Utilization of red mud and boron-containing liquid radioactive wastes of nuclear power plants

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Abstract. The physicochemical processes of red mud recovery using solid reducing agents were studied. A comparison was made of the effectiveness of obtaining functional materials from red mud with various reducing agents. The extent of recovery of red muds was investigated by X-ray phase analysis. The red mud of the “Alum” plant contains sodium, which has a positive effect when it is used in the process of liquid radioactive waste (LRW) cementation as a result of the partial neutralization of the acidic environment of boron-containing LRW. The use of red mud as a source of raw materials for the recovery process with solid carbon allows not only to solve the problem with the accumulation of technogenic waste, but also to reduce the costs of immobilizing LRW. Replacing the artificially produced nanosized iron hydroxide with red mud will reduce the cost of the feedstock while optimizing the process of obtaining the finished product. The obtaines functional materials can be used for immobilization of LWR of nuclear power plants in order to reduce the hardening time of cement compounds and increase their strength.

1. Introduction
Currently, one of the most important problems of environmental protection is the recycling of ever-increasing technogenic waste from various industries. It can be distinguished two the most hazardous to the environment and significant on the scale of the accumulated volumes groups of waste - radioactive waste and waste resulting from metallurgical production.

Among radioactive waste, a significant proportion is occupied by LRW. Currently, over 550 million m$^3$ of radioactive wastes have been accumulated in the Russian Federation [1]. 85% of these wastes are LRW. They include various organic and inorganic liquids. LRW are also formed during the recycling of spent nuclear fuel. Possible methods for the immobilization of LRW are: cementing, bituminization, deep evaporation and vitrification. The most common method of disposing of low and medium level LRW is cementing, which makes it possible to obtain a durable product in the form of a cement compound with low capital and operating costs [2]. The resulting compounds are prepared for long-term burial in specially equipped places [3].

Cementation of boron-containing LRW is associated with a number of difficulties. Low pH values of the solutions lead to a significant increase in the hardening time of cement compounds and a decrease in their strength. This leads to an increase in operating costs of the process of LRW recycling. Currently, a physical impact method is used to regulate the acidity of boron-containing
LRW [4]. A mixture of LRW with cement mortar is subjected to electromagnetic treatment in the vortex layer of ferromagnetic rods (VET). Extraction of ferromagnetic rods is associated with the need for their deactivation, which leads to the formation of secondary liquid radioactive waste and an increase in the total volume of radioactive waste.

Earlier, a technology for producing magnetic activators of the process of LRW cementation by the method of solid-phase carbon reduction of artificially prepared raw materials - nano-sized iron hydroxide, was developed [5]. The use of the obtained mixture in the process of boron-containing LRW cementation has reduced the setting time of the cement slurry with the addition of LRW, as well as improved the strength characteristics of the cement compounds, including due to the accelerated set of the early strength of the cement composition [6].

The obtaining of magnetic activators of the LRW cementation process is also possible from industrial waste with high iron content. The most promising raw material for these purposes is the waste of the aluminum industry - red mud, the iron content of which can reach 50%. Depending on the composition of the initial bauxite and technology, from 0.9 to 2.5 tons of these wastes are produced per 1 ton of alumina [7, 8]. The world has already accumulated from 2.7 [7,9] to 4 [10] billion tons of such waste, and every year the amount increases by 5-8 million tons. The storage volume of only Ural aluminum plants is 100-300 million tons [9]. The annual generation of such waste worldwide exceeds 120 million tons. Despite the large number of developed technologies for the recycling of red mud [11, 12], in most cases, they are unprofitable, with the result that the slimes continue to be dumped, which is dangerous for the environment. Due to the high alkali content for storage of red mud, special storage facilities are used. Each such storage is a reservoir with a height of 30-50 m, occupies 10-50 hectares of land area and holds tens of millions of tons of red mud [13]. Figure 1 shows an example of red mud storage. The cost of building new and maintaining old red mud dumps requires significant financial investments.

![Figure 1. Red mud storage](image)

The use of red mud as a precursor for the recovery process by solid carbon allows not only to solve the problem of accumulation of industrial wastes, but also to reduce the cost of obtaining activators of the process of LRW cementing. Replacing the artificially produced nano-sized iron hydroxide with red mud will reduce the cost of raw materials and optimize the process of obtaining the finished product.

2. Materials and Methods

High-alkaline red mud from the “Alum” plant (Romania) and low-alkaline red mud from JSC Ural Aluminum Plant (UAP) (Kamensk-Uralsky), containing up to 45% hematite, and aluminum oxides silicon, calcium and sodium were used. High-alkaline red mud has pH values from 10 to 13, which
allows partially neutralizing the acidic environment of boron-containing LRW solutions. The chemical composition of the red mud is given in table 1, and figures 1 and 2 show their radiographs.

**Table 1. The composition of the main components of red mud**

| Component   | “Alum” (Romania) (%) | UAP (Kamensk-Uralsky) (%) |
|-------------|-----------------------|---------------------------|
| Fe₂O₃       | 43.39                 | 36.9                      |
| Al₂O₃       | 21.51                 | 11.8                      |
| SiO₂        | 9.04                  | 8.71                      |
| CaO         | 4.63                  | 23.8                      |
| Na₂O        | 7.09                  | 0.27                      |
| TiO₂        | 2.92                  | 3.54                      |

**Figure 2. X-ray of “Alum” red mud**

**Figure 3. X-ray of UAP red mud**

Phase analysis of red muds and recovered samples was carried out using a ULTIMA IV diffractometer (Rigaku, Japan) on Cu-κα X-rays and a Diffray 401 diffractometer (JSC “Scientific Instruments”, Russia) on Cr-κα X-rays, a quantitative calculation of the phase content was carried out by Rietveld method. Mössbauer spectroscopy was carried out on a Ms-1104Em spectrometer (RSU, Russia) in the mode of constant accelerations with a Co-57 source in the Rh matrix. Studies have shown that the distribution of iron over iron-containing phases for the red mud “Alum”: hematite (α-Fe₂O₃) - 45%, lepidocrocite (γ-FeOOH) - 55%. For the UAP red mud, the iron distribution over the iron-containing phases is as follows: hematite (α-Fe₂O₃) - 80%, iron-alumino-silicate - 15% (ferrous iron) and iron hydroxide of complex composition - 5%.

The original mixture of red mud was mixed with carbon of various grades in different ratios and heated in a stream of argon to a temperature of 700 °C in a tubular furnace, followed by exposure for 30 minutes. The following were chosen as reducing agents: “Medisorb” activated carbon, BAU-A activated carbon, charcoal and sucrose. Table 2 shows the composition of the reducing agents.

**Table 2. Composition of reducing agents**

| Type of reducing agent     | Composition, wt.% | The main substance, formula |
|----------------------------|-------------------|-----------------------------|
| “Medisorb” activated carbon| carbon            | C 78 | 5 | 17 | - |
| BAU-A activated carbon     | carbon            | C 84 | 10 | -  | 6 |
| Charcoal                   | carbon            | C 85 | 10 | -  | 5 |
| Sucrose                    | C₁₂H₂₂O₁₁         | C 42 | 58 | -  | - |
Thermodynamic calculation of the amount of reducing agent required for the reduction of iron-containing phases to magnetite was carried out by the HSC Chemistry 5.11 program [14].

3. Results

Thermodynamic calculation showed that for complete reduction of the iron-containing phases of the red mud UAP to magnetite at a temperature of 700 °C and atmospheric pressure, 1 wt.% of carbon is sufficient and for red mud “Alum” – 0.5 wt.% of carbon. With such an amount of carbon, the magnetite content in the final mixture is maximal (Figure 4, 5). Along with magnetite, a small amount of iron compounds with titanium (Figure 4) and sodium (Figure 5) and magnetic aluminoferritic phases (Hercynite) may be present in the final product.

**Figure 4.** The change of the main iron-containing phases of UAP red mud depending on the change in the amount of carbon at 700 °C.

**Figure 5.** The change of the main iron-containing phases of UAP red mud depending on the change in the amount of carbon at 700 °C.

**Figure 6.** The results of X-ray phase analysis: 1 – “Alum” + 1% C; 2 – “Alum” + 2% C; 3 – “Alum” + 5% C; 4 - UAP + 1% C; 5 - UAP + 2% C; 6 - UAP + 5% C.
For the experiments, samples of mixtures of red mud with “Medisorb” activated carbon were prepared in ratios of 1, 2 and 5 wt.%. Depending on the exposure time and the carbon content in the initial mixture, the samples obtained had a different ratio of magnetic phases and nonmagnetic phases. The results of X-ray phase analysis of the recovered samples are shown in Figure 6.

Figure 6 shows the line of the spectrum most characteristic of the maghemite phase (γ-Fe₂O₃).

As a result of the experiments, it was shown that samples recovered using 1% carbon were only partially recovered, and samples with a carbon content in the initial mixture of 5% contain a significant amount of magnetic phase. Samples obtained from the red mud UAP, have in their composition a greater amount of magnetic fraction compared with similar samples of red mud from the factory “Alum”.

An increase in the mass fraction of carbon in the initial mixture to 10% leads to the complete transition of iron oxides to magnetite. Figure 7 shows the X-ray diffraction pattern of the “Alum” red mud sample, and Table 3 shows its quantitative phase composition.

![Figure 7](image_url)

**Figure 7.** The results of X-ray phase analysis for the sample “Alum” with a carbon content of 10% in the initial mixture.

| Structural formula                      | Quantitative content, % |
|----------------------------------------|-------------------------|
| Fe₂O₄                                  | 35.8                    |
| Na₇₋₆(Al₆Si₆O₂₄)(CO₃)₀₋₉₃(H₂O)₂₋₉₃ | 19.2                    |
| Na₇₋₂₆₂(CO₃)₀₋₉₂Al₆Si₆O₂₄            | 13.3                    |
| Na₆Ti₃.₅O₂(OH)₂(SiO₄)₄                | 11.8                    |
| Na₁₅₋₆Ca₃₋₈₆(Si₁₂O₃₆)               | 6.9                     |
| C                                      | 6.6                     |
| CaCO₃                                 | 4.3                     |
| CaTiO₃                                | 2.1                     |
From table 3 it can be seen that magnetite in the sample is present in an amount of 35.8% of the total mass, the remaining phases are mainly composed of complex sodium aluminosilicates.

The effect of the type of reducing agent on the reduction process of the iron-containing phases of red mud was also investigated. Samples of mixtures of red mud with 10 wt.% of activated carbon BAU-A, 10 wt.% of charcoal and 20 wt.% of sucrose were reduced by the described method.

Figure 8 and 9 shows radiographs of samples obtained with various types of reducing agents.

It can be seen from the figures that the results of the reduction of the iron-containing phases of the “Alum” and UAP red mud are different. In the “Alum” red mud, a noticeable amount of magnetic phases is present only in the sample reconstituted with activated carbon BAU-A, in the remaining samples there are practically no magnetic phases, and the main iron-containing phase is hematite. The UAP red mud recovered better, as evidenced by magnetite peaks on radiographs in all cases.

Taking into account the data of thermodynamic modeling in the samples, along with magnetite, hercinit (FeAl₂O₄) may be present. However, due to the similarity of types of crystal lattices of these compounds, it is not possible to separate them by X-ray phase analysis.

4. Discussions

The results of the experiments showed that to obtain magnetic phases, an excess of reducing agent is necessary, several times higher than that required by the results of thermodynamic modeling. This is most likely due to the low content of carbon monoxide in the gas phase, which is the main reducing agent for iron minerals at low temperatures. An increase in the amount of carbon in the mixture leads to an increase in the CO content in the gas phase and an increase in the degree of reduction. Also, a low degree of recovery may be associated with insufficient exposure time.

The influence of the type of reducing agent on the degree of reduction of iron-containing phases is due to the different rate of gasification of the coal under study. The speed of the gasification process is primarily determined by the value of the specific surface area, which is greatest for the activated carbons “Medisorb” (about 400 m²/g) and BAU-A (about 600 m²/g).

The low degree of recovery of red mud “Alum” is most likely due to the presence in its composition of a large amount of alkali and calcium, which, when reacting with iron compounds, can form hardly-recoverable iron-containing phases.

The presence of magnetite in this sample in the case of the use of activated carbon “Medisorb”, in contrast to samples obtained with other types of carbon, is explained by the composition of the activated carbon itself. Carbon contains up to 20% of organic additives in the form of sucrose and
starch, which act as binders. When heated, these substances begin to decompose in the temperature range from 170 to 250 °C with the formation of water and black carbon. As a result, the sample is saturated with a dispersed reducing agent in the form of black carbon, which contributes to the formation of the magnetic phase of iron oxide.

As a result, the recovery of the oxide phases of iron in the composition of the red mud provides for obtaining magnetic particles necessary for conducting the VEO. Reduced red mud from the “Alum” plant contains sodium, which has a positive effect when it is used in the process of LRW cementation due to partial neutralization of the acidic environment of boron-containing LRW.

5. Conclusion
It was determined that in the process of reduction with increasing temperature, the structure of iron compounds changes, accompanied by the transition of the nonmagnetic phase to the magnetic one. Thus, the magnetic phase of maghemite ($\gamma$-Fe$_2$O$_3$) is formed first, followed by its transition to magnetite (Fe$_3$O$_4$).

It was found that the most effective reducing agent is activated carbon "Medisorb", containing in its composition binders, in the form of sucrose and starch, the use of which contributes to the most complete recovery process of the iron-containing phases in the red mud with the formation of a magnetic phase in the form of magnetite.

As a result, the recovery of iron-containing phases in the composition of the red mud provides for obtaining magnetic particles necessary for conducting the VEO.

Joint utilization of such industrial wastes as LRW and red mud contributes to a significant reduction in the amount of accumulated waste and the prevention of environmental disasters, as well as lower costs for the disposal of LRW.

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