Mineral composition of bauxite residue and their surface for innovation materials

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Abstract
Natural aluminum ores and aluminosilicate residues are an important component in the development of strategies for the modification of composites, sorbents and other functional materials. The properties of bauxite and bauxite residue were studied by XRD, SEM and standard methods of mineral surface. The phase composition, magnetic, sorption and other properties of bauxite residue before and after exposure to chemical and physical methods to be used in industries are presented.

Keywords: bauxite residue, mineral composition, modification, advanced materials

1. Introduction

Alumina is an important raw material for the development of the national economy; however, alumina production can result in great environmental problems. Potentially, bauxites are complex ores for aluminum, titanium, gold and rare elements, which determines the combined processing technologies to extract all useful components and use their technological properties [1-4]. Bauxite residue (red mud) are the main by-product of alumina production. Annually, up to 40 million tons of bauxite residue are produced in the world, the bulk of which is still not used. The high alkalinity of such wastes adversely affects water, soil and air. Problems include the flow of alkaline solution and bauxite residue because of damaged pipelines or dams. High cost and large land area are also associated with the construction of dams. Bauxite residues removed from the alumina plant outside the territory in the form of pulp and stored in a specially equipped site - the so-called mud lake. Dried bauxite sludge can be an effective filler of insulation materials, paints, mastics, tile and roll materials for flooring, etc. [1-8]. A significant part of the researches is devoted to composites based on aluminosilicates and technologies for modifying physicochemical properties to meet current and future requirements by request of companies involved in processing of raw materials and production of goods in factories. The study of aluminum and other metals is promoted by their attractiveness for many structural components, where special technological properties are important (increased strength, lower weight, etc.) [9-12]. Bauxite residue is a waste from alumina production, which is characterized by a high content of finely dispersed Fe, Al, and Ti oxyhydrides [8].

In recent years, protecting people and the environment from harmful effects of industrial pollution has become increasingly important. The use of sorbents wins a special recognition to solve a number of problems. The most widely used sorbents are natural clays characterized by chemical stability, mechanical strength, high ion-exchange selectivity for various compounds, low cost in comparison to synthetic organic ion exchangers and other inorganic materials [13-24]. For example, the papers [15-20] were devoted to composites based on analcime-montmorillonite rocks and aluminosilicate wastes (coal fly ash). An important role of integration of mineralogical and technological features of the material composition for predicting behavior in the technological processes of composite formation and their operational characteristics were emphasized.

Bauxite residue is also studied as sorbent [8, 13, 21]. The specific surface area of bauxite residue is 23–25 m²/g, the density is 3.3–3.4 g/m³, and the melting point is 1350–1370 °C. It was determined that the maximum sorption capacity of bauxite residue for strontium is 420 ± 24 mg-Eq/100 g. The high sorption properties of bauxite residue allow using it as a sorbent in the construction of technogenic barriers in places of radioactive waste burial.

The bauxite residue ash, mineralogical characteristics (mineral and (or) phase composition), the form of occurrence of the useful component, morphostructural features that determine the strategy and tactics of their secondary use (Fig. 1):
- as raw without processing, for example, to recover valuable metals;
- as initial raw after additional processing to obtain industrial resources.

Even today we witness achievements in solving this problem, for example: storage, production of building materials, new materials to protect the environment, extraction of useful elements, etc. [1-22].
It is very important to study the surface of minerals of bauxite residue (in a fine state), taking into account their structural modification with the aim to process them efficiently. Sorption processes in the system (mineral-environment) were studied earlier. These processes (their mechanisms) are used, for example, to solve technological and environmental problems (for the extraction of non-ferrous metals from the effluents of metallurgical and other industries, the purification of liquid radioactive wastes, etc.) [10, 23], as well as in geochemical methods of searches for minerals, including migration and concentration (or dispersal) of various elements and formation of deposits [24].

Our task is to summarize the existing experience, including new data from our researches on bauxite residue, and to demonstrate the potential for practical implementation in various industries, to apply innovative methods for new materials.

2. Materials and experiments

2.1 Materials

Bauxite residue (red mud) – industrial wastes from the processing of bauxites from the Ural Aluminum Plant.

2.2 Methods of research

The chemical composition of the bauxite residue was determined by the silicate analysis. Phase diagnostics was carried out by X-ray diffraction (Shimadzu XRD-6000, CuK radiation). The microelement composition was determined by AES-ICP (ISP-22 Spectrograph). The specific surface area was determined by low temperature nitrogen adsorption method with the help of NOVA 1200e Quantachrome analyzer of surface area and pore size. The density was measured by the pycnometric method. The sorption of radionuclides was carried out according to the procedure described in [21]. Methods for studying the surface of minerals are described in [23, 24]. The surface study after laser processing was carried out by Raman spectroscopy (Raman scattering) using LabRAM HR800 high-resolution Raman spectrometer (Horiba, Jobin Yvon), and optical microscopy was performed with the help of Olympus BX41. The surface was modified by GOR-100M ruby laser with a wavelength $\lambda = 694.3$ nm and energy density of about 30 J/cm$^2$.

3. Results and discussion

3.1 Chemical and mineral composition

The chemical and mineral composition of bauxite residues determined by the composition of the initial bauxite and processing methods. The composition varies, but not much. Thus, for example, $\text{Fe}_2\text{O}_3 + \text{FeO}$, $\text{CaO}$, $\text{Al}_2\text{O}_3$ (Table 1) are main components of the chemical composition of the bauxite wastes of the studied samples, the loss on ignition was 12.77%. X-ray analysis was used to diagnose hematite, calcite, lepidocrocite/goethite, nosean, pyrite, garnets, and X-ray amorphous iron compounds. The specific surface area was 18.7 m$^2$/g, density 2.84–2.94 g/cm$^3$. According to AES-ICP data, the bauxite residue contains significant amounts of REE exceeding bulk earth values. The microelement composition is shown in Table 2.
minerals [23] in sorption processes. When minerals are heated at temperatures 100-150 °C, the hydroxyl coating is broken, and we observe a shift of the point of zero charge of the mineral surface. As a result, we observe a change in the magnetic properties of the samples.

For example, under normal conditions, berthierine and hematite (bauxite residue minerals) possess close magnetic properties and are ineffectively separated by magnetic separation methods. Bertierine significantly reduces the quality of the iron concentrate because of a low content of the latter. For comparison, we carried out magnetic separation of the initial sludge and calcined one for 2 hours at 150 °C. After separation and calcination, the chemical composition of the samples was slightly different from each other (Table 3). Changes occurred in the yield and mineral composition of the calcined samples. The non-magnetic fraction of the calcined sample increased by 22% compared to the non-calcined sample. The diffraction patterns of the non-calcined samples (non-magnetic and magnetic fractions) are slightly different from each other. The calcined samples showed a changed mineral composition. Two main minerals are diagnosed in the composition of bauxite residue: berthierine (often confused with chamosite, the difference is the absence of 14 Å reflex in berthierine diffraction pattern) and hematite. The intensity of the main peak of berthierine at (7.03 Å) in the calcined non-calcined sample is much lower than in the non-calcined and, conversely, in the calcined sample, the intensity of the peak of berthierine increases significantly. This gives reason to conclude that even a slight heat treatment (150 °C) (violation of natural long-lived radionuclides – uranium, radium, strontium, and rare earth elements).

### 3.2 Granulometric analysis

The bauxite residue is represented by a fine component, which complicates the extraction of useful minerals by traditional methods, such as magnetic separation. Gravity separation is preferable because it allows improving the content of berthierine in the tails and intermediate product of the separation. This is explained by significant differences in the concentration table 49-52%, against 43% related to magnetic separation methods. Bertierine significantly reduces the quality of the iron concentrate because of a low content of the latter. For comparison, we carried out magnetic separation of the initial sludge and calcined one for 2 hours at 150 °C. After separation and calcination, the chemical composition of the samples was slightly different from each other (Table 3). Changes occurred in the yield and mineral composition of the calcined samples. The non-magnetic fraction of the calcined sample increased by 22% compared to the non-calcined sample. The diffraction patterns of the non-calcined samples (non-magnetic and magnetic fractions) are slightly different from each other. The calcined samples showed a changed mineral composition. Two main minerals are diagnosed in the composition of bauxite residue: berthierine (often confused with chamosite, the difference is the absence of 14 Å reflex in berthierine diffraction pattern) and hematite. The intensity of the main peak of berthierine at (7.03 Å) in the calcined non-calcined sample is much lower than in the non-calcined and, conversely, in the calcined sample, the intensity of the peak of berthierine increases significantly. This gives reason to conclude that even a slight heat treatment (150 °C) (violation of the hydroxyl coating of the mineral) results in a change in the ratio of the yield of minerals in the non-magnetic and non-magnetic fractions.

### 3.3 Bauxite residue as source of alumina, caustic alkali, iron and rare earths

From the alumina workshop of the plants, sludge as pulp enters the sludge storages, which pollute the environment and increase the cost of the main products of the plants. With dump bauxite residue, 10–20% of the alumina, contained in the initial bauxite, and 60–200 kg of Na2O per 1 ton of marketable alumina are irretrievably lost. The annual loss of iron with bauxite residue from a large plant is about 0.5 million tons. Therefore, the bauxite residue should be considered as one of the potential sources of alumina, caustic alkali, iron and rare earth elements.

### 3.4 The effect of the condition of surface of bauxite residue minerals on the distribution of magnetic separation enrichment products

The finely dispersed state of bauxite residue unequivocally indicates a significant influence of the surface condition. Earlier, we studied the finely dispersed mineral–environment system [23, 24]. The value of the surface charge is important for sorption processes. The value and polarity of the surface charge depends on the position of the Fermi level. Thus, the Fermi level acts as a regulator of the activity of the surface of...
Thorium (U²³⁸, Ra²²⁶, Th²²³). The kinetics of sorption of radionuclides by bauxite residue [21] showed that more than 95 and 97% of uranium and radium, respectively, are extracted from the solution within 30 minutes of interaction. After 2 hours, more than 98.8% of radium (the content in the solution is below the detection limit) is sorbed by bauxite residue. The distribution coefficient for radium was more than 4040 ml/g. With increasing reaction time, uranium recovery increases slightly and reaches a value of 96.63%. Thorium sorption proceeds lower: after 1 h, about 20% is recovered, after 24 h – more than 60%. The study of desorption characteristics showed that sorbents had a high absorption strength (or low total desorption). When interacting with water and ammonium acetate, the desorption of radionuclides was less than 1%; during acid treatment, radium and uranium were most strongly retained (desorption was 6.3 and 11.6%, respectively), and radium was the least stable (up to 48.4% was desorbed into solution). The use of bauxite wastes as sorbents or additional material in various fields of technology does not solve the problem of processing large quantities of this waste product from alumina production. Therefore, in recent years, in many countries of the world, extensive research has been conducted on the recovery of valuable components from bauxite residue. A number of papers suggest to use bauxite residue as raw material for iron, gold, platinum, REE [2, 4, 8, 21, 25].

We studied the content of radioactive elements in bauxite and bauxite residue. For example, the thorium content in bauxite residue is about the same as in bauxite, uranium is 14 times lower, and radium is 10–6 times lower.

3.6 Modification of structure and properties

Bauxite residue is used as raw material for Fe production. For the effective development of this industrial product, technological enrichment schemes should provide for a low-waste process: along with obtaining iron-containing commodity concentrates, it is necessary to obtain concentrates of other available minerals, for example, valuable metals.

Bauxite residue, accumulated in tailings, undergo significant transformations during energy impacts in terms of micro- and nanodispersed oxyhydroxides of iron and REE, which optimizes a number of physical and technical properties of sludge and expands the potential for practical implementation in various industries, while creating new materials. For example, in [4, 8], mechanisms of the conversion of weakly magnetic iron-containing minerals (hematite, goethite) to highly magnetic minerals (magnetite, maghemite) under the influence of external physicochemical factors were considered.

The laser agglomeration technology proposed in [25] is an alternative to cyanidation and amalgamation technologies, which has a negative impact on the environment.

We determined that in the area of laser irradiation, the intensive formation of a new phase is taking place. According to Raman spectroscopy data, the newly formed phase is magnetite (Fig. 2). In this case, it is worth noting the heterogeneity of the magnetite film at the nanoscale level. The irradiation surface is a magnetite matrix interspersed with silica, hematite, pyrite.

The impact of laser irradiation on finemined raw materials (bauxite residue) containing hard-to-enrich, colloidal gold and other noble metals, REE and RME results in agglomeration processes with the formation of coarse particles in the form of a drop-like shape with particle sizes one to two orders of magnitude larger than the original ones. As a result of laser melting, the substance is redistributed with the concentration and agglomeration of valuable metals (gold, platinum, hafnium, tungsten, bismuth, etc., the list depends on the experimental conditions), which are “invisible” before processing [25].

4. Conclusions

This article is devoted to the prospects of using bauxite residue as a source of metals and advanced materials. An important role of integration of mineralogical and surface features of rad mud for innovative new material were emphasized. Complex forms of occurrence of useful components of bauxite residue and their technological properties were revealed. We emphasized the influence of the surface state of bauxite residue minerals on their physical and chemical properties. It was noted that various physical and chemical influences on bauxite residue
can result in a fundamental improvement of their useful properties. The use of bauxite residue as an additional material (in composites, cement, etc.) does not solve the problem of processing large quantities of this dump product of alumina production. Therefore, we suggest using bauxite residue as raw material for metals, REE, etc. The use of bauxite residue as sorbent (radionuclides, heavy metals, etc.) is one of the promising areas of waste utilization.

Acknowledgements

The authors are thankful to Geonauka Center for Collective Use, where we conducted our studies. The reported study was funded by RFBR and NSFC according to the research project RFBR № 20-55-53019 and NSFC № 4191101331, 41672039. The studies were supported by the program “Main directions of integrated assessment and efficient use of georesources of Timan-Northern Ural-Barents Sea Region” GR AAAA-A19-119031390057-5.

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Ref:

Kotova, Olga B. – Razmyslov, Ilia N. – Ibrahim, Jamal Eldin F. M. – Shushkov, Dmitry A: Mineral composition of bauxite residue and their surface for innovation materials

Építőanyag – Journal of Silicate Based and Composite Materials

Építőanyag – Journal of Silicate Based and Composite Materials, Vol. 72, No. 4 (2020), 135–139. p. https://doi.org/10.14382/epitoanyag-jsbcm.2020.22