more and more magnetite is required to obtain it. The most common method of obtaining magnetite by chemical condensation makes magnetic fluid very expensive, one liter of which is sold for more than 500 USD. To reduce its cost, the paper proposes the methods of high-temperature reduction of iron-containing wastes to magnetite, which are metallurgical dust caught by electrofilters. As a reducing agent the waste activated carbon and carbon black (soot) are used the codes of which are included in the Federal classification catalog of waste (FKKO) and reflect a significant amount of their formation. After mixing iron-containing waste, activated carbon waste and carbon black, they are gradually heated to a temperature of 900 °C. These conditions create the possibility of the appearance of ferrous iron ions, which, occupying vacant places in the crystal lattice of iron oxide (III), contribute to the formation of magnetite. The magnetite was identified by X-ray technique and evaluated by the indicator of saturation magnetization in comparison with the natural magnetite appeared to be almost identical. The resulting magnetites were dissolved in hydrochloric acid and precipitated with ammonium hydroxide. Repeated determination of saturation magnetization did not show any difference in its level. In the suspension of magnetite, a dispersant in the form of oleic acid and a dispersion medium – kerosene was introduced during heating and stirring. The saturation magnetization and stability of the obtained magnetic fluid satisfied its application for water purification from oil and oil products spill.

Introduction

The potential need for magnetic fluid (MF), and hence magnetite, is primarily related to its effectiveness in removing oil and petroleum products from the surface of increasingly polluted water bodies [1-6]. It is quite productive to use magnetic fluid to separate a mixture of materials with different densities, since MF increases its density when the strength of the external magnetic field increases [7, 8]. MF is used in shock absorbers in the automotive industry;



replacement of conventional oils with oil-based magnetic fluid provides a more comfortable ride if there are any bumps on the road by reducing the amplitude of wheel movement in the vertical plane [9, 10]. Magnetofluid seals are widespread and are the most common technical device paired with MF, which is held within the strong magnetic field and forms a liquid plug, separating two volumes with different media or pressures. Most often, magnetofluid seals are used to separate gas media or gas medium and vacuum [11, 12]. In order to save the used magnetic fluid, there were attempts to regenerate it [13], but this required the creation of strong magnetic fields and was associated with technological difficulties which are sometimes impossible to overcome. Therefore, for example, captured magnetized petroleum products are now used as a complex ingredient of rubber blends [14, 15]. Magnetite is also used in the preparation of magnetic fluids based on therapeutic substances such as dextran, penicillin solution and some others in order to deliver them under the action of a permanent magnet to the affected area [16, 17].

Such wide possibilities of magnetic fluid application are limited by its high cost (about 500 USD per 1 dm³). It seems quite important to find a cheap source raw material for obtaining magnetite, which is the basis of the cost of magnetic fluid [18].

This paper proposes one of the variants for its solution by replacing the method of obtaining magnetite by chemical condensation of salts of divalent and trivalent iron with thermal reduction with carbon of trivalent iron oxide contained in the wastes.

Experimental methods

A composite is prepared in a bead mill to produce magnetite: metallurgical dust from electrostatic precipitators (Table 1), reducing agent and sodium carbonate in the ratio of 1 : 0.5 : 0.3.

Table 1. Composition of metallurgical dust

No.	Name of component	Result of measurement	Relative error at $P=0.95$	Measurement method
1	Total iron, %	56.000	± 22.000	PNDF 16.3.24-2000
2	Wt % of moisture	0.630	± 0.120	PNDF 16.1:2.2:2.3:3:52-08
3	Copper, %	0.123	± 0.040	PNDF 16.3.24-2000
4	Petroleum products, %	0.080	± 0.170	PNDF 16.1:2.2:2.3:3:64-10
5	pH	11.30	± 0.100	PNDF 16.2:2.2:2.3:3:33-02
6	Chrome, %	0.110	± 0.020	PNDF 16.3.24-2000
7	Zinc, %	18.800	± 4.100	PNDF 16.3.24-2000
8	Sieving on a 63 μm sieve, %	1.500	± 0.200	-

Reducer – activated carbon waste and carbon black waste from FWCC - Federal Waste Classification Catalogue. Sodium carbonate creates an inert environment in the form of carbon dioxide during subsequent calcination. Stirring time is 20 minutes. The resulting composite is loaded into a rotary three-zone hardening furnace: Zone 1 – heating to at least 900 °C; Zone 2 – soaking at the reached temperature for at least one hour; Zone 3 – cooling.



Trivalent iron oxide Fe_2O_3 retains its crystalline structure up to $1565\text{ }^\circ\text{C}$, which is 26° above the melting point of iron ($1539\text{ }^\circ\text{C}$). It can act as a solvent in the formation of solid embedding solutions. In this case, the atoms of the dissolved substance (in this case, carbon) can be located inside the crystal lattice (volume diffusion), along the crystal faces (from the inner side), and along the crystal faces from the outer side (surface diffusion).

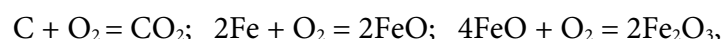
The small atomic radii of the metalloid (0.077 nm for carbon) compared to the atomic radii of iron (0.126 nm) and the shortest distance between the nuclei of neighboring atoms of 0.249 nm with ionic type of chemical bonds allow the formation of a solid solution.

Fe_2O_3 , which makes the main part of the metallurgical dust, has a gamma-modification, crystallizes in a cubic lattice with the parameter $a=0.832\text{ nm}$, and has ferromagnetic properties. Heating the composite and having a reducing environment, it is possible to form magnetite Fe_3O_4 ($\text{Fe}_2\text{O}_3 \cdot \text{FeO}$), which also forms solid solutions with Fe_2O_3 .

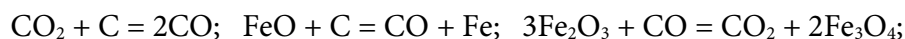
Results and discussion

Supposedly, the diffusion of the carbon atoms into the Fe_2O_3 crystal lattice with a dense face-centered packing of negative oxygen ions with the octahedral and tetrahedral spaces between them creates favorable conditions for the following reactions to take place:

oxidation:



reduction:



The presented reactions show that the redox processes make way for procuring magnetite.

The obtained samples were subjected to X-ray diffraction studies using a Bruker DZ Phaser benchtop powder diffractometer with a cobalt anode. The results of magnetite identification obtained by calcination of metallurgical dust and activated carbon with sodium carbonate are presented in Table 2.

Table 2. Results of diffraction analysis of calcined mixture of metallurgical dust and activated carbon

No.	X axis degree	Substance	Chemical formula	Relative height of radiograph peaks
1	32.400	Hematite	$\alpha\text{-Fe}_2\text{O}_3$	11.29
2	35.410	Magnetite, hematite	$\text{Fe}_3\text{O}_4; \alpha\text{-Fe}_2\text{O}_3$	30.98
3	41.656	Magnetite, hematite	$\text{Fe}_3\text{O}_4; \alpha\text{-Fe}_2\text{O}_3$	100.00
4	50.700	Magnetite, hematite	$\text{Fe}_3\text{O}_4; \alpha\text{-Fe}_2\text{O}_3$	19.41
5	63.720	Magnetite, hematite	$\text{Fe}_3\text{O}_4; \alpha\text{-Fe}_2\text{O}_3$	14.13
6	67.820	Magnetite, hematite	$\text{Fe}_3\text{O}_4; \alpha\text{-Fe}_2\text{O}_3$	15.78
7	74.800	Magnetite, hematite	$\text{Fe}_3\text{O}_4; \alpha\text{-Fe}_2\text{O}_3$	25.09

Table 2 shows the reduction of iron oxide to magnetite and there is some part of the non-ferromagnetic phase $\alpha\text{-Fe}_2\text{O}_3$. However, the saturation magnetization data presented in Table 3



showed this parameter to be only slightly lower than that of natural magnetite, indicating a significant predominance of the Fe_3O_4 phase.

Table 3. Saturation magnetization of a sample obtained by reduction of metallurgical dust with activated carbon

Types of samples for testing	Sample of natural magnetite	Samples from one batch of magnetite-containing composition				
		1	2	3	4	5
Saturation magnetization, kA/m	406.80	396.50	398.20	386.40	389.30	392.20

The results of diffraction analysis of the sample obtained by calcination of a mixture of metallurgical dust and waste carbon black with sodium carbonate, given in Table 4, show the presence of Fe_3O_4 phase only.

Table 4. Results of diffraction analysis of calcined mixture of metallurgical dust and waste carbon black

No.	X axis degree	Substance	Chemical formula	Relative height of radiograph peaks
1	17.962	Magnetite	Fe_3O_4	9.91
2	29.579	Magnetite	Fe_3O_4	28.54
3	34.842	Magnetite	Fe_3O_4	100.00
4	36.452	Magnetite	Fe_3O_4	7.88
5	42.321	Magnetite	Fe_3O_4	22.11
6	52.500	Magnetite	Fe_3O_4	6.87
7	55.958	Magnetite	Fe_3O_4	25.41
8	61.442	Magnetite	Fe_3O_4	29.35
9	72.650	Magnetite	Fe_3O_4	3.99

The Mössbauer spectrum was also taken. Iron nuclei in the octahedral position correspond to a sextet with effective magnetic field parameters of 36.8 kA/m, isomeric shift 0.64 mm/s; in the tetrahedral – 39.2 kA/m and 0.32 mm/s. Accordingly, the isomeric shift reflects the valence of iron, from which it follows that the octahedral position contains Fe^{2+} and Fe^{3+} ions.

The greater completeness of trivalent iron oxide reduction to magnetite in this case is obviously related to the contact of nanometric particles of metallurgical dust with nanometric particles of technical carbon, providing a large interaction surface. The results in Table 5 show that in this case the saturation magnetization is even slightly higher than that for natural magnetite.

Table 5. Saturation magnetization of a sample obtained by reduction of metallurgical dust by waste carbon black

Types of samples for testing	Samples taken from one batch of magnetite-containing mixture				
	1	2	3	4	5
Saturation magnetization, kA/m	400.20	401.13	405.20	407.10	402.30

Magnetite samples of both types were used to prepare magnetic fluid. For this purpose, they were dissolved in hydrochloric acid with some insoluble precipitate filtered out and re-salted with ammonia water. The suspension was watered down to pH=8-9 and mixed at 95 °C



with oleic acid and a carrier fluid, which in this case was kerosene (Fig. 1). Table 6 provides the parameters of the obtained magnetic fluid.

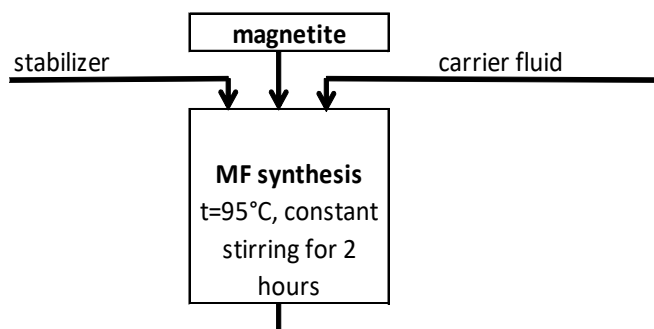


Fig. 1 Flowchart of magnetic fluid synthesis

Table 6. MF parameters

Sample N	Reducing agent	Liquid carrier	Magnetite volume, %	Saturation magnetization, kA/m
MF-1	Activated carbon	Kerosene	5.10	15.6
MF-2	Waste carbon black	kerosene	6.00	16.81

Magnetic liquids with such magnetization saturation are quite suitable for cleaning water surface from oil and oil products contamination.

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