Composite materials on the basis of silica-modified systems with high sorption activity for water surface cleaning

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Synthesis of magnetic sorbents for heavy oil collecting and for cleaning waste water has significant importance. We have developed a novel mechanical-chemical treatment of silica-rich raw minerals and wastes to synthesize, in a single stage, magnetic sorbents, displaying high efficiency at low cost. Crystalline silica assumes the role of the matrix during development of structure and functional properties of the magnetic adsorbent. It was found, that the polymer film used to cover the quartz particles, includes regions with embedded iron nanoparticles as well as other regions enriched with active carbon. The iron nanoparticles react during grinding in the mill with modifiers and develop iron-organic compounds on the quartz surface in conjunction with functional radicals, thereby offering superior high adsorption catalytic properties.

Keywords: petroleum, magnetic, sorbents

1. Introduction

Overflow, spillages or leakages of petroleum and its products during mining, transportation or storing has always catastrophic consequence to surrounding nature. This has led to the development of a range of, often complex, methods for cleaning water surfaces from petroleum spillages.

Spillages of petroleum on the ocean surface harms many types of water life; because of its nature, it also significantly reduces penetration of light and concentration of diluted oxygen [1]. For removing petroleum spillages (which may have a layer thickness of 10cm or more) first of all floating barriers with pumps are used. But this pumping method can't take away petroleum spots from the water surface. For complete cleaning usually various additional sorbents are used, which are distributed on the surfaces of the water and then collected. There is large consumption of sorbents in this case and sorbent loss can be significant. Therefore the sorbent material should be cheap with high adsorption capacity, preferable for multiple uses. Sorbents produced from wastes of local production would preferable.

Carbon sorbents have high adsorption capacity [2]. They are produced from food sources (rice and buckwheat husk, corn stem) and wood-working industrial wastes. Such wastes are exposed to carbonization and hydrophobization by different inorganic salts and organic compounds. Such sorbents are usually applied for floating barriers in an arrangement called "sorbents in a sack". More effective is the application of materials with high adsorption capacity (up to 300mg/g) such as preliminary frothed perlite and vermiculite, volcanic slag, zeolite and claydite [3], which had undergone hydrophobization. Mechanical methods for collecting the sorbents with adsorbed petroleum or petroleum products are used.

From such porous sorbents, petroleum and petroleum products are extracted by centrifuging. Possibility of regeneration of such sorbents by heating is a significant advantage, but the low kinetics of adsorption and their need for good contact with polluted water are disadvantages.

Application of magnetic sorbents offers a new approach for collecting petroleum and petroleum products from water surface. The mechanical method can be replaced by a magnetic method. Most of usual magnetic sorbents are produced by pyrolysis of mixtures of the sorbent material and the magnetic material in an inert atmosphere. Ferromagnetic substances increase the adsorption capacity of the system and result in more complete separation of sorbent and petroleum or petroleum product during magnetic separation of the mixture, but the cost of the magnetic adsorbents is relatively high -up to US$1000 per ton.

Recently, we have developed a magnetic powder with sufficiently effective characteristics (absorption capacity, hydrophobicity, magnetic characteristics, regeneration properties, low cost) by a relatively simple mechano-chemical treatment in a mill-activator, from quartz-containing mixtures, including wastes of metallurgical and thermoelectric power stations [4]. This inorganic powder material consists of particles with a specific layered structure: a quartz nucleus-carrier covered with layers of various compounds (carbon, polymers, iron-contained compounds) providing magnetic properties. Besides this, the new material has high coagulation characteristics because of electrostatic charge, which help to shrink oil and petroleum spots overflow on the water and it has good affinity for the sorbent-petroleum system. By varying the mechano-chemical production treatment and the composition of the quartz particles completely new properties can be obtained, for many applications [5].

2. Experimental

The raw materials for the production of these magnetic sorbents are natural quartzite and ash slag, containing amorphous and crystalline silica oxide. Mixtures of oxide materials with organic modifying additives were treated mechano-chemically in a centrifugal-planetary dynamic mill. Influence of different conditions of treatment in dynamic mill on the density, dispersity, specific surface and specific volume of the pores were studied for quartz and quartz-containing materials. Microscopy was used for the measurement of material dispersity by particle size (60% percent of the powder volume). Determination of adsorptivity was obtained by measurements of the specific surface, carried out by desorption of argon and by measurement of the specific volume of pores measured by benzene vapor. Composition and structure of the material were measured by Electron microscopy analysis, Electron determined by resonance (EPR), Infrared (IR), Mossbauer spectroscopy (MS) and XRD analyses.

3. Results and Discussion

Detailed study of the synthesized material shows that its properties depend on the morphology of the surface layers. First of all, the adsorption capability of the material depends on the particle surface condition and on the specific adsorption surface. Particle size of the dry crushed quartz after 5, 25, and 50min is 20-30μm, after 15 and 40 min treatment it is 5-15 μm. Particle size of the dry crushed quartz in the presence of butanol after 5 min is 10-20μm, and after 20 min treatment it drops to 5-10 μm. Thus, the dependence of the particle size on crushing time doesn't change monotonically. The same kind of irregularity was observed for the density and other structure-sensitive characteristics of material [6].

The most significant changes observed on the particle surface reaching an optimum surface structure for adsorption after 20 min treatment of quartz in a centrifugal-planetary mill. Particle dispersity and defect content also affect the density of material. The results of picnometric density measurement in comparison with apparent density of the powder are presented in Table 1.

Quartz powder density decreases and structure defects increase by the presence of alcohol during the treatment process. Additives of activated coal and polystyrol increase this effect even more. The density of quartz treated with 5% polystyrol decreased down to 0.63g/cm3, indicating evidence of significant changes in quartz particles and especially its surface layers (e.g. formation of polymers on the quartz particles surface). Decreasing of picnometric density and significant differences between picnometric and apparent density are evidence of increased adsorptivity of the material, probably due to increasing of internal pore volume. But this dependence is not absolute and not linear [7], on pore size and their form.

Table 1 Apparent (ρa) and picnometric (ρp) density of quartz - containing mixtures activated by 20 min milling.

№	Material	Density ρ, g/cm3	
		ρ_a	ρ_p
1	Quartz	2,55	2,65
2	Quartz + ethanol (5 %)	2,10	1,95
3	Quartz + butanol (5 %)	1,69	1,67
4	Quartz+5%ethylene glycol	1,70	1,59
5	Quartz + 5% activated C	0,91	1,03
6	Quartz + polystyrol (5 %)	0,63	0,65
7	Quartz (20 %) + ash slag	1,29	1,91
8	Quartz (30 %) + ash slag	1,21	1,91
9	Quartz (20%)+ polystyrol (5 %) + ash slag	0,91	0,93
10	Quartz (20 %) + Fe2O3 (10 %)+ ash slag	1,86	1,80
11	Quartz(20%) + Fe2O3(10 %)+ ethylene glycol (5 %)+ ash slag	0,94	0,95

More precise determination of adsorptivity may be obtained by measurements of the specific surface, and by measurement of the specific volume of pores. The results of measurements for some quartz- containing mixtures are presented in the Table 2.

Quartz treated with polystyrol has relatively high specific surface (210м²/g) (Table 2). The highest measured characteristics were found for materials mixture (ash slag, quartz, iron oxides and alcohol additive). The values (340 - 350 m²/g) are close to the characteristics of known synthetic aluminum silicate adsorbents which are used for the adsorption cleaning of water from petroleum products.

Observed changes in density, specific surface and volume of modified quartz particles can be explained by specific morphology of the surface layers of the dispersed quartz particles. Electron microscopy analysis shows that quartz particles are initially dense crystals with clearly marked facets. After mechano- chemical treatment in the presence of butanol thequartz particles have friable laminated surface structure (of thickness 10 - 40 nm), saturated with carbon, which contain dense ultra-dispersed impurities of iron or iron compounds (Figure 1). Iron came in the dispersed mixture from the walls and spheres of the mill.

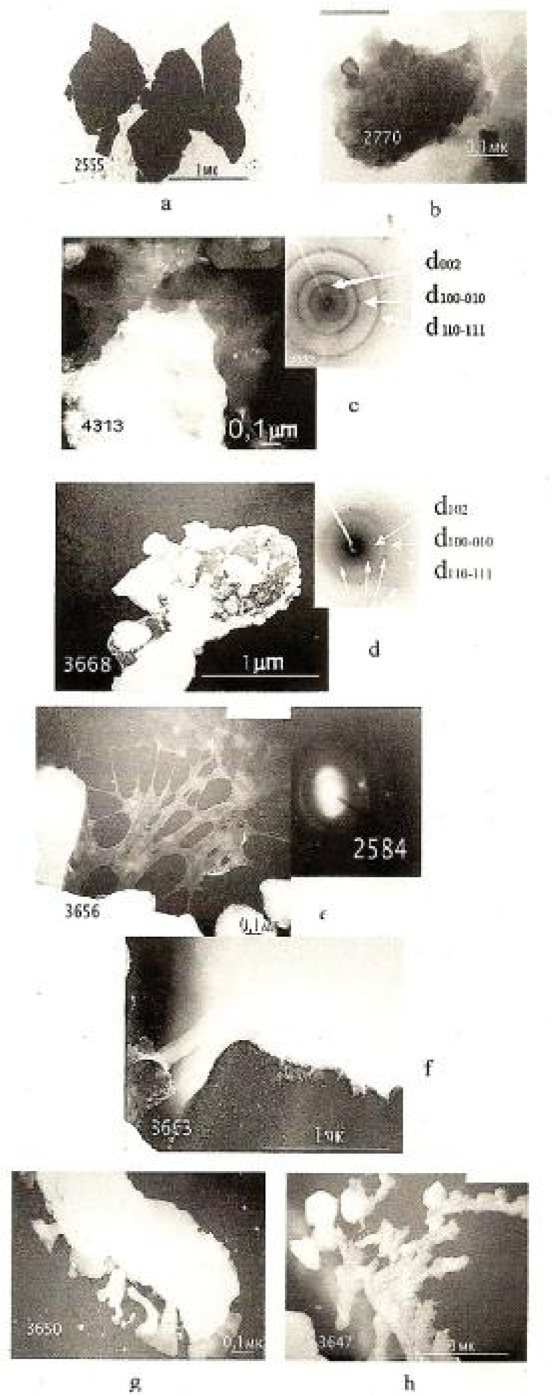

Figure 1. Electron-microscope photos and electron micro-diffraction of quartz particles in initial state (a) and modified in the presence of butanol (b), acrylic acid (c, d) and polystyrol (e-h)

Table 2 Specific surface and specific pore volume for activated quartz containing mixtures.

№	Material	$t_{act.}$, min	S, м^2/g	V, cm^3/g
1	Quartz	Init.	1,5	0,01
2	Quartz	10	3,5	0,04
3	Quartz	20	5,2	0,11
4	Quartz + 5 % ethanol	20	5,4	0,32
5	Quartz + 5 % butanol	20	6,5	0,14
6	Quartz +5% ethylene glycol	20	10,5	0,24
7	Quartz + 5 %activated C	20	77,6	0,29
8	Quartz + 5 % polystyrol	20	210	0,39
9	Quartz (20 %) + ash slag	20	310	0,36
10	Qartz (20%) + polystyrol (10%) + ash slag	20	340	0,65
11	Qartz (20%) + Fe_2O_3 (10%) + ash slag	20	270	0,50
12	Qartz (20%) + Fe_2O_3 (10%) + 5%ethylene glycol + ash slag	20	350	0,45

The result of mechano-chemical treatment of quartz particles modified by polyatomic alcohols or acrylic acid is the formation of dense, homogeneous organic film and crystallites in the surface polymer layer. The morphology, structure and carbon content on the particle surfaces are similar after mechanical treatment of quartz in carbon or butanol. Surface particle micro-diffraction picture show three dimensional regulated carbonic substance. At different modification conditions electron diffraction analysis indicate the presence of metal-silicon-carbon composition or a weakly crystallized silicon-carbon material.

A variety of structural surface forms of modified quartz is observed when polystyrol is used as modifier.

The quantity of modifier (3-10%), duration of mechanical treatment and level of applied force all influence the formation of structured or fret films on the particle surface, or coagulated as different configuration microtubes, whose size reach 50-70nm (Figure 1e and f). Increasing treatment duration results in coagulation of dispersed particles with a modified surface layer and formation of dendrites (Figure1g and h) which grow according to the fractal structure principle. The main element, which is present in the nanostructured particles morphology after quartz mechano-chemical treatment is carbon.

The distinctive peculiarity of carbon structures on the quartz surfaces after mechano-chemical treatment with polystyrol is due to textured carbon particles oriented inside films (Figure 1e and f). Maximum content of bonded carbon in the modified quartz particle layer (2, 6%) was measured in the samples modified by polystyrol and they display a variety of structured forms.

Changes observed in the IR-spectrum of activated quartz are connected with the transformation of the surface layer structure and appear first as decreasing of low frequency intensity of valence and deformation oscillations and as increasing of high frequency oscillations (Figure 2a). The intensity of the complete IR-spectrum increases after 20 min treatment. At the same time the contribution of low frequency oscillations is relatively low, particle surface dehydration takes place and the spectrum shifts towards higher frequency. Disappearance of OH- lines can be explained with formation of siloxane bonds:

$$\equiv Si\text{-}OH + OH\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O,$$

which confirmed by the increasing of the intensity of

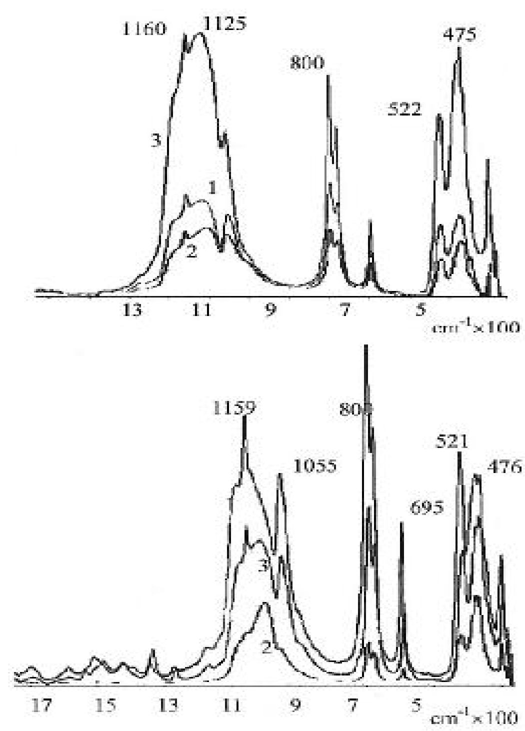

Figure 2. IR- spectrum: a – quartz in initial condition (1) and after 10(2) and 20(3) minutes activation; b – after activation in the butanol (1), polystyrol (2) and acrylic acid (3) presence

all Si-O-Si lines, valence (1000–1200cm^{-1}) and deformation (700–800cm^{-1} and 400–600cм$^{-1}$) oscillations of activated powders.

Modifying quartz treatments with organic additives lead to degeneration of the 1160 cm^{-1} line, shifting of other lines to higher frequencies in case of alcohols and to even higher frequencies in case of polystyrol. Of greatest interest is the region higher than 1400 cm^{-1}, which is related with the presence of different carbonate and carboxyl groups on the surface of Si-O-Si. Modified with acrylic acid quartz, the IR-spectrum has absorptions lines at 1400-1700 cm^{-1} of iron acrylate, synthesized during mechano-chemical treatment. Iron appeared in the mixture and then in the synthesized compounds during mechano-chemical treatment, probably from surface of the mill and the milling balls.

XRD-analysis shows that the iron content in quartz powder depends on treatment time and type of modifier. Organic modifiers during mechanical treatment apparently increase the iron from walls and balls. Maximum quantity of iron in the powder (more than 10%) is present in the quartz surface structureafter treatment of at least 20min with mono-atomic alcohols.

Electron paramagnetic resonance (EPR), Mossbauer spectroscopy (MS) and XRD analyses have helped to determine the conditions in which iron exists in modified quartz. The results of EPR analysis show that, except the signal of the valence 3 iron in the field of distorted octahedral (g=2,14) and in strong crystal field of low symmetry due to rhombic distortion of coordination nut (g=3,9), a signal of ferromagnetic resonance and observed absorption of microwave power in the region of low fields is present. With increasing quantity of ultra dispersed iron particles the absorption microwave power intensity increases. The strongest non-resonance absorption in the region of weak fields was received on quartz powder modified in the presence of acrylic acid and polystyrol. These organic additives are characterized by mechanical destruction and by synthesis of new polymers with participation of crashed inorganic materials.

Mossbauer spectroscopy represents direct evidence of the existence of iron nano-particles in the metal state and in different compounds on the quartz surface. Up to 0.8% of iron impurities in the initial quartz powder were detected (Figure 3a) as compounds Fe_2O_3-hematyte and FeS_2-pyryte. After quartz activation, lines of these compounds became wider, which is related to the local heterogeneity of iron atoms in the matrix, in other words with defect structure. Besides that, in the activated samples spectrum α–Fe present (fig 3b), its content increases with time of activation.

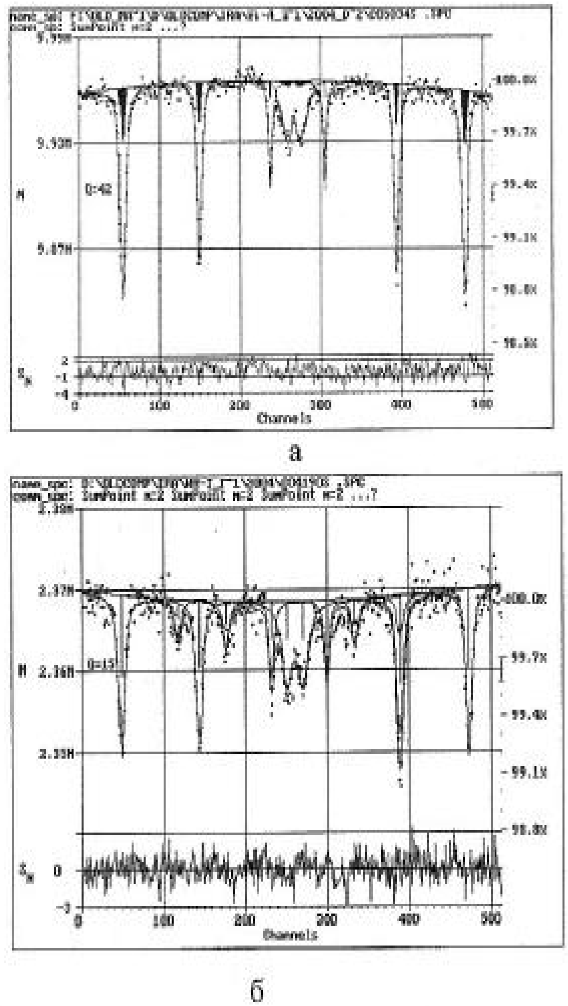

Figure 3. Mossbauer quartz spectra in initial (a) and activated (b) conditions

After quartz treatment with different modifiers, the Mossbauer spectra change with the phase composition of surface iron-containing compounds, but also with spectrum parameters. Spectra distinguish the peculiarity of quartz modified with butanol and acrylic acid is absence of hematite and presence of small quantity of pyrite, due to intensive reduction of iron from compounds to metallic phase. In the presence of polystyrol as modifier observed distortion of the sub α–Fe spectrum and formation of iron carbide Fe_3C (fig 4).

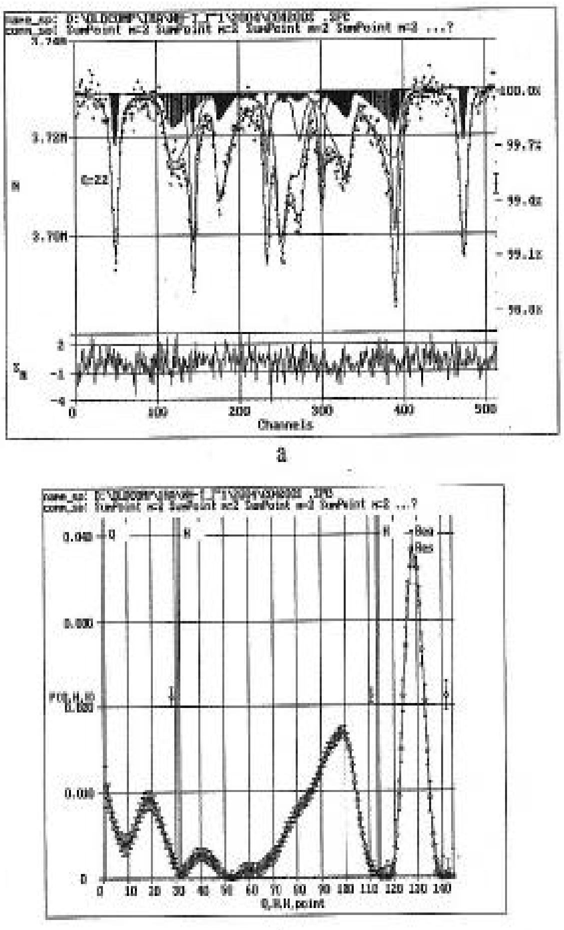

Figure 4 – Mossbauer quartz spectra (a) and distribution functions (b) of super- thin magnetic fields p (Hn), quadrupole shifts p (ε) in polystyrol modified quartz

Thus, the results of Mossbauer spectroscopy clearly demonstrate the presence in treated quartz (with or without modifier) of dispersed iron in metallic state in different compositions. Carbon, produced by destruction of polystyrol, actively reacts with iron with the formation of solid solutions and carbides, which was also confirmed by the results of XRD analysis.

The detailed study of the activated and modified quartz powders demonstrate, that in the process of mechano-chemical treatment the particle surface is saturated by nano-dispersed iron particles or their oxides and also by supersaturated solid solutions of carbon in iron. All these formations are ferromagnetic. The presence of ferromagnetic compounds in “carbon saturated” the quartz particle surface layer provides the magnetic properties of the synthesised nano-composite powder material [7].

The magnetic properties of quartz particles after mechano-chemical treatment were evaluated by measurement of their magnetic permeability (μ) in powder samples. The relative magnetic permeability μ of quartz powder after activation is about 2 - 3. The magnetic properties of the quartz particles increase after mechano-chemical treatment with modifying additives (Figure 5).

The degree of quartz magnetization after mechano-chemical treatment in presence of different modifying

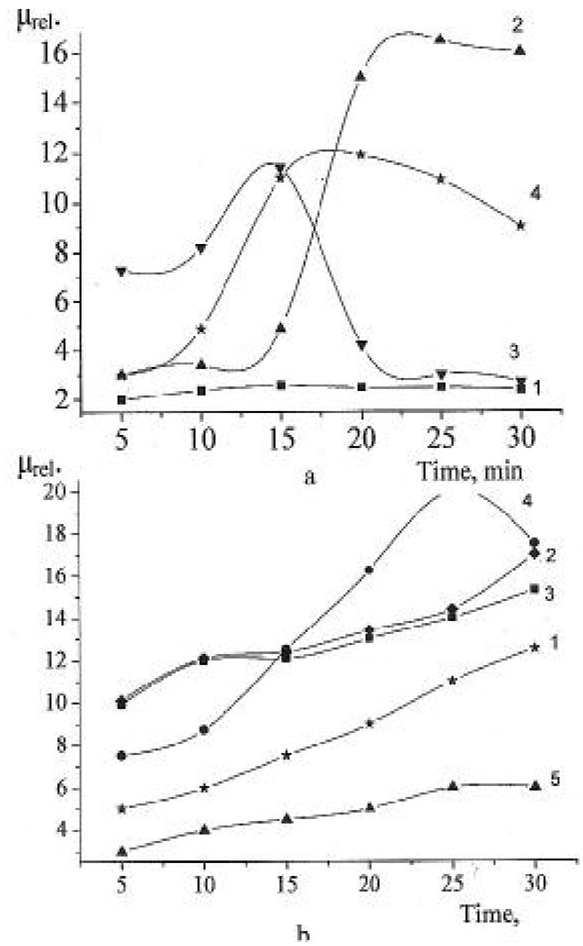

Figure 5. Dependence of magnetic permeability on duration of mechano-chemical treatment: a – quartz (1),quartz with butanol (2), ethylene glycol (3), carbon(4); b – quartz with 5 (1), 10(2) и 20(3) mass.% of polystyrol, with 5 (4) and 15 mass % of acrylic acid (5)

additives is non-linear function of the duration. Treatment with carbon and butanol increases the magnetic permeability up to 12 and 17 units respectively. The highest µ values are observed in samples modified by acrylic acid and polystyrol. Polystyrol as modifier for quartz powder appears to offer the greatest promise as it displays the highest magnetic properties (highest level of µ) and also high stability.

The iron-containing compounds are not the only reason of quartz powder magnetization. Important role play also the conditions of treatment and type and quantity of modifier. At the optimum conditions, regulated nano-composite structures of ferromagnetic compounds are formed on the surface of the quartz particle. For practical application of the synthesized material very important is the factor of stabilization of the magnetism obtained during mechano- chemical treatment.

Effectiveness of properties is determined by optimum ratio of the elements participating in structural transformations in the surface layers. It was found, that the optimum ratio of silicon, iron and carbon in the quartz system with modified surface layer with the maximum magnetization is 41- 42%, 6 - 10% and 4 - 6%, respectively. The transformed surface structure, enriched by carbon and carbon containing compounds, has new physical and chemical properties giving enhanced sorption activity to the synthesized material.

The mechano-chemical treatment results in highly dispersed surface modification of quartz particles and obtains ferromagnetic systems with high specific surface, porosity and good sorption properties. The calculated hydrocarbons (benzene) adsorption capacity, using the specific volume pore measurements for the synthesized materials (Table 2), vary according to the conditions of mechano-chemical treatment, from 0,54 to 0,78 g/g. Treated ash slag, which contains mixtures of oxides (SiO_2, Al_2O_3, Fe_2O_3) and some quantity of unburned coke, increases sorption properties of the powder. Mechano-chemical treatment of ash slag with quartz, iron oxide and modifier (ethylene glycol, polystyrol) provides a high value of specific surface and specific pore volume (Table 2), which characterizes adsorption material capability, and also high values of magnetic permeability. Maximum magnetizing effect (µ=28) of quartz-containing mixture on the basıs of ash slag was obtained at the optimum quartz content in the mixture of 45 % [8]. SiO_2 in ash slag is mainly in an amorphous state and it is necessary to add 20, 30 or 40% of quartz and polystyrol as modifier in order to receive satisfactory values of magnetic permeability (Figure 6).

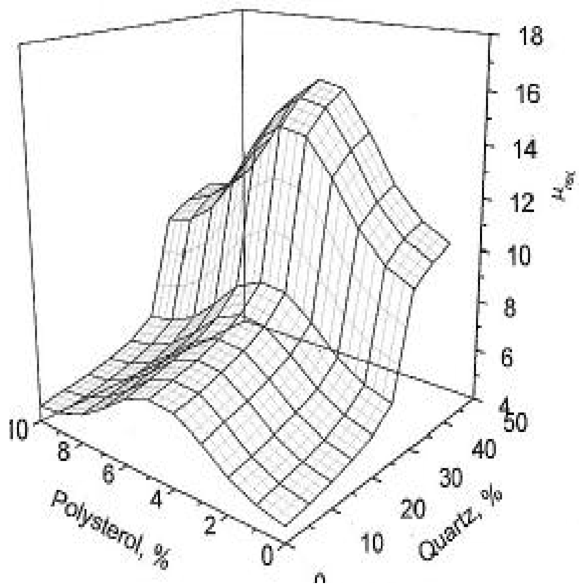

Figure 6. Dependence of magnetic permeability of mechano-chemically treated ash slag on the added amounts of quartz and modifier.

Increasing quantity of quartz from 20 to 40%, the magnetic permeability of the system increases from $\mu_{relative}$= 6-8 to $\mu_{relative}$=16-18 (depending on the duration of the mechano-chemical treatment and concentration of modifier). Addition of modifier in the system has different influence on magnetic permeability. For example, if there is 20% of additional SiO_2, the maximum magnetic permeability value was reached after 20 minutes of treatment with 10% of polystyrol as modifier. For the system with 30% of additional SiO_2, the maximum magnetic permeability ($\mu_{отн}$ =14,5) value was reached after 20 minuets treatment with 5% of polystyrol as modifier. Similar results were received for the system with 40% content of additional added quartz, but magnetic material permeability increased to 17,5. Therefore, in order to receive high values of magnetic permeability it is necessary to add quartz to mechanically treated ash slag, because in this case formation of special microstructure (or nano-structure) with ferromagnetic compounds on the quartz particles surface takes place.

In conclusion, the obtained results show how the magnetic properties of mechano-chemically treated ash slag depend on optimal quantity of quartz added in it. This indicates that the magnetic properties of the synthesized materials depend not so much on iron-containing compounds, but on the peculiarity of the quartz particle surface structure, which contain ferromagnetic compounds protected with an organo-elemental (polymer) film. Quartz in this case acts as a kind of matrix, the basis for the synthesis of magnetic sorbent with mechano-chemical method. Ash slag is a raw material, which contains all necessary components, such as organic (carbon) and iron oxides for quartz particles surface modification. The optimum quartz quantity (crystal SiO_2) for the synthesis with ash slag of a system with effective magnetic properties is 45%. Magnetic permeability μ of such mixture reaches values of 27,5 - 28 .

The synthesized powder systems were used to determine their efficacy in collecting petroleum spillages from water surface. The petroleum adsorption capacity of sorbents was measured as ratio of collected to total spilled petroleum (in %). Such method of evaluation was selected because, during cleaning of water from petroleum products with such materials, a colloid solution is preferentially formed, which reduces the mobility of the adsorbent particles. A number of compositions were prepared on the basis of quartz activated with ash slag and modifying additives, with satisfactory adsorption, coagulation and magnetic properties of produced material. The results of repeated experiments collecting petroleum overflow from water surfacec (M_{volume}) for two compositions are presented in Table 3. It is evident that the material produced by mechano-chemical activation is an effective sorbent at even after 2-3 repeated petroleum collections from water surface.

Table 3. Results of collecting petroleum overflow at the multiple use of synthesized magnetic powder

Number of collection	Quantity of collected petroleum (M_{volume}), % For compositions:	
	I	II
1	92	95
2	92	87
3	45	45
4	33	42

Results of further studies [9, 10] of the application of developed magnetic powder adsorbent of various compositions show effectiveness of their application for the cleaning of petroleum spillages from water surface in a laboratory pilot installation. Water cleaning effectiveness reaches 92 - 98 %. The sorbent was regenerated and used for repeated applications after 1 hour heating at 200 - 250 ^{O}C.

4. Conclusions

Mechanochemical treatment activation of quartz and quartz-containing mixtures in the presence of a series of organic and inorganic additives results in well magnetized adsorptive powder, which is due to the formation of ferromagnetic compounds on the surface of the quartz particles. The structure and properties of quartz-containing material depended on activation treatment duration and type of additives providing particle surface modification. The variation of magnetic permeability was a non-linear function of treatment duration. Density and dispersity measurements show non monotonic changes of the dispersed substances as a result of mechano-chemical processes. This is probably connected with gradual processes of quartz crystal lattice deformation, accumulation of defects and relaxation and structure formation on the particle surfaces. Powder mixtures with high magnetic, coagulation and adsorption properties for petroleum and petroleum products were produced. Their application on laboratory pilot installation show that they can be successfully used for repeated cleaning of water surface from petroleum spillages.

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