Mechanochemical Synthesis of Composite Magnetic Materials on the Basis of Quartz-Containing Systems

N.N. Mofa, Z.A. Mansurov

Institute of Combustion Problems,
050012, Almaty, 172, Bogenba batyr Kazakhstan

Abstract
Mechanochemical treatment of quartz and its mixtures with ash-slag and iron oxides in the presence of various modifying organic additives was carried out. Quartz and mixtures based on it exhibit ferromagnetic properties and are distinguished by good sorption ability toward organic substances. 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, which is used to cover the quartz particles, includes regions with embedded iron nanoparticles as well as other regions enriched with active carbon. The synthesized sorbents were used to collect petroleum spill over water; high water purification degree (up to 98 %) was achieved.

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. 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. 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 [2].

All the changes in the status of solids due to mechanical action are due to the accumulation of various kinds of defects in the structure of the substance, such as vacancies, dislocations in lattice, rupture of bonds in chemical compounds, distortion of the order and density of electronic state in defect sites [3]. 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 [4]. They are efficiently used as powder but not granules, which allows one and ash-slag. The phase composition of the ash-slag is represented by the following compounds: SiO₂ (14 %), mullite (7.5%), CaCO₃ (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 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.

Electron-microscopic analysis was carried out using an electron translucent microscope Jem – 100CX; U-100kv. The samples were prepared by the method of suspension in distilled water followed by ultrasound dispersion. In the process of investigation it was stated that water interacts with alcohol residues, after grinding quartz, with the formation of silicon acid which not only dissolves the surface layer but also penetrates into the inside part of quartz particles. Therefore, further preparation of the samples for investigation was carried out by the method of dry preparation. Particles of rock crystal prepared by grinding in an agate mortar without a dispersing medium were studied as reference non modified quartz.

To measure magnetic permeability of material modified powder express method was developed for determining this characteristic based on the principle of the device work MT-40NC to define magnetic film thickness [6]. The development and use of this method is caused by that the material after mechanochemical modifying treatment is in
metal stable state. It is very difficult to achieve the stability of measuring characteristics using generally common methods in measuring magnetic permeability.

Results and discussion

It is known [7] 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 /g^541m, after 15 and 40 min of treatment it was 5–15 /g^541m. When ground with butanol for 5 min, particle size was 10–20 /g^541m; after treatment for 20 min, it was 5–10/g^541m. 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 [8]. 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 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.

| Material | Density, ρ g/cm^3 |
|----------|------------------|
|          | ρ_a              |
| Quartz   | 2.55             |
| Quartz + ethanol (5 %) | 2.10             |
| Quartz + butanol (5 %) | 1.69             |
| Quartz + ethylene glycol (5 %) | 1.70             |
| Quartz + activated carbon | 0.91             |
| Quartz + polystyrene (5 %) | 0.63             |
| Quartz (20 %) + ash-slag | 1.29             |
| Quartz (30 %) + ash-slag | 1.21             |
| Quartz (40 %) + ash-slag | 1.57             |
| Quartz (20 %) + Fe_2O_3 (10 %) + ash-slag | 1.86             |
| Quartz (20 %) + Fe_2O_3 (10 %) + ethylene glycol (5 %) + ash-slag | 0.94             |

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 alchololic additive. The obtained values (340–350 m^2/g) are close to the characteristics of the known aluminosilicate synthetic adsorbents used for adsorptive purification of petroleum products and higher than those for the known magnetic adsorbents [9] used to purify water from petroleum products.

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 clarity marked facets. After mechanochemical treatment in the presence of butanol the quartz 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 (Fig. 1). Iron came in the dispersed mixture from the walls and spheres of the mill.
The result mechanochemical 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 surface are similar after mechanical treatment of quartz in carbon or butanol. 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 tubes, whose size reach 50-70nm (Fig. 1d,e). The main element, which is present in the nanostructured particles morphology after quartz mechanochemical treatment is carbon. 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.

The detailed study of the activated and modified quartz powders demonstrate, that in the process of mechanochemical treatment the particle surface is saturated by nanodispersed iron particles or their oxides and also by supersaturated solid solutions of carbon in iron. Mossbauer spectroscopy represents direct evidence of the existence of iron nanoparticles 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 (Fig. 2a) as compounds FeO-hematite and FeS2-pyrite. 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 2b), its content increases with time of activation.

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 Fe3C (Fig 3). 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.

![Fig. 2. Mossbauer quartz spectra in initial (a) and activated (b) conditions](image)

![Fig. 3. Mossbauer quartz spectra (a) and distribution functions (b) of super-thin magnetic fields μ (Hn), quadruple shifts μ (c) in polystyrol modified quartz](image)
All these formations are ferromagnetic. The presence of ferromagnetic compounds in “carbon saturated” the quartz particle surface layer provides the magnetic properties of the synthesized nanocomposite powder material [10].

The magnetic properties of quartz particles after mechanochemical treatment were evaluated by measurement of their magnetic permeability ($\mu$) in powder samples. The relative magnetic permeability $\mu$ of quartz powder after activation is about 2 – 3. The magnetic properties of the quartz particles increase after mechanochemical treatment with modifying additives (Fig. 4).

The degree of quartz magnetization after mechanochemical treatment in presence of different modifying 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 $\mu$ 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 $\mu$) and also high stability.

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 [11]. 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 Mössbauer and EPR spectroscopy, the authors of [12] stated encapsulation of quartz particles in metal-polimer coatings with magnetic properties.
providing ferromagnetism in mechanically treated quartz. 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.

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 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 (SiO₂, Al₂O₃, Fe₂O₃) and a definite amount of unburned 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 (μ = 28) of quartz-containing mixtures based on ash-slag was obtained with an optimal quartz content of the mixture 45 % [13].

Previously published results [11, 14] 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 [20]. 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.

References

1. Nelson-Smith A. Sea petroleum pollution. Gidrometeoizdat, Leningrad. 1973.
2. Heinike G. Tribochemistry. Akademie-Verlag. Berlin 1984. 584p.
3. Baramboim N. K. Mechanochemistry of high molecular compounds. M.: Chemistry, 1978, 384p.
4. Chubar T.V., Ovcharenko F.D., Himchenko U.I., Vysotskaya V.I. Carbon sorbents and their industrial application. Nauka, Moscow, 1983, p. 92-99.
5. Tarasevich U.I., Ovcharenko F.K., 1983. “Application of natural sorbents for purification of petroleum products and water”, USSR sorbents conference, Moscow, p.173-179.
6. Chervyakova O.V., Mofa N.N., Ketegenov T.A., Stahov O.V. Vestnik Kaz. Naz. NU. Chem. Series. 20: 145 (2000).
7. Avvakumov E.G. Mekhanicheskiye metody aktivatsii kimicheskikh protsessov, Nauka, Novosibirsk (1986).
8. Mofa N.N., Ketegenov T.A., Shabanova T.A., Mansurov Z.A. Mechanochemical synthesis of nanocomposition systems: quartz nucleus, carbon-containing coating / III International Conference “Fundamental Bases of Eurasian ChemTech Journal 12 (2010) 55-62
9. Mofa N.N., Shabanova T.A. Modeling of the process of mechanochemical synthesis of quartz and carbon-containing hybrid nanocomposition systems // The International carbon Conference, Carbon 2006, Aberdeen, Scotland 16th-21st July – CD.

10. Mofa N.N., Shabanova T.A., Mansurov Z.A. Nanocomposition quartz containing materials / Structural chemistry of partially ordered systems, nanoparticles and nanocomposites. June 27-29 2006, Saint-Petersburg, Russia - 86 p.

11. Mofa N.N. Chervyakova O.V., Ketegenov T.A., Mansurov Z.A. Mechanochemical synthesis of magnetic quartz containing adsorbents modified by carbon compounds. // Novosti nauki Kazakhstana. Scien.-tech. coll. Research Institutes of al-Farabi KazNU. Issue 2 (81). Almaty, 2004. - -P.59-65.

12. Mofa N.N., Ketegenov T.A., Ryabikin Yu.A., Chervyakova O.V., Ksandopulo G.I. // Magnetism of iron containing particles in a quartz matrix after mechanochemical treatment. Inorganic materials, 2002, V.38, № 2, P. 1-6.

13. Mofa N., Mansurov Z., Xanthopoulou. G. Composite materials on the basis of silica-modified systems with high sorption activity for water surface cleaning // Euro-Asian Journal of Sustainable Energy Development Policy 2010. - V 2, №1. - P. 39 – 47.

14. Soh D., Mofa N., Ksandopulo G., Lan B., Ketegenov T. Reclaiming property of magnetic adsorbent for oil spill recovery and pollution control. / Proceeding of the KIEEME Annual Autumn Conference, 2001. v. 14, issue 1, p. 296 – 299.

Received 27 may 2009.