Characterization of Bayer red mud from Guizhou, China

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Abstract
Bayer red mud is derived from the Bayer cycle, the major industrial approach to producing alumina from bauxite. The chemical and mineral composition of Bayer red mud varies greatly with respect to the type of bauxite ores and processing parameters. Bayer red mud from Guizhou, China, was investigated using XRF, ICP-MS and XRD. The mineral composition of Bayer red mud samples was studied using transmission electron microscope (TEM). It was found that the Guizhou Bayer red mud sample mainly consisted of vishnevite, garnet (grossularite, almandite), titanite, calcite, perovskite, larnite, iron oxides and a small amount of amorphous materials.

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Introduction

The Bayer process is the principal commercial technology to produce alumina. Red mud, also known as bauxite residue, is a major byproduct during refining aluminum ore by means of the Bayer process. For every ton of alumina produced, 1–1.5 t of red mud is generated. It is estimated that about 119 Mt of red mud was produced worldwide in 2007. In China in 2009 alone, about 30 Mt of red mud was generated, with only 4% of it utilized (Power et al., 2009; MIIT and MOST, 2010). The disposal costs as per regulations may add up to 5% of the alumina production cost (Kumar et al., 2006). Furthermore, red mud is harmful to water, land and air of the surrounding area because of its high alkalinity. The disposal of red mud remains a great environmental concern. The treatment and utilization of red mud is of environmental and economic significance.

In recent years, many studies have investigated different applications for red mud. Red mud is being used as an additive for building materials, which opens the potential to use red mud in industries such as ceramics (Sglavo et al., 2000a; Pontikes et al., 2007), cements (Tsakiridis et al., 2004) and clay bricks (Dass and Malhotra, 1990; Somlai et al., 2008).

It is essential to know the basic chemical and mineral composition of red mud for its comprehensive use in industrial applications. No report has yet been published about the mineral characterization of Bayer red mud from Guizhou, China. The objective of this investigation is to characterize Guizhou Bayer red mud, so as to provide necessary data and a scientific basis for its comprehensive use.

Materials and methods

Materials. Bayer red mud samples used in this study were provided by Guizhou Enterprise of China Aluminum Co. Ltd., which is one of the largest alumina-producing companies in China, and produces more than 1.2 Mt of red mud per year. Bayer red mud starts as slurry and then forms large hard agglomerates when dried. Before experiments, the homogeneous samples were dried at 105° C for 24 hours, then ground and milled into powders below 74 μm.

Analytical methods. The main chemical composition and trace elements of the Bayer red mud sample were determined using an Axios (PW4400) X-ray fluorescence spectroscopy (XRF) and quadrupole inductively coupled plasma mass spectrometer (ICP-MS), respectively (Gu et al., 2012). A Malvern Mastersizer 2000 laser scattering particle size distribution analyzer was used to determine the particle size distribution of Bayer red mud. X-ray diffraction (XRD) analysis of Bayer red mud was performed on a D/Max-2200 diffractometer. For microscopic observation of Bayer red mud, samples were fixed on a copper supporting net, coated with graphite and then readied for observation and identification on a TEM instrument (JEM-2000FXII, Japan) equipped with an EM-ASID20 scanning and imaging system and an energy dispersive spectroscope (Oxford Link ISIS) at a maximal accelerating voltage of 200 kV.

Results and discussion

Main chemical composition. Guizhou Bayer red mud was found to consist mainly of CaO, Al_2O_3, SiO_2, Fe_2O_3, TiO_2, Na_2O, K_2O and MgO, and it had higher CaO, Na_2O, K_2O and Al_2O_3 than those from other countries, but was lower in Fe_2O_3 (Table 1). The differences in the constituents may be attributed to the variations of bauxite ores and the specific processing conditions, such as temperature, pressure and so on. Bauxite in China, including Guizhou province, is diaspore-type bauxite, which usually contains less than 10% hematite. According to *Chinese Guidelines for Comprehensive Utilization of Red Mud*, only red mud with a high iron content (usually Fe_2O_3>30%) can

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Table 1 — Main chemical composition (wt %) of Guizhou Bayer red mud and comparison with studies in other countries.

Components	Al_2O_3	SiO_2	Fe_2O_3	CaO	TiO_2	Na_2O	K_2O	MgO	L.O.I.	Other	Total	Reference
Guizhou RM	27.45	15.86	7.23	21.58	4.93	15.94	2.89	1.44	3.53	-	100.85	Gu et al. (2012)
Spanish RM	20.20	7.50	47.85	6.22	9.91	8.40	0.11	0.33	-	-	100.52	Pascual et al. (2009)
Greek RM	19.95	6.80	40.80	12.60	5.80	2.70	0.14	0.20	10.54	0.58	100.11	Tsakiridis et al. (2009)
Greek RM	17.04	7.79	44.34	11.64	5.12	3.17	0.07	0.57	9.77	-	99.51	Pontikes et al. (2007)
Italian RM	20.00	11.60	35.20	6.70	9.20	7.50	-	0.4	7.30	2.10	100.00	Sglavo et al. (2000b)
Birac RM	14.14	11.53	48.50	3.96	5.42	7.50	0.06	0.05	7.25	0.61	99.02	Cablik (2007)

L.O.I.: Loss on ignition.

Table 2 - Concentrations of trace elements in Guizhou Bayer red mud (μg g^{-1}).

Element	Amt	Element	Amt	Element	Amt
Li	43.2	Nb	97.2	Tb	3.86
Be	7.22	Mo	13.2	Dy	21.4
Sc	82.0	Ag	2.07	Ho	4.84
V	494	Cd	0.805	Er	13.4
Cr	388	In	0.466	Tm	1.97
Co	14.8	Sn	24.6	Yb	13.0
Ni	51.4	Sb	1.97	Lu	1.98
Cu	91.2	Cs	1.59	Hf	35.9
Zn	56.1	Ba	187	Ta	7.20
Ga	42.5	La	199	W	18.6
Ge	5.51	Ce	390	Tl	0.161
As	10.7	Pr	44.2	Pb	93.7
Rb	23.1	Nd	156	Bi	2.74
Sr	1.24×10^3	Sm	29.4	Th	99.9
Y	129	Eu	5.34	U	26.1
Zr	1.29×10^3	Gd	23.6	Hg*	0.458

* Analyzed by cold vapor atom fluorescence spectrometry.

Figure 1 — Mineral crystals of vishnevite under TEM.

be processed by reduction to recover iron; therefore, low-iron oxides in Guizhou Bayer red mud (7.23%) made it impossible to recover iron under present technological constraints.

Trace element composition. Red mud is a hazardous material, but might also be considered a secondary raw material (Castaldi et al., 2008). With the exhaustion of many natural resources, some rare elements such as Ga, Sc, Y and the lanthanides in red mud could be a potential resource (Table 2), if the extraction of these elements can be made economically acceptable (Ochsenkühn-Petropulu et al., 1996).

A leaching procedure test to determine toxic characteristics such as Cr, Cu, Zn, Pb, Cd, Hg and Mn indicated that red mud from the Shandong Aluminum Corporation was not hazardous (Zhao et al., 2009). However, the metal concentrations, leachable metals and leachable ratios of red mud could vary from plant to plant, along with the mineral origins, occurrence states and amounts of toxic metals contained.

The concentration of Th and U in Guizhou Bayer red mud was 99.9 and 26.1μg g^{-1}, respectively. The dominant source of natural radioactivity in red mud is based on the presence of Th and U (Akinci and Artir, 2008). Due to Th, U and members of their decay chains, red mud may emit ionizing radiation above natural background levels, which restricts it from use as an additive for building materials.

Particle characteristics. Particle analysis showed that 10% of the red mud grains had a particle size below 1.146 μm, 50% below 5.897 μm, and 90% below 36.663 μm. The red mud had a specific surface area of 1.46 $m^2 g^{-1}$, with a mean surface diameter of 2.932 μm and a mean volume diameter of 13.224 μm. The particles of red mud were aggregated with multiple fine grains having different constituents.

Mineral composition. Mineral composition of red mud mainly depends on the mineral composition of the source material – bauxite. Bauxite is a multiphase ore that may contain more than one hundred minerals (Cablik, 2007). The major mineral phases of Guizhou red mud include vishnevite, calcite, tiantanite, perovskite, larnite, kaolinite, quartz and a few amorphous materials.

TEM analysis. Silicates, aluminosilicates, iron oxides and oxyhydroxides, and titanium oxides were the major constituents of Guizhou Bayer red mud. The most common mineral that appeared under TEM was vishnevite, with a short six-sided prism (Fig. 1). Vishnevite is one of the cancrinite group minerals, and its chemical formula is $(Na,K)_8[AlSiO_4]_6(SO_4)\cdot nH_2O$.

Besides aluminosilicates, Al-containing minerals in the sample existed as oxides and hydrates, such as corundum, diaspore (α-AlOOH), gibbsite ($Al(OH)_3$) and boehmite (γ-AlOOH) (Gräfe et al., 2009). Corundum (with a table-shaped feature) formed during Bayer processing, whereas aluminum hydrates could be residues from bauxite ores.

There were several kinds of calcium minerals in the Bayer red mud, such as calcium silicate, calcium carbonates, calcium sulfates and perovskite. Calcite was newly formed during the Bayer process.

Titanite is a calcium titanium nesosilicate mineral, occurring as a common accessory mineral in many igneous rocks. Trace impurities of iron and aluminum are typically present in titanite. Titanium, which was also observed in perovskite and rutile, could be partly replaced in titanite from Bayer red mud by iron and aluminum. Perovskite usually had a small crystal size, with complicated components (Figs. 2 and 3), some of which contained zirconium, strontium and trace impurities of thorium and REE. Some rutile minerals in this study contained trace niobium and iron.

Zircon and monazite, which are usually regarded as the source of natural radioactivity in Bayer red mud, were found under TEM. Quartz in Bayer red mud was metamict, with small spots on the surface of minerals. Halite was one of the trace phases in Bayer red mud, as well as gypsum, which was present as plate-like crystal (Fig. 4). Xenotime, cassiterite,

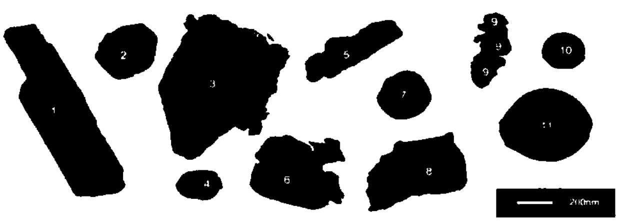

Figure 2 — TEM photograph of minerals in Guizhou Bayer red mud. 1: vishnevite, 2: titanite, 3: fluorapatite, 4: monazite, 5: cassiterite, 6: grossularite $Ca_3Al_2[SiO_4]_3$, 7: smithsonite, 8: perovskite, 9: oxides of Ni, Cr, Zn, Fe, Cu, Mo, 10-11: glass.

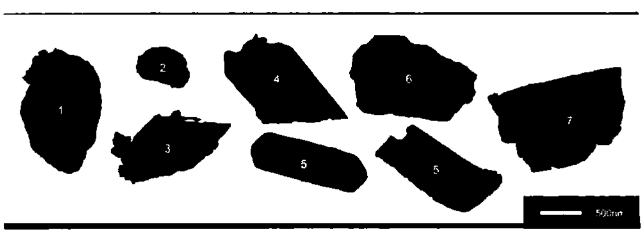

Figure 3 — TEM photograph of minerals in Guizhou Bayer red mud. 1: corundum, 2: perovskite, 3: rutile, 4: calcite, 5: zircon, 6: xenotime, 7: gypsum.

Figure 4 — TEM photograph of minerals in Guizhou Bayer red mud. 1: quartz, 2: halite, 3: almandite.

smithsonite and amorphous phases were also observed under TEM as minor or trace constituents in Bayer red mud.

Conclusions

Bayer red mud from Guizhou was found to consist of CaO, Al_2O_3, SiO_2, Fe_2O_3, TiO_2, Na_2O, K_2O and MgO. It is difficult to recover iron from Guizhou Bayer red mud because of its low concentration. The mud also contained complex trace elements, of which some may be economically valuable, while others could be hazardous to the environment. The natural radioactive elements (Th and U) in Bayer red mud were as high as 99.9 and 26.1 $\mu g\ g^{-1}$, respectively.

The mineral composition of Guizhou Bayer red mud is complex. The major minerals are vishnevite, garnet, titanite, calcite, perovskite, larnite and iron oxides; the minor minerals are zircon, monazite, xenotime and cassiterite. The amount of minerals in Guizhou Bayer red mud was similar to other clays. It can be mixed with other raw materials for building materials.

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