

Magnetic Sorbents Obtained by Mechanochemical Treatment of Quartz-Containing Mixtures

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Abstract

Mechanochemical treatment of quartz and its mixtures with ash-slag and iron oxides in the presence of various modifying additives (alcohols, activated carbon, polystyrene) was carried out. The dependence of specific surface, density and specific pore volume of quartz-containing mixtures on the time of treatment and a kind of modifying additive was investigated. Quartz and mixtures based on it exhibit ferromagnetic properties and are distinguished by good sorption ability toward organic substances. The synthesized sorbents were used to collect petroleum spill over water; high water purification degree (up to 98 %) was achieved.

INTRODUCTION

Adsorption of the dissolved organic substances is the basis of many technological processes. The use of sorption processes in the technology of deep purification of waste water from organic substances is especially urgent. The development of petroleum production, transportation and refining provides the necessity to synthesize new sorbents of higher efficiency. Silicate materials in different modifications (polymeric, crystalline, amorphous), both as individuals and in combination with other substances including organic ones, have been and still are most frequently used to purify water from oil and petroleum products. Silicate particles readily get covered with an oil film and either can be mechanically removed from water surface or go down to the bottom of a water reservoir (body) where oil, petroleum and oil products undergo natural decomposition [1].

Various methods are under development to increase the sorbing ability of silicon-containing materials. They are processed in mills to achieve fine dispersed state and are treated

with various organic compounds to form the coatings on particle surface to provide high hydrophobic properties and to increase their sorbing properties [2, 3]. The materials with modified surface find increasingly wide application as sorbents the uniqueness of which is determined by the individuality of a compound grafted to the surface and by the properties of the supporting material. In addition to chemical modification of the surface of powder particle surface, mechanochemical modification is carried out, involving structural and phase changes on the surface of freshly formed particles during grinding. That is why among the variety of methods of action on a solid aimed at changing its state, structure and properties, mechanical treatment occupies exclusively important place. Combination of the extent and kind of deformation, as well as the temperature of the material under treatment is an efficient means to change its mechanical and physical properties and provides the basis for many technological processes of obtaining new compounds with required properties [4].

All the changes in the status of solids due to mechanical action are due to the accumula-

tion of various kinds of defects in the structure of the substance, such as vacancies, dislocations in lattice [5], rupture of bonds in chemical compounds [6], distortion of the order and density of electronic state in defect sites [7]. Under mechanical action, the rate of diffusion of fluxes of a substance from the internal layers to the surface exceeds the diffusion during thermal treatment by several orders of magnitude. A consequence of this fact is the possibility of the formation of principally different structure of the surface, and therefore the possibility of changes in the properties of well-known materials. In particular, new sorbing compounds can be obtained on the surface of particles.

Much attention is paid to the sorbents possessing also magnetic properties. Magnetic sorbents in many cases are distinguished by increased absorbing capacity toward both organic and inorganic substances [8]. They are efficiently used as powder but not granules, which allows one to separate the worked out sorbent from the solution by means of magnetic separation. The application of a magnetic sorbent is especially promising for the purification of water surface from petroleum and oil products. These substances cover the particles of a magnetic material and can be collected with electromagnetic devices [9]. Rather large number of magnetic sorbents and methods of water purification with their help have been developed till present. The sorbents are obtained as powders containing the adsorbing and ferromagnetic components [8, 10]. The sorbing constituent is a carbon-containing material (active carbon, polystyrene, polyurethane, *etc.*) and inorganic substances (pearlite, claydite, *etc.*). The magnetic constituent is represented by finely dispersed powders of iron, magnetite or any ferrite.

Another method of obtaining these sorbents involves impregnation of various sorbing substances by salts of iron, followed by thermal treatment till the elemental iron is formed by reduction; this iron covers the whole sorbent surface thus rendering magnetic properties to the sorbent [11]. To provide high efficiency of collecting petroleum products from water surface, a ferromagnetic sorbent should contain not less than 30 % of metallic iron or another

ferromagnetic component [8]. It is rather difficult to conserve buoyancy of such a material. The particles saturated with iron (or ferrite) sorb oil or other organic substances, stick together and go down. To provide collection on the surface, it is necessary to use a light-weighted sorbent with small amount of the heavy ferromagnetic component but the latter should ensure high efficiency of magnetization of the floating petroleum products. Quartz powder with hydrophobized particle surface is known as a cheap and efficient material for water purification from oil and other petroleum products [10].

The goal of the present work was to reveal the conditions of possible magnetization of the quartz particles by mechanochemical treatment, to study the dependence of changes in the structure and properties of quartz-containing materials on the time of mechanical action during grinding and on the kinds of additives introduced into the mixture under treatment, providing purposeful modification of the surface of particles. The final goal was to obtain quartz-based mixtures possessing both magnetic properties and good sorption ability toward organic substances, and to use these materials for highly efficient purification of water surface from petroleum products.

EXPERIMENTAL

Quartz sand of the following chemical composition was used, %: SiO_2 , Fe_2O_3 – 0.39, Al_2O_3 – 0.55, TiO_3 – 0.12, calcination loss 0.10 %, with particle size not larger than 200 μm , as well as a mixture of quartz with ferrous and ferric oxides, and ash-slag. The phase composition of the ash-slag is represented by the following compounds: SiO_2 (14 %), mullite (7.5 %), CaCO_3 (1.7 %), anorthite, kaolinite, cristobalite (up to 1 %), the rest is X-ray amorphous phase consisting of the glass phase unburnt carbon (up to 5 %). Modifying additives were alcohols (mono- and dihydric), activated carbon and some polymeric materials (in particular, polystyrene).

Mechanical treatment of the mixtures was carried out in a centrifugal planetary mill with the platform rotation frequency of 700 rpm.

The rotation frequency of milling vessels was 1200 rpm. Acceleration of treatment in the centrifugal mill was up to 20 *g*. The time of action was varied from 5 to 60 min with a stop every 5 min. The structure and disperse state of the material under treatment in the mill were determined with an optical microscope POLAM R-211. In order to measure the magnetic characteristics of the powder material, F-5063 ferrometer was used. The sample under investigation was placed into the primary winding of an inductance coil; alternating voltage of 0.5 to 5.0 V with a frequency of 100 to 500 Hz was fed from a GZ-12 generator of standard signals.

The elemental composition of the material was estimated with a SRM-20 spectrometer under the decomposition of X-ray radiation into the crystal diffraction spectrum with the use of flat lines (Soller's arrangement) or bent crystals (Johann's arrangement). The intensity of the characteristic radiation of the element under analysis is proportional to its concentration. Pycnometric and apparent density values of the material were measured according to the GOST 2211-94 (State Standard), specific pore volume was measured with benzene vapour according to TU 3810119-97 and specific surface was determined with argon desorption method [12].

RESULTS AND DISCUSSION

It is known [13] that quartz gets rather good adsorption characteristics after grinding. The adsorption ability of a material is determined first of all by the state of particle surface and the size of adsorbing surface. Because of this, we measured the density, dispersity, specific surface and specific pore volume of quartz and quartz-containing mixtures after different modes of treatment. The dispersity of a material was estimated according to the size of particles comprising more than 60 % of the volume of quartz powder ground dry and with the addition of 5 % butanol. After 5, 25 and 50 min of treatment of the dry-ground quartz, particle size was 20–30 μm , after 15 and 40 min of treatment it was 5–15 μm . When ground with butanol for 5 min, particle size was 10–

20 μm ; after treatment for 20 min, it was 5–10 μm . It follows from the results of measurements that particle size changes non-monotonously *versus* treatment time. Periodicity similar to changes in particle size was also exhibited by the changes in the density of the material, as well as other structure-sensitive characteristics [14]. It should be noted that the treatment of quartz for 20 min in a centrifugal planetary mill causes the most substantial changes in the state of quartz surface which provide optimal surface characteristics for adsorption. Dispersity and defect concentration are exhibited in the changes in the density of the material. The results of measurements of pycnometric density and its comparison with the apparent density of the material are presented in Table 1.

The treatment of quartz in the presence of alcohols leads to a decrease in the powder density and an increase in defect concentration. The use of activated carbon and polystyrene as additives enhances this effect. The density of quartz treated with 5 % polystyrene decreases to 0.63 g/cm^3 , which is an evidence of substantial changes in the structure of quartz particles and especially their surface layers (the formation of polymers on quartz surface).

A decrease in pycnometric density and a large difference between pycnometric and apparent density are the evidences of an increase in adsorbing ability of the material due to an increase in the internal pore volume in the powder under analysis. However, this dependence is known [15] to not absolute and non-linear (due to the shape and size of pores). The adsorbing ability is more accurately determined by measuring the specific surface and specific volume of pores. The results of these measurements for some quartz-containing mixtures are shown in Table 2.

It was established that quartz treated with polystyrene has rather large specific surface (210 m^2/g). However, higher characteristics were obtained for the material composed of a mixture of ash-slag, quartz, iron oxide and alcoholic additive. The obtained values (340–350 m^2/g) are close to the characteristics of the known aluminosilicate synthetic adsorbents used for ad-

TABLE 1

Apparent (ρ_a) and pycnometric (ρ_p) density (g/cm^3) of quartz-containing mixtures activated for 20 min

Material	ρ_a	ρ_p
Quartz	2.55	2.65
Quartz + ethanol (5 %)	2.10	1.95
Quartz + butanol (5 %)	1.69	1.67
Quartz + ethylene glycol (5 %)	1.70	1.59
Quartz + activated carbon (5 %)	0.91	1.03
Quartz + polystyrene (5 %)	0.63	0.65
Quartz (20 %) + ash-slag	1.29	1.91
Quartz (30 %) + ash-slag	1.21	1.91
Quartz (40 %) + ash-slag	1.57	1.91
Quartz (20 %) + Fe_2O_3 (10 %) + ash-slag	1.86	1.80
Quartz (20 %) + Fe_2O_3 (10 %) + ethylene glycol (5 %) + ash-slag	0.94	0.95

sorptive purification of petroleum products and higher than those for the known magnetic adsorbents [16] used to purify water from petroleum products.

The results of our previous investigations showed that after the treatment of quartz in a mill of centrifugal planetary type it acquires magnetic properties [17]. In order to estimate the magnetic characteristics of the treated quartz, we measured the dependence of magnetic conductivity (μ , rel. units) on the frequency and strength of magnetic field. For comparative estimation of magnetization degree of quartz after mechanical treatment, the measured magnetic conductivity values for a number of non-metallic magnetic powdered materials (up to the frequency of 500 Hz) are shown in Fig. 1.

For magnetite, m changes from 33 to 5 at the magnetic field strength of 160 A/m. It should be taken into account that the powder is not a pure magnetite, it contains 20 % FeO. When iron oxides are diluted with quartz with particle size $d < 100 \mu\text{m}$, magnetic conductivity of the quartz-magnetite mixture (50 : 50) decreases changing within the indicated measurement range from 8 to 1.5. With an increase in quartz content of the mixture up to 70 %, magnetic conductivity decreases to 4.5–0.7. Magnetic conductivity of quartz magnetized as a result of intensive grinding in planetary mill is 6.0–2.0 within the limit of 500 Hz and then remains rather stable ($\mu = 2\text{--}2.5$) till 1000 Hz. Magnetic conductivity of ferrite of 200 SCh grade decreases within the range 100–500 Hz from 8.0 to 1.0, while that of iron powder with liquid

TABLE 2

Specific surface (S) and specific pore volume (V) of activated quartz-containing mixtures

Material	τ_{act} , min	S , m^2/g	V , cm^3/g
Quartz	10	15	0.04
»	20	52	0.11
Quartz + ethanol (5 %)	20	54	0.32
Quartz + butanol (5 %)	20	65	0.14
Quartz + ethylene glycol (5 %)	20	105	0.24
Quartz + polystyrene (5 %)	20	210	0.39
Quartz (20 %) + ash-slag	20	340	0.36
Quartz (20 %) + Fe_2O_3 (10 %) + ethylene glycol (5 %) + ash-slag	20	350	0.45

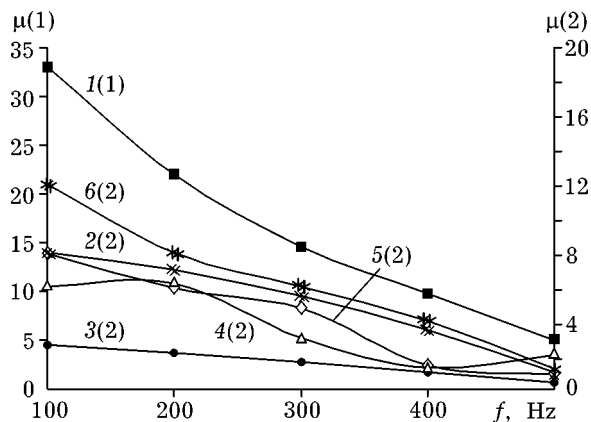


Fig. 1. Dependence of magnetic conductivity of magnetic powders on the frequency of magnetic field: 1 (1) - Fe_3O_4 ; 2 (2) - 50 % Fe_3O_4 + 50 % SiO_2 ; 3 (2) - 30 % Fe_3O_4 + 70 % SiO_2 ; 4 (2) - SiO_2 ; 5 (2) - Fe + liquid glass; 6 (2) - ferrite of 200 Sch grade.

glass coating from 12.0 to 1.2. So, the level of magnetic conductivity of quartz treated in the mill corresponds to the same characteristics of the magnetic-dielectric composite (iron powder coated with liquid glass).

The addition of alcohols into quartz during mechanical activation has different effects on its magnetization (Table 3). Almost in all the cases some periodicity of magnetization takes place. The most stable values were obtained with the voltage in ferrometer coil 1 V. The results of these measurements at the magnetic field frequency of 100 Hz are shown in Table 3. The use of ethylene glycol provides the most substantial magnetization effect, which increases continuously with treatment time. The treatment of quartz in the presence of alcohols and polystyrene leads to more intensive dispersion and magnetization of particles. The latter is a consequence of the formation of magnetic compounds in the surface layer. Similar changes in the state of a substance during

mechanochemical treatment are likely to be due to polymer grafting on quartz surface thus providing its modification [18]. In addition, magnetization of quartz is affected by the presence of iron, which gets into quartz during grinding from the surface of balls and walls of milling vessels.

The amount of iron in quartz was determined by X-ray spectral analysis. Its results showed that the amount of iron in samples depends both on treatment time and on the types of the organic additives used. With an increase in grinding time, the concentration of iron admixtures increases (most sharply within the first 5 min). In the initial quartz, the mass concentration of iron admixtures was 0.1 %; after grinding for 5 min, it increased to 3.07 %, after 30 min to 5.36 %, and after grinding for 1 h it increased insignificantly (up to 5.666 %). Grinding in the presence of organic additives helps increasing iron admixture concentration in quartz. After grinding quartz with ethanol for 30 min, mass concentration of elemental iron in mixture was 11.62 %, with butanol 14.66 %, with polystyrene 15.7 %, while with ethylene glycol only 4.94 %. However, the highest magnetic conductivity was observed with quartz treated in the presence of ethylene glycol, that is, with the minimal iron content of the material. Therefore, the presence of iron in quartz subjected to mechanochemical treatment is a substantial but insufficient factor for magnetic properties to be exhibited by the dispersed material. On the basis of analysis of the results of M \ddot{u} ssbauer and EPR spectroscopy, the authors of [19] stated encapsulation of quartz particles in metal-polymer coatings with magnetic properties providing ferromagnetism in mechanically treated quartz.

TABLE 3

Magnetic conductivity (at 100 Hz) of quartz activated in the presence of modifiers

Material	Activaton time τ , min			
	5	10	15	20
Quartz + ethanol (5 %)	4.48	2.69	0.60	2.99
Quartz + butanol (5 %)	3.95	3.77	3.77	11.3
Quartz + ethylene glycol (5 %)	3.19	5.83	6.28	17.04
Quartz + polystyrene (5 %)	3.58	6.45	6.94	12.5

So, mechanochemical treatment resulting in modification of the surface of finely dispersed quartz particles allowed obtaining a ferromagnetic with high specific surface, developed porosity and good adsorption properties. The adsorption capacity for hydrocarbons (benzene) calculated according to the above-mentioned results of determination of specific pore volume showed that this parameter of the synthesized materials changes depending on the conditions of mechanochemical treatment from 0.54 to 0.78 g/g. The use of ash-slag, which is a mixture of a number of oxides (SiO_2 , Al_2O_3 , Fe_2O_3) and a definite amount of unburnt coke, enhances the sorbing properties of the powder. Mechanochemical treatment of ash-slag with the additional introduction of quartz, iron oxide and the modifier exhibiting the highest effect (ethylene glycol) provided not only high specific surface and specific pore volume (see Table 2) characterizing adsorbing ability of the material but also high magnetic conductivity. Maximal magnetization ($\mu = 28$) of quartz-containing mixtures based on ash-slag was obtained with an optimal quartz content of the mixture 45 % [20].

Experiments were carried out on water surface purification from oil spill and the capacity of adsorption of petroleum products by sorbents was determined as the ratio of masses of the collected and spill oil (in per cent). Such a method of estimation was chosen because preferable formation of colloid solutions decreasing the mobility of the particles of substance to be adsorbed occurs during water purification from petroleum products with such a material. We prepared several compositions

TABLE 4

Results of the collection of petroleum spills with multiple use of two compositions (I and II) of the synthesized magnetic powder

Stage of test	Mass fraction of the collected petroleum, %	
	I	II
1	92	95
2	92	87
3	45	45
4	33	42

based on quartz activated with ash-slag and modified with the additives enhancing adsorption, coagulation and magnetic properties of the resulting material. Table 4 shows the results of multiple collection of petroleum from water surface using two compositions. One can see that the material obtained by mechanochemical activation is an efficient sorbent for two-, three-fold collection of petroleum from water surface.

Previously published results [21] on the use of the developed powder magnetic sorbent with different components showed the efficiency of its application for water purification from petroleum spill with a laboratory pilot set-up. Water purification degree was 92–98 %. In addition, the sorbent is suitable for multiple use after annealing for an hour at the temperature of 200–250 °C.

CONCLUSION

Thus, mechanochemical activation of quartz and quartz-containing mixtures in the presence of a number of organic and inorganic additives results in magnetization of the powder under treatment, which is due to the formation of ferromagnetic compounds on the surface of quartz particles [19]. A dependence of the changes in structure and properties of quartz-containing material on activation time and on the kinds of additives introduced into the mixture under treatment to provide purposeful modification of the particle surface was established. Magnetic conductivity depends on powder treatment time non-linearly. Determination of density and dispersity also provided the evidence of non-monotonous character of changes occurring during mechanical treatment in the state of the substance under treatment. This is likely to be due to the sequence of stages of the processes involving deformation of the crystal structure of quartz, accumulation and relaxation of defects and the formation of structures on particle surface. Powdered mixtures with high magnetic, coagulation and adsorption characteristics toward petroleum products have been obtained. Their tests with a laboratory pilot set-up showed that they can be successfully used for the purification of water surface from the spills of petroleum products.

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