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Conference Paper

Hydrothermal Resource-saving Processes in Complex Processing of Bauxite and Red Mud

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Abstract

The Bayer bauxite residue (red mud, RM) is environmentally hostile and hazardous to human health. Red mud can be viewed as an important and promising source of scandium, yttrium, zirconium and other elements rather than a solid waste. Due to a high content of iron in bauxites and especially in RM, the conversion of hematite into magnetite in Bayer liquor plays a key role in the exploration of a cleaner technology of alumina production. Thus, RM and raw bauxite were used for hydrothermal digestion in an original one-stage method of magnetite production during co-recovery of alumina. The yield of alumina reaches 80% from RM and more from bauxites during digestion with addition of lime and Fe(II) or Fe^0. The saturation magnetization of a bulk sample of magnetized bauxite is 40.5 emu/g, two orders of magnitude higher than that of a raw red mud sample. Moreover, magnetite containing a residue has a high crystallinity, which contributes to better deposition and magnetic separation in the development of an overall flowsheet for RM utilization.

Keywords: Red mud, bauxite, hydrothermal treatment; enrichment, extraction, magnetization, hematite, magnetite, rare elements

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The limited amount of high-quality bauxites and the increasing alumina production volumes call for an approach for sustainable use of mineral raw materials. All over the world bauxite processing is limited only to extraction of alumina and storage of red mud (RM) characterized by a multicomponent composition. For example, the bauxite residue that was produced after processing at the Bogoslovsky Aluminum smelter in the Urals (Russia) contains (wt.%) 45.0 Fe_2O_3; 14.0 Al_2O_3; 9.5 SiO_2; 11.0 CaO; 3.5 Na_2O; 4.6 TiO_2; 1.1 MgO; O.7 P_2O_5. The weight percent of Al_2O_3 in residues of other manufacturers can exceed 20% and that of SiO_2 is more than 25%. A significant content of rare and other non-ferrous metals makes RM a promising source of these elements [1, 2]. At this time, the emission of alkaline toxic RM in existing technologies is much higher than the amount of alumina produced. The resulting RM is pumped into the ground storage occupying hundreds of hectares of land. The high alkalinity of RM with Na_2O content of 3.5-7.5% adversely affects both the subsequent use of the bauxite residue and the

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ecology. The toxic solutions containing arsenic, vanadium, chromium, mercury, alkali and radioactive elements can penetrate into the aquifers. Destruction and leakage in the barrier dams can lead to flooding of the area with toxic pulp (Hungary, Aika; China, Ping-Go) and in arid regions (China; Ukraine) – to dust storms.
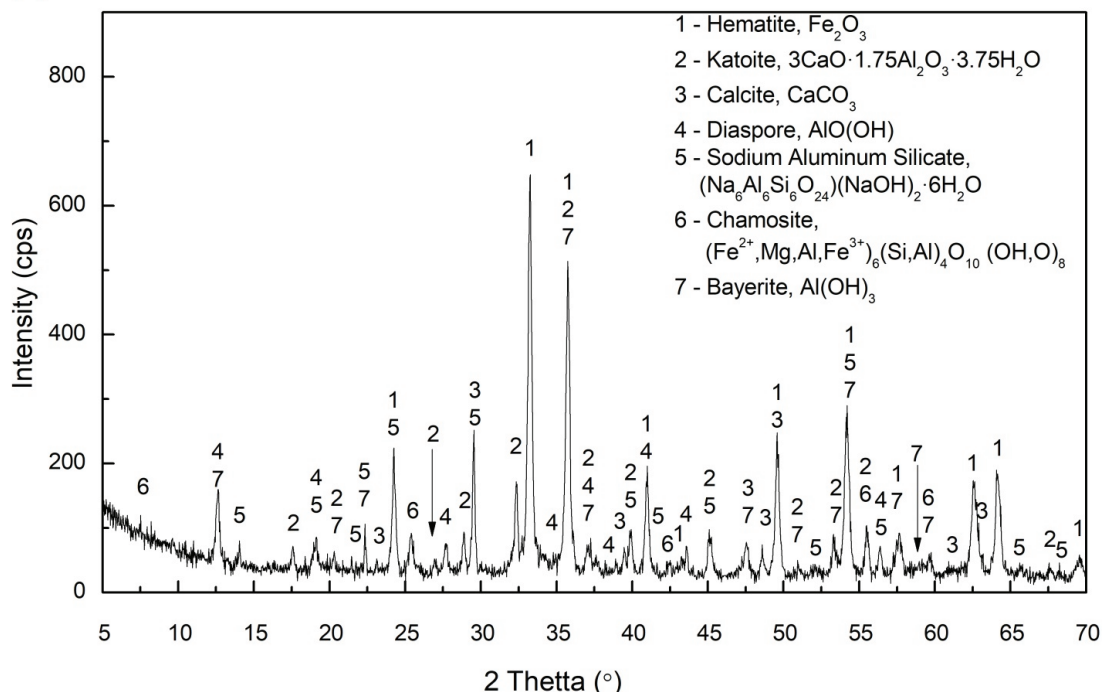
Methods of waste-free processing of red mud and bauxite are developed in the Institute of Solid State Chemistry of the Ural Branch of RAS, which are aimed at the reduction of alumina losses, obtaining of magnetite in the composition of sludge, selective extraction of rare metals, separation of amorphous silica "white carbon", etc. [3–5]. This work focuses on mineralogical reconstruction of red mud and adjusting transformations of minerals in bauxite during a Bayer digestion process with synchronous addition of lime and reductant to provide efficient digestion of alumina minerals and conversion of hematite into magnetite in resulting RM.

The high content of iron oxides (45-55 wt.%) makes some types of RM or initial bauxite a promising feedstock for ferrous metallurgy [6]. However, the use of iron-rich RM as a raw material directly for smelting of cast iron leads to the loss of aluminum and sodium as secondary wastes (slags) and impairs the process variables. Therefore, the extraction of aluminum and sodium at the first stage may be promising if these elements are returned to the main alumina production. Future application of iron-rich RM without alkalis could be more effective for the separation of iron oxides with magnetic properties from non-magnetic calcium and silicon minerals. Note that the production of iron materials such as magnetite and hematite from industrial waste is attractive for commercial and environmental purposes.
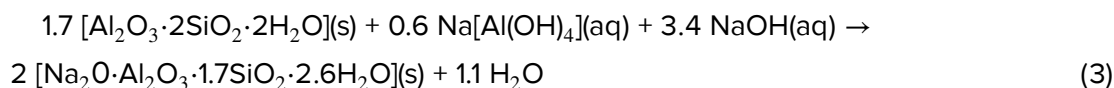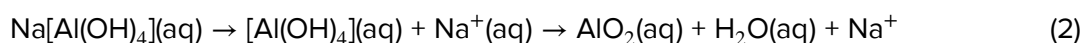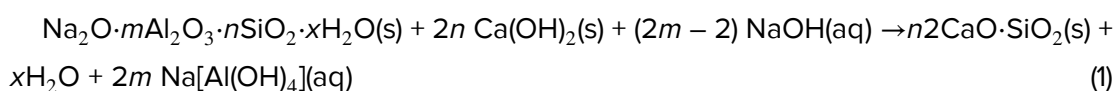
Recently, we have developed a hydrothermal method for the synthesis of magnetite with alumina recovery from RM [7]. We put a special emphasis on the establishment of reaction mechanisms for mild hydrochemical leaching practices in various conditions (mole ratio of CaO to SiO_2, temperature, duration), accounting for the removal of alumina and soda and for the enhancement of the total iron content in RM. The mechanism and conditions of the phase transition from Fe_2O_3 in RM to magnetite using a seed amount of ferrous iron were examined simultaneously during the leaching process (at the target mole ratio of CaO to SiO_2). Then, the strongly magnetic fraction was separated from magnetized and hydrochemically treated RM. Finally, the improved magnetic properties of chemically derived magnetite products were studied in comparison with those of the concentrate isolated from initial RM only by magnetic enrichment. The obtained results are important for the development of a technology for hydrochemical conversion of hematite into magnetite which would be appropriate for large-scale application of RM and effective ore beneficiation.

The XRD pattern (see **Figure 1**) unveils the main crystalline phases of RM used including (wt.%) 40 hematite (αFe_2O_3), 22 katoite (($CaO)_3(Al_2O_3)_{1.75}(H_2O)_{3.75}$), 11 calcite ($CaCO_3$), 10 diaspore ($AlO(OH)$), bayerite ($Al(OH)_3$), 7 sodium aluminum silicate ($Na_6(Al_6Si_6O_{24})\times 2NaOH\times 6H_2O$) and 7 chamosite ($(Fe,Al,Mg,Mn)_6(Si,Al)_4O_{10}(OH)_8$). The Al_2O_3 content in RM after bauxite processing is still 14.1 wt. % in insoluble form of diaspore and secondary compounds such as bayerite and katoite. All these phases provoke the loss of alumina with RM during the Bayer process.

Heterogeneous reactions like those in the Bayer process can occur during hydrochemical treatment of RM with addition of lime for extraction of Al_2O_3 from the most soluble aluminum hydroxides $Al(OH)_3$ (bayerite and gibbsite). The calcium hydroxide additive can lower the digestion temperature and intensify the decomposition of complex aluminosilicates during alumina dissolution reactions (Eqs. (1),(2)). A lack of lime in the alkaline aluminate solution in the Bayer processing leads to sodium hydroxide waste and to a lower yield of alumina in the form of aluminosilicates according to Eq. (3) [8].

Figure 1: The XDR pattern of initial RM.

$$Na_2O\cdot mAl_2O_3\cdot nSiO_2\cdot xH_2O(s) + 2n\ Ca(OH)_2(s) + (2m-2)\ NaOH(aq) \rightarrow n2CaO\cdot SiO_2(s) + xH_2O + 2m\ Na[Al(OH)_4](aq) \tag{1}$$

$$Na[Al(OH)_4](aq) \rightarrow [Al(OH)_4](aq) + Na^+(aq) \rightarrow AlO_2(aq) + H_2O(aq) + Na^+ \tag{2}$$

$$1.7\ [Al_2O_3\cdot 2SiO_2\cdot 2H_2O](s) + 0.6\ Na[Al(OH)_4](aq) + 3.4\ NaOH(aq) \rightarrow$$
$$2\ [Na_2O\cdot Al_2O_3\cdot 1.7SiO_2\cdot 2.6H_2O](s) + 1.1\ H_2O \tag{3}$$

To induce the decomposition of aluminosilicates, e.g. sodalite $Na_6(Al_6Si_6O_{24}) \cdot xNaOH \cdot (8-2x)H_2O$, an even greater excess of lime up to 2.5 is required. The silicon of aluminosilicate is caught by lime into calcium silicate; simultaneously, aluminum is recovered into solution.

The Al_2O_3 extraction from RM during hydrochemical digestion with different amounts of lime additives is shown in **Figure 2**. The alumina dissolution with the yield of Al_2O_3 above 75% is achieved at a small amount of lime when the ratio increases from 0 to 0.28 and it falls abruptly to 40% when the CaO/SiO_2 ratio grows from 0.28 to 1. A further increase in the amount of lime reduces the extraction of alumina to less than 30% [9].
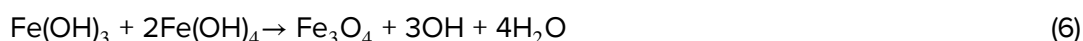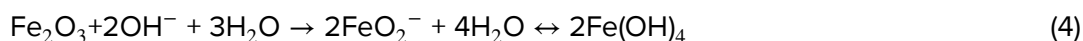
The research reveals that the addition of ferrous ion is of great importance for the investigation of the reaction of Al_2O_3 leaching from diasporic bauxite and the mechanism of iron reduction (magnetization) during high-pressure Bayer digestion [10]. Besides, the addition of ferrous ion is of great significance for the conversion of Fe_2O_3 into Fe_3O_4.
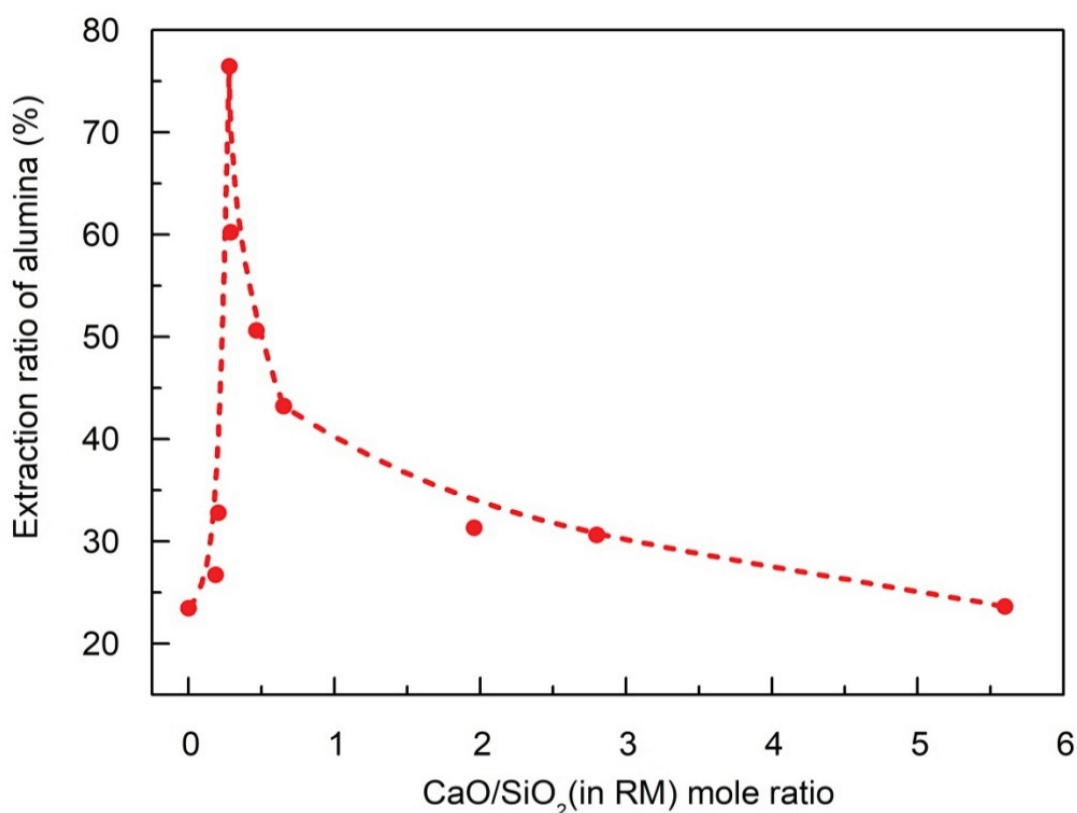
Figure 2: Leaching of Al_2O_3 from RM at various CaO/SiO_2 ratio

The transformation of Fe-rich RM by magnetization was studied during RM digestion with simultaneous addition of CaO (for Al_2O_3 recovery) and salts of Fe(II) or Fe^0. The formation of Fe_3O_4 during RM digestion proves the existence of active and accessible ions FeO_2^- or $Fe(OH)_4^-$ in alkaline aqueous solution due to Fe_2O_3 hydrolysis by Eq.

(4). The ferrous sulfate is not a stable phase in NaOH solution in this process, and $HFeO_2^-$ or $Fe(OH)_3^-$ ions are formed according to Eq. (5). Thus, in the absence of reducing atmosphere, the formation of magnetite proceeds as chemical co-precipitation by reaction (6). The as-precipitated powder iron Fe^0 is oxidized in water-alkaline medium giving rise in the first place to ions $Fe(OH)_3^-$ (Eq. (7)).

$$Fe_2O_3 + 2OH^- + 3H_2O \rightarrow 2FeO_2^- + 4H_2O \leftrightarrow 2Fe(OH)_4 \tag{4}$$

$$Fe^{2+} + 3OH \rightarrow HFeO_2 + H_2O \leftrightarrow Fe(OH)_3 \tag{5}$$

$$Fe(OH)_3 + 2Fe(OH)_4 \rightarrow Fe_3O_4 + 3OH + 4H_2O \tag{6}$$

$$Fe^0 + H_2O + OH = HFeO_2 + H_2\uparrow \tag{7}$$

The XRD analysis shows that hematite (27 wt.%) and magnetite (22 wt.%) are the main phases in the RM sample after transformation with $Fe(II)/Fe_{RM}$ mole ratio 0.067 (Fe_{RM} is the total Fe content in the RM used). After magnetization, a separate part of RM containing 33 wt.% Fe_3O_4 shows a medium ferromagnetic behavior with the saturation magnetization 29.5 emu/g and residual magnetization 5.45 emu/g. The magnetic concentrate isolated by the enrichment method with 6% yield has the highest value, 65.5 emu/g, at Fe_3O_4 content similar to that in magnetic part of leached RM, 33-34%. The coercive force decreases from 20 Oe to 10 Oe and the residual magnetization remains constant, 5.45 emu/g, as for RM.

The reductive Bayer digestion of bauxite by using as-precipitated iron powder as a reductant (Fe^0) was proposed. The results show that the growth of the amount of reductant favors the transformation of hematite to magnetite. According to the XRD analysis, the characteristic peaks of unreacted hematite and magnetite were detected in the obtained product. The relative recovery of alumina in Bayer digestion remains high, not less than 95-98%, which was achieved by an optimized process with subsequent leaching with water at 50°C. The residual alumina content in magnetized RM did not exceed 10 wt.%.

The morphology and surface elements distribution of magnetized RM was studied by SEM using a JEOL-JSM LA 6390 scanning electron microscope coupled with an energy dispersive X-ray analyzer (EDX). The hematite particles in the initial RM are nearly spherical with a fine particle size of less than 800 nm which obviously becomes finer owing to dissolution by Bayer re-digestion and re-deposition. The magnetite particles converted by hematite in Bayer process are octahedral and obviously have coarser granularity than hematite particles. **Figure 3a** shows the magnetite particles with a high degree of crystallinity and significant aggregation behavior caused probably by the high gradient effect between fine magnetite particles. Nevertheless, other particles (of hematite and calcite) have very fine granularity, and adhesion among particles occurs. Moreover, according to the EDX results in **Figure 3b**, iron is a predominant component in

the product of reductive Bayer process of bauxite, in which as-precipitated iron powder is used. The observations of crystallinity suggest that the transformation of iron minerals is responsible for the differences in the physical and chemical composition of the mud samples, which control the settling properties of RM. In the future, the predominance of magnetite over hematite in the magnetized RM sample can significantly contribute to its excellent deposition. With the use of such high crystalline product, the high gradient superconducting magnetic separation of extremely fine RM particles into a high iron content part and a low iron content part will be more effective [11].
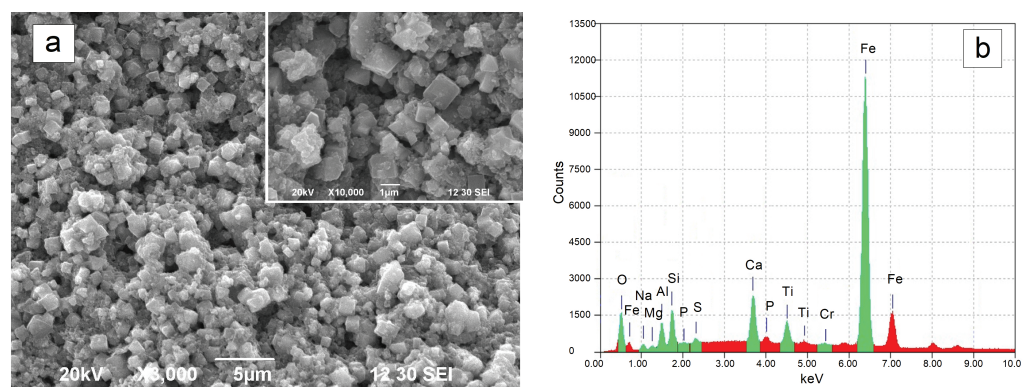

Figure 3: **a** – SEM image of magnetized RM with a magnification of ×3000 (in the insert ×10 000), **b** – EDX-spectra for the selected region

The VSM analysis using a Cryogenic VSM-5T magnetometer at room temperature (see **Figure 4**) further illustrates that the saturation magnetization of Bayer bauxite residue is only 2.9 emu/g, whereas magnetized RM shows a typical ferrimagnetism, signifying that reductive Bayer digestion promotes iron recovery from bauxite. The saturation magnetization of the bulk sample is 40.5 emu/g, two orders of magnitude higher than that of the raw red mud sample (0.34 emu/g). The saturation magnetization of the reduced sample is lower than that of magnetite concentrate [σ(MC) = 65 emu/g] and pure magnetite [σ(Fe_3O_4) = 110 emu/g] at T = 300 K. As this sample of magnetized RM contains several other mineral phases, this is quite expectable and therefore we can make a rough estimate that the sample is composed of approximately 40 wt.% magnetite. According to the X-ray analysis, the magnetite content in RM residue is increased to 40 wt.%, the initial Fe_2O_3 content in the bauxite being 25%.

The strong magnetic fractions from the magnetized RM at a varying amount of Fe(II) have been isolated under a constant magnetic field of ferrite magnet. The share of the separated strong magnetic fraction actually increases with increasing ferrous-ions dosage. Thus, a greater amount of hematite from RM is transformed to magnetite when the amount of Fe(II) additive increases. However, it should be pointed out that the

hematite phase is not completely removed since extremely fine particles could be captured in the magnetic fraction.
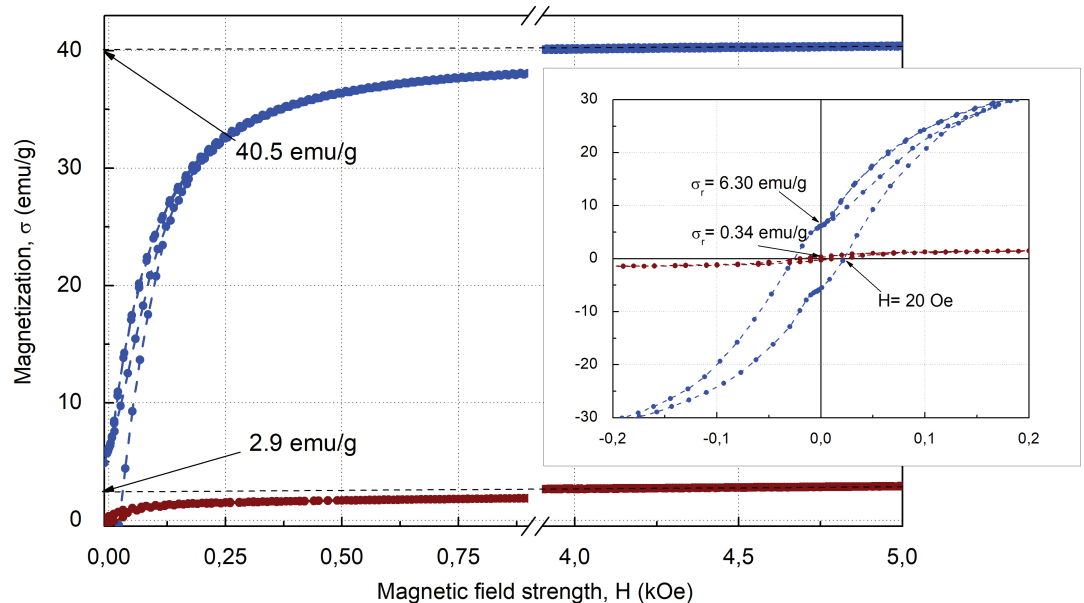
Figure 4: Part of the magnetic hysteresis loops in an extended range and the same data in a limited range measured at T = 300 K for samples of magnetized RM (blue) and initial RM (brawn); H – coercive force, Oe; σ_r – residual magnetization, emu/g.

1. Conclusions

Different iron transformations may take place in the Bayer process depending on the digestion conditions or the properties of resulting products. To minimize adverse environmental impacts, the conditions of the Bayer process should be such that the resulting red mud has nature-friendly physical properties. The red mud should also have the chemical properties that prevent leaching of red mud chemicals, accelerate the settling of particles and eliminate the amorphous content, as well as strong magnetic properties.

In this study, we have received the magnetite products with good crystallinity from both initial red mud and raw bauxite in the process of Bayer digestion simultaneously with high alumina extraction. The magnetic properties of magnetized samples show that even if the properties corresponding to the magnetite concentrate were not fully achieved, the synthesis of hematite-derived magnetite from red mud of alumina production seems quite promising. The results suggest that the conversion of hematite into magnetite during digestion of RM and bauxite can significantly enhance the magnetic property of iron minerals, laying the foundation of the separation of iron minerals in weak magnetic field from RM produced by reductive Bayer digestion.

Acknowledgements

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