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Obtaining Synthetic Magnetite and Ferromagnetic Fluid from Industrial Waste to Purify Water from Petroleum Products

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ABSTRACT

In the article, the authors describe three methods for producing synthetic magnetite from industrial iron-containing waste: chemical condensation, electrochemical method and heat-reducing carbon treatment. The results of the study of the structure and properties of the obtained magnetic particles are presented. From the magnetite obtained from the waste, a magnetic liquid was synthesized on various bases (water, oil, kerosene). Magnetic fluids are used to remove petroleum products from the water surface. The efficiency of purification of water contaminated with petroleum products was 90-96%.

Keywords: Synthetic magnetite; Magnetic liquid; Oil products; Waste water; Purification

INTRODUCTION

Magnetite is the most popular magnetically soft ferromagnetic material [1] because it is widely used to make transformer cores, induction coils, filters, circuits, magnetic antennas, stators and rotors of high-frequency motors, parts of deflecting systems in television equipment and other high-frequency and pulse-based devices, as well as ferromagnetic fluids [2]. However, due to its intensive use in various areas, the reserves of natural magnetite found in erupted rock are on the decline at an accelerated rate, especially in foreign regions [3,4]. Therefore, it is very important to study the possibility of obtaining magnetite from iron-containing industrial waste [5-7].

METHOD

We obtained synthetic magnetite in various ways.

Obtaining magnetite by chemical condensation with waste containing Fe^{3+} and waste containing $Fe^{2+}$is described by the following reaction equations [8,9]:

1. The dissolution of iron-containing waste (ICW) in hydrochloric acid

$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$;

2. A mixture of salts of bivalent and trivalent iron with subsequent treatment of magnetic phases with a concentrated ammonia solution

$2FeCl_3 + FeSO_4 + 8NH_4OH \leftrightarrow Fe_3O_4\downarrow + 6NH_4Cl + (NH_4)_2SO_4 + 4H_2O$

To exclude corrosives (HCI, NH_4OH), we developed a more environmentally friendly method of obtaining magnetite - electrochemical method [10-12], the point of which is to carry out the electrolysis in a pre-heated (80-85°C) NaCl solution as an electrolyte during the oxidation of the intermediate compounds with atmospheric oxygen.

The main process at the anode is the dissolution of iron waste (an electrode made out of scraps or iron filings):

$Fe^0 \rightarrow Fe^{2+} + 2e^-$

Hydrogen evolves at the cathode, which leads to alkalization of the solution:

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

When the products of the anodic and cathodic reactions interact with each other, iron hydroxide (II) is formed, which is partly oxidized by atmospheric oxygen:

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

$2Fe(OH)_2 + H_2O + ½O_2 \rightarrow 2Fe(OH)_3$

The next formula is how magnetite is formed when bivalent and trivalent hydroxides interact with each other:

$2Fe(OH)_3 + Fe(OH)_2\ FeO\cdot Fe_2O_3\ (Fe_3O_4) + 4H_2O$

To obtain magnetite, we used high temperature recovery of ICW (galvanic sludge) [13,14]. The composition of ICW is shown in Table 1. As a carbon-containing reducing agent, we used the waste of activated carbon from the Federal Waste Classifier (FWC): code 4.42.104.01.49.5 "Activated carbon, exhausted after drying

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air and gases, not contaminated with hazardous substances"; code 3.71.126.11.20.3 "Activated carbon, exhausted during the manufacture of printed circuit boards"; code 3.14.143.11.49.4 "Activated carbon, exhausted during cleaning of the carbon dioxide absorber in the manufacture of ammonia". The exhausted activated carbon was pulverized, sifted through a sieve with the side of a cell 63 microns and introduced into the ICW paste at 1:2 ratio to a dry substance. To create an inert atmosphere, we added sodium carbonate during its decomposition at recovery temperatures. The obtained mixture was treated with heat in a three-zone rotary calcining furnace: the first zone was heated to 900 °C, the second zone was kept at 900 °C for one hour, the third zone was cooled to 50°C.

We studied the structure and properties of the obtained magnetic particles.

Dried to a constant weight at 105°C, the sludge (magnetite) was subjected to X-ray phase analysis in an X-ray machine DRON-UM-1 with CoK-α radiation (α=0,17902 nm). X-ray diffraction pattern is shown in Figure 1. X-ray clearly shows a reflection indicative of magnetite (41,656°).

RESULTS AND DISCUSSION

One of the most important features of magnetite and FF is saturation magnetic moment. Properties of the obtained magnetic nanoparticles are presented in Table 2.

Table 1: Composition of iron-containing waste (galvanic sludge).

Elements	**Fe**	**P**	**Cr**	**Ca**	**Cd**	**Zn**	**Sn**	**Mg**
Content ratio, %	58.279	11.871	6.217	5.750	4.653	4.531	2.084	1.503
Elements	**Si**	**Ni**	**Cu**	**S**	**Pb**	**Mn**	**K**	**Sr**
Content ratio, %	1.482	1.234	1.003	0.467	0.439	0.375	0.084	0.028

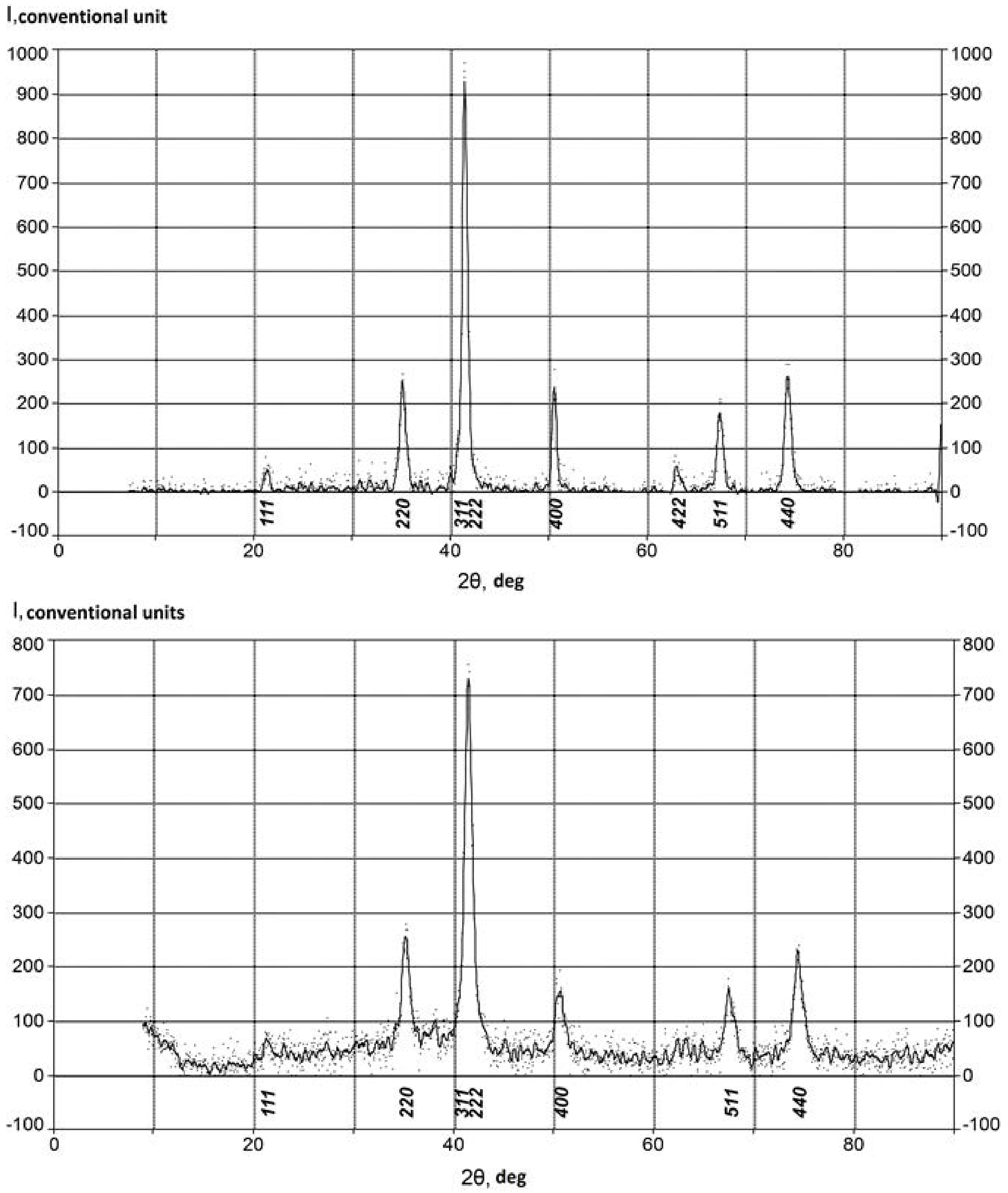

Figure 1: X-ray diffraction patterns of the samples of dispersed magnetic materials obtained by electrochemical method (a) and chemical condensation (b) from ICW.

As you can see in Table 2, the magnetic particles obtained by chemical condensation and electrochemicallly are nanosized. The magnetic particles obtained electrochemically have higher saturation magnetic moment compared to particles obtained by chemical condensation.

Based on the fact that the obtained magnetite is a magnetically soft material, we attempted to improve the distribution of particles based on their size after its self-pulverization during the treatment in the electromagnetic device (EMD). As you can see in Figure 2, a short-time treatment with the specified parameters significantly increases the amount of fine particles.

However, it should be noted that if the time of pulverization becomes more than 2 minutes, the saturation magnetic moment decreases sharply (Figure 3).

The magnetite obtained by these three methods was used to obtain ferromagnetic fluids (FF) which are a suspension of nano dispersed particles of a magnetic material (magnetite) of about 5-100 nm stabilized in the carrier liquid. ferromagnetic fluids have an unusual combination of properties of magnetic materials, fluids and colloidal solutions, they do not age, decompose, they remain liquid in a magnetic field and restore their properties after removing the field. FF could have quite a wide range of applications; however, its use is limited by its very high cost (about $1,000 per litre) because

Table 2: Properties of magnetic particles obtained by chemical condensation and electrochemical method from ICW.

Properties of magnetic particles : A method of producing magnetic particles	The average particle size, nm	Temperature, °C	Saturation magnetic moment, kA/m
1. Chemical condensation a) using pyrite cinder	7±2	20	211.56
b) using the industrial waste of titanium dioxide and the waste of JSC "Severstal"	7±2	20	197.34
c) using the industrial waste of titanium dioxide and galvanic sludge	9±2	20	187.35
d) using the rock mass of rock waste disposals	9±2	20	241.10
e) using industrial waste of magnetite (Olenegorsk GOK)	14±2	20	229.42
e) from reactive raw materials	9±2	20	246.80
2. Electrochemical	24±2	40	227.77
		60	247.54
		80	282.71
3. High temperature recovery	5±2 microns	900	211.32

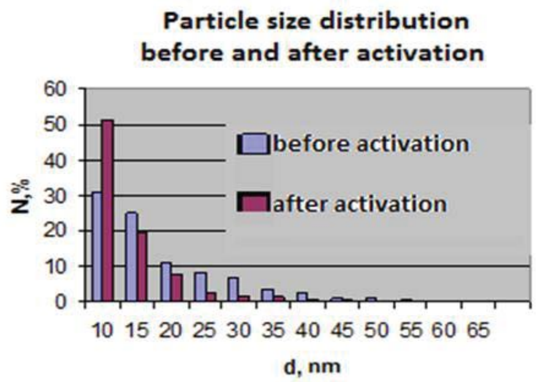

Figure 2: Distribution of the magnetite particles based on their size before and after its activation in a magnetic field (voltage–75V, frequency–50 Hz, magnetic induction–0.11 TL, time–2 minutes).

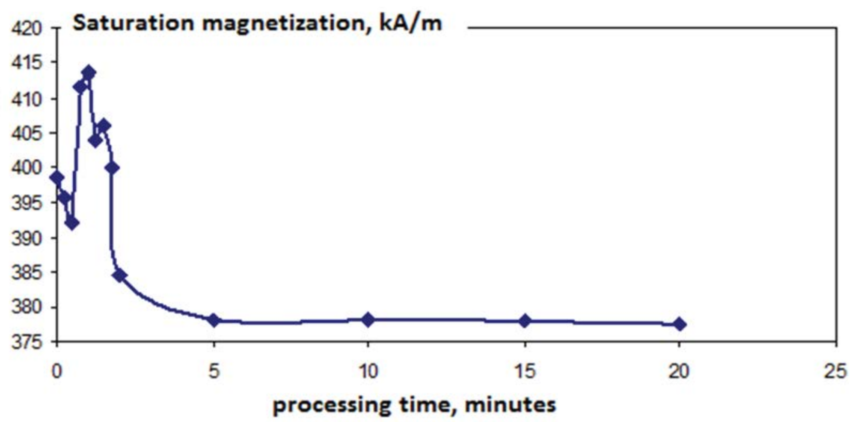

Figure 3: Interdependence of the saturation magnetic moment in magnetite and the time of its treatment in the electromagnetic pulverizer.

the dispersed phase of FF (magnetite) is made of reactive materials. Therefore, the synthesis of magnetite from waste that already exists in larger quantities and contains Fe^{2+} and Fe^{3+} would not only reduce the anthropogenic impact on the environment but also the cost of ferromagnetic fluid, thus expanding its scope of application.

to preserve the original particle size of the obtained magnetite in nanosized range and prevent their aggregation, we treated them with a surfactant immediately after obtaining the magnetite. The effectiveness of this technique is shown in Figure 4. This provides greater stability of the ferromagnetic fluid over the time.

Based on the technology developed [15], we obtained ferromagnetic fluids with various bases (water, oil, kerosene). The parameters of the kerosene-based ferromagnetic fluids obtained from industrial ICW are presented in Table 3.

As you can see from the results in Table 3, the ferromagnetic fluids obtained using ICW are close in their values to the ferromagnetic fluids obtained from the reactive raw materials.

The obtained ferromagnetic fluids were used to remove petroleum products from the water surface.

The problem of collecting petroleum products from water surface is still very important. To purify water from petroleum products, almost all known treatment methods are used depending on how contaminated the water is; in particular, mechanical, biological, sorptive. However, the analysis of existing methods of collecting petroleum products from water surface shows that currently there is no method of collecting PP from water surface that meets most requirements.

There is a method of water purification from petroleum products using ferromagnetic fluids (FF) [16] which cleans the water from the petroleum products much better. With this method, FF is sprayed through special spray devices over an oil film (OF), and the "magnetized" petroleum products are collected with an electromagnetic device. For successful magnetization, the carrier fluid must be soluble in PP and insoluble in water. For this purpose, kerosene-based FF is more suitable. Such treatment technology requires using large amounts of ferromagnetic fluid. The high cost of industrial ferromagnetic fluids made from "clean" raw materials is one of the factors impeding wide spread of the environmental technology mentioned above. It is economically feasible to replace the ferromagnetic fluid synthesized from the "clean" raw materials with a similar material obtained from the recycling of harmful industrial waste.

In the course of our research, we studied the process of collecting petroleum products from water surface with FF obtained from industrial ICW. The research was conducted with an experimental machine [17].

The collection of "magnetized" PP occurs across the moving water surface and the rotation of a drum with permanent magnets (Figure 5).

The waste water with "magnetized" PP moves across the rocker with a speed of 4-5 mm/s. When it reaches the drum, the "magnetized" PP sticks to it and is removed with the scraper into the collector of magnetized PP. The results of the study of efficiency of water purification from industrial oil are shown in Figure 6.

For PP up to 10 mm thick, the most appropriate parameters of purification are – FF:PP ratio = 1:7, settling time after FF treatment – 5-7 minutes, drum rotation speed with permanent magnets to collect the "magnetized" PP – 30 RPM. The treatment efficiency is 90-96%. The residual concentration of OF in water is no more than 8-10 mg/dm^3 compared to the existing industrial oil separators – 50-70 mg/dm^3, and flotators – 20-30 mg/dm^3.

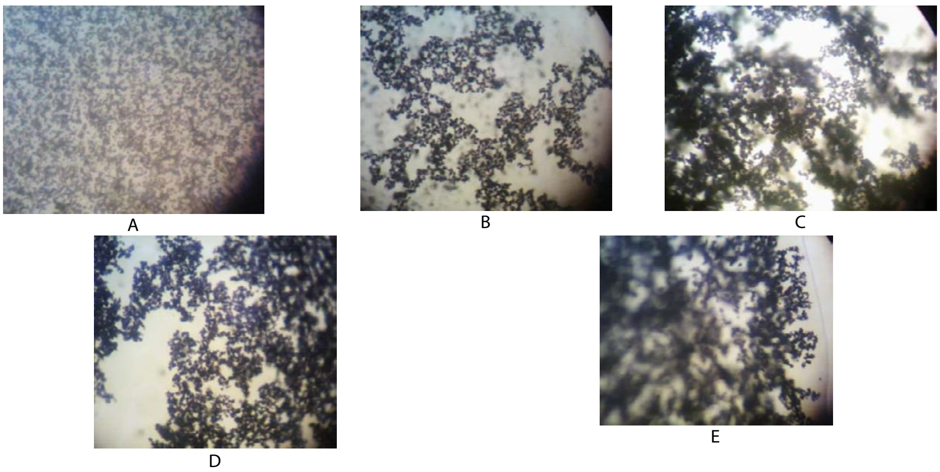

Figure 4: The study of how time of settling before surfactant treatment affects the aggregation of magnetite particles (magnification 300). (A) a sample of a magnetite slurry which particles are covered with a surfactant (B) a sample of the magnetite suspension after 30 minutes of settling (C) a sample of the magnetite suspension after 1 hour of settling (D) a sample of the magnetite suspension after 4 hour of settling (E) a sample of the magnetite suspension after 4 hour of settling

Table 3: Characteristics of the obtained ferromagnetic fluids.

Magnetite production process	Density, kg/m^3	Total magnetite volume, %	Saturation magnetic moment, kA/m
Electrochemical	970	6.40	14.10
High temperature recovery	1170	12.05	22.75
Chemical condensation of iron-containing waste	1200	11.98	23.30
Chemical condensation of the reactive $FeCl_3$ and $FeSO_4$	1177	12.25	24.10

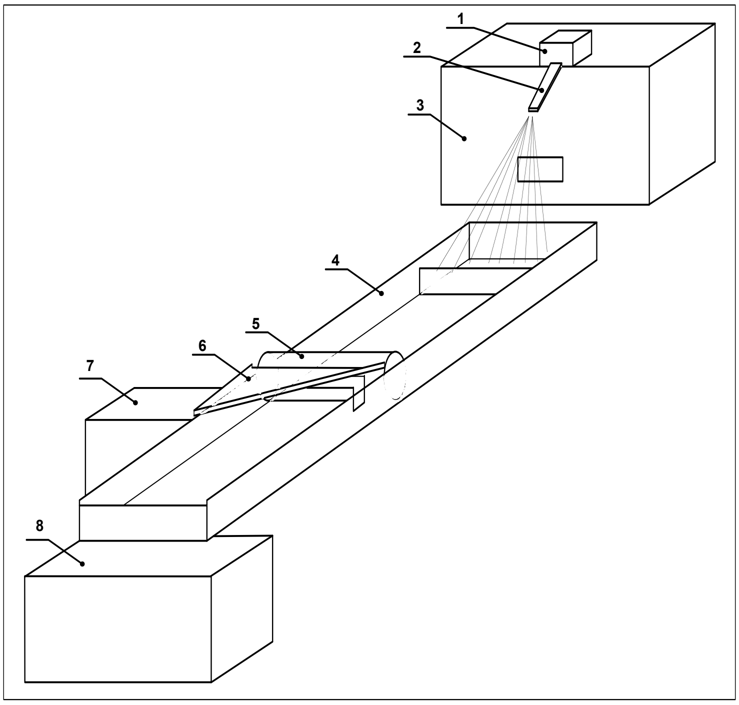

Figure 5: Schematic diagram of the experimental machine for FF water purification from petroleum products. (1 – a tank with ferromagnetic fluid; 2 – a spray device; 3 – a tank for waste water contaminated with PP; 4 – a rocker; 5 – a drum with permanent magnets; 6 – a scraper; 7 – a collector of magnetized PP; 8 – a tank with clean water).

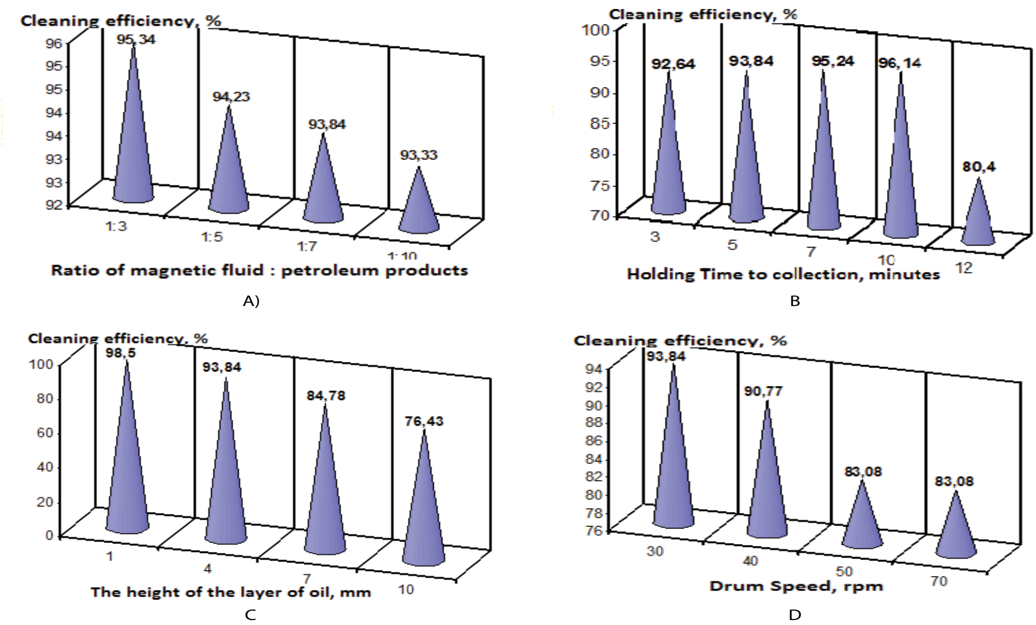

Figure 6: The dependence of the efficiency of water purification from industrial oil with a ferromagnetic fluid on parameters of purification (A) on FF : PP ratio (B) on time of settling before collection (C) on the thickness of the layer of petroleum product (D) on drum rotation speed

CONCLUSION

Thus, we found a source of magnetite, which is large iron-containing waste. We developed the technology of obtaining cheap ferromagnetic fluids, and this technology expands the ways to use them in areas that require a lot of them; for example, to treat water from oil products.

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