New adsorbent materials on the base of minerals and industrial waste

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Abstract. At present, when environmental problems become more pronounced, we need to find special solutions. One of the ways is to use cheap adsorbents that do not need to be restored. An example of developing a class of adsorbent materials is technology for synthesizing nanotubes from refractory ilmenite-leucoxene ore. Another example of the development of a class of zeolite as advanced materials is the technology of their synthesis from ashes of thermal power plants. Synthesis conditions create necessary parameters of adsorption properties to remove heavy metals and radionuclides. “Clean” technologies are formed to replace natural and commercial zeolite. Production of such materials at the national level can be an important source of profit, can create new jobs and increase competitiveness of the industry.

1. Introduction
Sorption and ion exchange technologies are widely used to solve environmental problems (wastes from hazardous hydrometallurgy production, in environmental protection technologies, etc.). The effectiveness of sorbents depends on many factors; the most important are their selectivity and application conditions of sorbents as a consequence of their material composition and structure [1, 2].

The use of sorbents includes various operations from prefiltration with separation of mechanical impurities or oils to supercleaning. Both mineral and synthetic sorbents are used for this purpose. As a rule, mineral sorbents have lower sorption properties, but they are much cheaper than synthetic materials. When using synthetic sorbents, it is possible to obtain more stable results for wastes water treatment, and to increase their service life due to the possibility of their regeneration.

One of the promising directions for creation of sorption materials is the technology of using wastes from the extraction and processing of ores and rocks. The importance of development of this direction lies in increasing stability of the regional development (reducing volume of wastes disposal, additional resources for sorption materials, new jobs for industry).

Production of such materials at the national level can be an important source of profit, can create new jobs and increase competitiveness of the industry. All this stipulates the necessity, firstly, to obtain a deeper knowledge about minerals as carriers of sorption properties, about their actual crystal structure; secondly, to understand the mechanisms of changes of the parameters of the minerals under the influence of natural and anthropogenic impacts; thirdly, to obtain new products competitive in the world market [2–6].

The aim of this work to obtain new knowledge in the field of phase transformations and aggregation of ultrafine mineral substances to create the adsorption materials with desired properties based on natural (ilmenite-leucoxene ore, Pizhenskoe deposit, Russia) and technogenic (fly ash, Pechora coal basin, Russia) materials.
2. Methods and approaches
1. Technology of nanotube synthesis (based on TiO$_2$) based on the methods and approaches of hydrothermal synthesis. They are adapted for non-magnetic fraction of gravity concentrate of titanium ore from Pizhemskoe deposit [5, 6].
2. Technology of zeolite synthesis (hydrothermal synthesis) from coal fly ash (Pechora coal basin) was described in detail [7]. In short, using a magnetic separator we removed ferriferous phases, which do not participate in the synthesis of zeolites. The suspension (after mixed thoroughly with the solution of sodium hydroxide) was placed in an autoclave.
3. Information on the morphology of raw and processing products was obtained using a scanning electron microscope (TESCAN VEGA 3 LMH) equipped with Oxford Instruments X-Max energy dispersive device. Chemical composition was determined using XRF method (Shimadzu XRF-1800). The mineral composition was determined by XRD (Shimadzu XRD 6000, CuK $\alpha$ radiation).
4. The surface roughness of the samples, shape and dimensions of the electric and magnetic micro- and nano-regions and their topology were determined by ARIS-3500 atomic-force microscope (AFM), magnetic power microscope (MPM) - upgraded AFM.

3. Mineralogy – a basis for interactive control of ore and adsorbent materials
Ores from Russia are predominantly complex, in which useful minerals can be both main and accompanying. The complexity of their mineralogical study is determined by the natural features of the ores:

- a complex textural-structural pattern, a significant amount of fine, metacolloidal units formed by mineral individuals and aggregates of micro- and nanometer-size,
- a polymineral composition, conditioned by simultaneous presence of minerals of different parageneses,
- a variable chemical composition of both the ore and nonmetal minerals caused by wide isomorphous substitutions of atoms of chemical elements in the crystalline structure of minerals,
- phase heterogeneity of mineral grains, conditioned by various causes (decomposition of solid solutions, zonal growth, partial recrystallization, solid-phase secondary transformations, etc.)
- development of metamictization processes of ore minerals containing radioactive elements, with the formation of metamictic (loosing crystal structure) and partially metamictic (with a damaged crystal structure) forms.

**Initial ore.** Determination of the mineral composition of ore, its texture pattern (mutual orientation of mineral aggregates), structural characteristics (dimensions of useful minerals, nature of their inter-growths with other mineral phases), determination of the nature of distribution of useful elements over ore minerals), determination of properties of minerals) [8].

4. Results and Discussion
As an example we consider ilmenite-leucoxene ore, the Pizhemskoe deposit. Upper Proterozoic and Devonian deposits, which are almost everywhere overlain by Quaternary sediments of various thickness (from 0.2 to 40 m), take part in the geological structure of the Pizhemskoe deposit. A titaniferous productive horizon is determined in the lower part of Devonian section. The titaniferous stratum is considered to be an ancient paleoplacer formed by erosion and redeposition of the weathering crust on underlying Riphean schists [4]. The average content of titanium minerals reaches 200 kg/t. The content of leucoxene in the sandstones reaches 15%. The titaniferous stratum is overlain by Middle Devonian alluvial quartz sandstones.

In [4] the mineralogical and technological properties of ilmenite-leucoxene ore are considered. According to optical-mineralogical analysis, the heavy fraction is formed by ilmenite, rutile, anatase, zircon, epidote, magnetite, chromespinelide, tourmaline, pyrite, monazite.
Ilmenite and leucoxene, diagnosed in the ilmenite-leucoxene ore, are represented by polymineral aggregates of pseudorutile, rutile, quartz and aluminosilicates. The distribution of titanium and iron in the ilmenite is uniform except of local substitution of ilmenite by rutile. In leucoxene, iron is concentrated within the aggregates and probably associated with relics of pseudorutile. Grains of zircon, xenotime, native gold, copper up to 15 μm in size are found on the surface and in the volume of the aggregates. Quartz and aluminosilicates are represented by mechanical inclusions less than 10 μm in size and constitute about 35 % of the aggregate volume.

The established morphostructural features should be taken into account when choosing methods for processing and separating minerals. The physical parameters of the constituent minerals of the ilmenite-leucoxene ore (density, magnetic susceptibility, etc.) indicate promising physical methods of enrichment. Ore components of mineral sands have a high density (more than 2.85 g/cm³) and can be quite easily separated from lighter components, such as quartz and aluminosilicates, provided that the intergrowths are well opened. However the established boundary particle size (10 μm) requires, firstly, considerable energy consumption. Secondly, adhesion forces increase and impede separation of particles. The losses of titanium dioxide, associated with ilmenite and leucoxene, are estimated at 20 % of the initial content, the content of titanium dioxide in the collective concentrate does not exceed 62 %. At the same time further processing requires concentrates with a higher content of TiO₂. Thus the chloride technology uses concentrates from 85 % of titanium dioxide. Therefore the use of combined enrichment methods is increasingly being proposed.

A higher degree of desilification is achieved by applying chemical methods (autoclave leaching and fluorination). The main titanium-containing phase is rutile, which, apparently, does not participate in reactions, retaining its crystalline form. It was established that the degree of desilification during fluoridation is higher (90 %), the fluorination products of the heavy fraction of titaniferous sandstones are more crystalline [7].

The applied technologies do not satisfy modern processing plants and provide expensive final products. Work is underway to change properties of minerals and (or) to find new methods for their utilization. Alongside with ilmenite, leucoxene and other polymorphs of TiO₂ useful products now include zircon, quartz and others. Active progress is to obtain high-tech materials based on inexpensive raw (leucoxene) including titanium dioxide nanotubes [7, 9].

We obtained structures of nanodisperse structures of titanium minerals using anatase as an example, for them we revealed features of physical-chemical properties resulted from structural reorganization at the nanolevel (surface topography, sorption, electronic properties, including width of forbidden zone, etc.) [9].

**Description of practical ideas:** The high cost of TiO₂ nanoparticles and their relevance in industry determines the importance of the hydrothermal synthesis method of nanotubes of titanium dioxide from cheap sand (titanium ore, Pizhemskoe deposit).

Leucoxene is a rutile microcrystalline matrix saturated with minute inclusions of quartz, the XRD analysis indicated a high crystallinity of the phases. The synthesized materials are a mixture of two phases: quartz and sodium titanate Na₂Ti₆O₁₃, and presented structure of nanotubes of titanium dioxide. Synthesized TiO₂ nanotubes possess a highly developed surface, which makes the material a good adsorbent and photocatalyst for wastewater purification with organic compounds [6, 9]. Also the
changed band gap allows considering the obtained material as raw for production of optical fibers [9].

Other important application of synthetized materials by hydrothermal methods is dialysis of blood. Our laboratory technologies imitate natural “production” - halloysite, found in nature as a hydrated mineral, consisting of rolled in coils aluminum sheets. Halloysite nanotubes are nontoxic and have fast adsorption rates. The nanotubes have a lot of applications: environment protection, anticancer therapy, cosmetics, nanotemplate for biocatalyst, tubular container for the corrosion inhibitor, additive in paints, coating material, etc.

The method of zeolite synthesis. When the state of the mineral system changes (P-T-V), phase transformations occur (substance transition from one phase to another). The substance changes its composition and properties. Researches in this area will be useful for the development of theory and experiment of obtaining advanced materials with certain properties. As an example of phase transformations we consider the technology for the synthesis of zeolites from fly ash - wastes of thermal power plants of Pechora coal basin. Synthesis conditions create necessary parameters of adsorption properties for removing heavy metals and radionuclides. We have studied morphology and chemical composition of initial, intermediate and final products.

X-ray diffraction (Fig. 2) showed quartz, mullite, magnetite and hematite in the coal fly ash. The broad "hump" (area of increased background) on the diffractogram in the area 15–35 º2θ indicates the presence of amorphous phase (probably silicate or aluminosilicate glass). The main components of the chemical composition are SiO₂ (57.78 %) and Al₂O₃ (18.25 %), iron oxide content is about 9.0 %, oxides of other elements - 7.42 %, loss on ignition - 7.90 %.

The fly ash morphology and composition. The fly ash is represented under the electron microscope by globules (Fig. 3). The globules are divided by the chemical composition to aluminosilicate and iron containing. The aluminosilicate globules composition is predominated by SiO₂ (from 41.82 to 61.27 %) and Al₂O₃ (from 17.03 to 22.8 %); FeO and Fe₂O₃ (up to 8.31 %), MgO (up to 4.83 %), K₂O (up to 3.05 %), TiO₂ (up to 1.04 %) and Na₂O (up to 0.93 %) are also present. Globule size varies from the first to about hundred micrometers; on the surface bubbles and elongated structures are observed.
On the surface of iron containing globules both flat areas and skeletal forms are observed, which are significantly different from each other by their chemical composition. The skeletal forms have a high content of iron oxides (68.14-74.66 %) and low SiO$_2$ (1.06-6.22 %), Al$_2$O$_3$ (1.33-4.17 %) and CaO (0.48-3.59 %) contents. On the flat areas iron oxides content is greatly reduced (19.29-31.81 %), SiO$_2$ and Al$_2$O$_3$ content increases (27.12-37.86 and 2.06-6.22 %, respectively); CaO presents in amounts of 10.45-25.3 %. Globule size ranges from several to tens micrometers. Globules, which contain smaller globules within, are often observed.

Hydrothermal synthesis. Two sets of experiments were carried out. In the first set the effect of temperature of hydrothermal reaction on zeolite synthesis was studied. The second set of experiments studied the influence of reaction time and concentration of alkali on synthesis process. The synthesis results in powders consisting of the mixture of zeolite and unreacted residue in different proportions, in which output was 70-80 % of the weight of the initial fly ash.

Effect of reaction temperature on the synthesis of zeolites. At reaction temperatures from 95 to 180 °C several species of zeolites were obtained, different by their morphology and porosity (Fig. 4). It
was found that increasing temperature leads to reducing pore size of the zeolites. Thus, at 95 °C zeolites X (a synthetic analogue of natural faujasite, pore size 0.74 nm) formed with an admixture of zeolite P (a synthetic analogue of natural gismondine, pore size 0.31×0.45 and 0.28×0.48 nm). At 140 °C zeolites P formed with an admixture of analcime (pore size 0.26 and 0.42×0.16 nm [10]). At 180 °C, analcime crystallizes with an admixture of cancrinite (a non-zeolitic phase). According to the classification of zeolites by pore size [11, 12], analcime and zeolite P refer to narrow-porous, zeolite X - to wide-porous species.

**Effect of reaction time and alkali concentration on zeolite type.** The wide porous zeolites X are formed by 4 hours of reaction at a high concentration of alkaline solution (4.5 mol/dm³). Longer reaction leads to the disappearance of the metastable phases of zeolite X and the occurrence of more thermodynamically stable - zeolite P and then analcime. Zeolite P is crystallized under a wide range of reaction conditions. At the same time, the fields of crystallization of analcime and zeolite P are significantly overlapped, that is, at the same conditions of the hydrothermal reaction, the mixture of zeolites in various quantitative relations is formed. Higher concentrations of alkali results in the increase of the content of narrow porous phases (analcime) compared to zeolite P, and contributes to the formation of non-zeolitic phase - hydrosodalite.

**Sorption properties.** Synthesized zeolites are characterized by a high sorption activity with respect to long-living natural radionuclides and possess low desorption of uranium and radium. The extraction degree of radium from solutions is 98, thorium - more than 89, uranium – more than 80 %. Thorium is retained in the structure of synthesized sorbents the least strongly. The sorption capacity for barium has values from 113.3 to 157.5 mg/g (1.65-2.29 meq/g), for strontium – 85.9 mg/g (1.94 meq/g), for ammonium 32.2 mg/g (1.78 meq/g). By selectivity of sorption, the above cations can be arranged in a line: Ba²⁺ > Sr²⁺ > NH⁴⁺ [13].

5. **Conclusion**

1. We underline an important role of integration of mineralogical and technological research of ores and treatment product, identification of mineralogical features for forecasting of behavior in technological processes.
2. We show that the mechanism of phase transformations in minerals (ores) (example of hydrothermal synthesis of TiO₂ nanotube from ilmenite-leucoxene ore, Pizhemske deposit, and example of zeolite synthesis (hydrothermal synthesis) from fly ash (coal of Pechora basin) can form new minerals (new phases), which physical and chemical parameters will satisfy requirements of new adsorbing materials with desired properties and reduce environmental risks and expand the list of market products of coal mines - sorbents of various toxicants.

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