Magnetic iron oxides in the cementation technology of the boron-containing radioactive waste

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Abstract. Two ways of synthesis of non-detachable dispersed particles of magnetic materials useful for the boron-containing waste cementation process regulation were developed. Powder XRD showed that the method of carbothermic recovery of nanoscale iron hydroxide allows obtaining a mixture of iron oxides with content of the magnetic phase up to 70%. Method of low-temperature hydrogen reduction of the raw materials allows obtaining various compositions of α-iron and iron oxides with the possibility to change the size of the final particles in a wide range. The possibility of using composites of magnetic iron oxides and metal oxide compositions instead of ferromagnetic rods with VEP of boron-containing liquid radioactive waste in the fluidized field was studied. It was shown that the use of fine and nano particles of the iron oxides in the pre-treatment of the boron-containing LRW increases the strength of the final compounds and accelerates the cement setting compounds from 13 to 5-9 days.

1. Introduction
At the nuclear industry enterprises various of radioactive waste (RW) has been formed. A significant amount of liquid and solid radioactive waste has been already accumulated in Russian Federation [1]. The long-term controlled storage and final disposal of the radioactive waste (RW) require their preservation in the form that prevent their interaction with the environment and be sustainable throughout the storage time. And it is important to minimize the volume of the conditioned RW. In Russia, the liquid radioactive waste (LRW) primarily goes to cementation [2]. This is the most cost-
effective solution for disposal of low and intermediate level radioactive waste, although the technology of cementation increases the total volume of the stored waste. To obtain a cement compound that meets the requirements of the normative documents, it is important to determine the recipe of the cementation. The optimal compound recipe provides the maximum inclusion of waste. The minimum amount of stored compounds must consider the chemical properties of different types of waste and as well as the established national standards.

The boron-containing radioactive waste with low pH<6 values cannot be cemented without alkaline additives that neutralizes the acidic form of the borate compounds. The introduction of the alkaline additives increases the volume of the final cement compound several times, which significantly increases the financial and operational costs.

The process of hardening of the borate cement matrix can be accelerated by reducing the effects of the borates in electromagnetic processing of the LRW in the vortex field with ferromagnetic rods. But this leads to the formation of secondary LRW after the decontamination of the reusable rods. Their replacement by non-separable dispersed particles of the magnetic iron oxides allow to accelerate the cement compounds setting, to improve their mechanical properties and to prevent the formation of secondary LRW [3].

The aim of this work is to develop the technology of preparation of dispersed magnetic iron oxide particles suitable for using instead of ferromagnetic rods in the process of the vortex of electromagnetic processing (VEP) boron-containing liquid radioactive waste, and testing obtained dispersed magnetic iron oxide particles for changing the state of aqueous solutions of borates after processing in the vortex electromagnetic field.

2. Magnetic iron oxides and methods for their preparation

Two ways of synthesis of non-detachable dispersed particles of magnetic materials useful for the boron-containing waste cementation process regulation were developed. The resulting materials are composites of dispersed magnetic iron oxides or composites with the presence of dispersed α-iron. The process of obtaining such materials is based on reduction of nanoscale raw material in the form of iron hydroxide by solid or gaseous reducing agents. Magnetic iron oxide phases are γ-Fe₂O₃ (maghemite), Fe₃O₄ (magnetite) and dispersed iron. The geometrical dimensions of the magnetic particles are controlled by reduction temperature.

Dispersed iron oxide magnetic particles synthesis process is separated into two phases. (Process for preparing the particulate magnetic iron oxide particles is separated into two phases). The first step is preparing a raw in the form of iron hydroxide by precipitation of iron chloride FeCl₃ or iron nitrate Fe(NO₃)₃ with ammonia aqueous solution. The result is a colloidal solution of ferric hydroxide Fe(OH)₃. In the second step the ferrous hydroxide is reduced with activated carbon. For this purpose, ferric hydroxide is mixed with crushed carbon in various proportions and heated to a temperature of 500 - 600 °C. The result of reduction is obtained nanoscale iron oxide powder with an average particle size of about 50 nm, which are composed of iron oxide phase α-Fe₂O₃, γ-Fe₂O₃ and Fe₃O₄, there is also soot carbon, sedimenting on the iron oxide particles. Reflections of magnetite and hematite are presented on the powder XRD (figure 1). The content of hematite (α-Fe₂O₃) in the resulting composite of iron oxides is not more than 2%. Maghemite (γ-Fe₂O₃) was detected by using Mössbauer spectroscopy.

Another process that allows obtaining composites of magnetic iron oxide is low-temperature hydrogen reduction of nanosized iron hydroxide. This process also involves the preparation of nanosized raw material as a first step. The method allows obtaining composites of magnetic iron oxides γ-Fe₂O₃, Fe₃O₄, as well as various iron oxide phase composites with metallic iron. It is possible to vary the geometrical dimensions of the obtained particles in a wide range. As an example, the Mössbauer spectrum of nanosized particles of different iron phases is shown on figure 2 [4].
The possibility of using composites of magnetic iron oxides and metal oxide compositions instead of ferromagnetic rods with VEP of boron-containing liquid radioactive waste in the fluidized field was studied.

3. The effect of iron oxide mixtures on the properties of the boron-containing liquid radioactive waste which goes to cementation

The properties of the boron-containing LRW are regulated using mixtures of dispersed magnetic iron oxides during the electromagnetic processing in the vortex field. Figure 3 shows the IR spectra of boron-containing LRW before and after VEP.

The spectra confirm the changes of the forms of the hydrate oxygen boron compounds. Due to the electromagnetic interference in the hydrogen bonds dissociation of the crystal hydrates and characteristic boron bonds (B-O-B), the magnetic and electromagnetic water activation may change the crystal phases and the pH of the solutions [5-8]. Thus, in the IR spectra peaks of 3640 cm\(^{-1}\) and 920 cm\(^{-1}\) disappeared. Vibration of 3640 cm\(^{-1}\) corresponds to stretching vibration of the free single end bond -O-H, and the vibration of 920 cm\(^{-1}\) correspond to the deformation vibration of -A-O-H bond (where A is the atom of boron). Moreover, peaks in the range of 1450 cm\(^{-1}\) to 750 cm\(^{-1}\) have changed, reflecting the state of the bonds of boron atoms. During the electromagnetic processing of the LRW the free end -O-H bond has disappeared, and there was a partial destruction of the crystal hydrates, which increases pH.
To determine the effect of the magnetic iron oxides obtained from the initial mixture of different composition, samples were selected of the o-boron acid solution to determine the change of the pH values, that were prepared using iron chloride and iron nitrate, and as well as with various proportions of carbon. The pH changes and conductivity of the solutions are given in table 1. The processing was performed within 180 seconds. Using nano particles of iron oxides as activators in the electromagnetic processing of the solutions of o-boric acid, pH value increased to 1.6 - 1.7 times, and the conductivity increase of 10-20 times depending on the composition of the initial mixture. The use of raw material of the various salts of iron (NC-1 and NC-2) has practically no effect on pH, while increasing the amount of carbon in the initial mixture NC-2 compared to NC - 3 has a positive effect on the increase of pH. So, using powders of iron oxides as activators in electromagnetic processing it improves the reactivity of the cement minerals in the presence of a solution of o-boric acid.

Table 1. Changes in pH and conductivity of the aqueous solutions of o-boric acid after the VEP depending on the type of activator

| Activator type | pH      | Electrical conductivity γ (μkS/cm) |
|----------------|---------|-----------------------------------|
| No VEO processing | 3.35    | 119                               |
| NC-1 (the ratio of the iron chloride FeCl$_3$ to the activated charcoal 1:1) | 5.73 | 2410 |
| NC-2 (the ratio of iron nitrate Fe(NO$_3$)$_3$ to the activated carbon 1:1) | 5.71 | 1700 |
| NC-3 (the ratio of iron nitrate Fe(NO$_3$)$_3$ to the activated carbon 1:0.5) | 5.43 | 1260 |

In the structure of the hardened cement compound with a boron-containing LRW the magnetic particles can act as reinforcing materials. Figure 4 shows the results of the cement compounds strength measurements. It is obvious, that the use of fine and nano particles of the iron oxides in the pre-treatment of the boron-containing LRW increases the strength of the final compounds. This is confirmed by the scanning electron microscopy data of the cement compounds on the basis of the VEP boron containing LRW (figure 5), indicating of a denser and orderly structure of the cement matrix already in the early stages of the hardening (10-14 days).

In cementation process using VEP the hardening dynamics of the compounds varies depending on the used activator. The use of a mixture of iron oxides instead of the separable ferromagnetic rods...
accelerates the cement setting compounds from 13 to 5-9 days. The iron oxide nanoparticles show better results after the boron containing LRW cementation using VEP, observed early setting and uniform strength. The mixture of nanoscale iron oxides act as well as dispersion strengthened elements that increase the mechanical strength of the cement compounds.

![Figure 5. Ordered structures of the new cement formations in the presence of magnetic iron oxides and VEP boron containing LRW](image)

4. Conclusions

There are two ways to obtain non separable dispersed particles of magnetic materials suitable for regulation of the cementation processes of the boron-containing LRW.

Method of carbothermic reduction of nanoscale iron hydroxide allows obtaining a mixture of iron oxides with content of the magnetic phase up to 70% and particles with an average size of 50 nm.

Method of low-temperature hydrogen reduction of the raw materials allows obtaining various compositions of $\alpha$-iron and iron oxides with the possibility to change the size of the final particles in a wide range.

It is shown that a result of the electromagnetic processing (VEP) in the vertical field of magnetic iron oxides through changes in the boron atoms bonds in hydrated compounds, the pH values increase in 1.6-1.7 times in the borate aqueous solutions, which leads to improvement of the properties of the cement compounds with boron containing LRW.

Replacement the ferromagnetic rods with dispersed mixture of magnetic iron oxides in the vortex electromagnetic processing of the boron LRW does not lead to the loss of positive effect and helps to simplify the technological process of processing the boron containing LRW using the method of cementation and to avoid the formation of secondary liquid radioactive waste.

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