Waste Management & Research
http://wmr.sagepub.com/

Radiological restrictions of using red mud as building material additive

Hannian Gu, Ning Wang and Shirong Liu

Waste Manag Res 2012 30: 961 originally published online 29 June 2012
DOI: 10.1177/0734242X12451308

Short Report

Waste Management & Research
30(9) 961–965
© The Author(s) 2012
Reprints and permission:
sagepub.co.uk/journalsPermissions.nav
DOI: 10.1177/0734242X12451308
wmr.sagepub.com

Radiological restrictions of using red mud as building material additive

Hannian Gu,[1,2] Ning Wang[1] and Shirong Liu[3]

Abstract

Red mud remains as residue from the processing of bauxite using different methods. The chemical composition of red mud varies widely with respect to the types of bauxite ore and processing parameters. Red mud samples from Guizhou, China, were investigated using a X-ray fluorescence spectroscope, a quadrupole inductively coupled plasma mass spectrometer and a electron probe microanalyzer. The results showed that red mud consisted of eight main chemical components—CaO, Al_2O_3, SiO_2, Fe_2O_3, TiO_2, Na_2O, K_2O and MgO—and dozens of trace elements, including natural radioactive elements, such as uranium and thorium. Gamma spectrometric analysis showed that the values of internal exposure index I_{Ra} and external exposure index I_γ of Guizhou red mud were 1.1–2.4 and 2.3–3.5 respectively. Thus, it should not be used as a main building material indiscriminately. The amount of red mud from Guizhou when it is used for main building materials in China should be less than 28–44%.

Keywords

Red mud, natural radioactivity, building materials, dose exposure, utilization

Introduction

Red mud is a major waste by-product of bauxite processing for alumina production. According to the different processing methods, red mud can be classified as Bayer red mud (BRM) and red mud from sintering alumina process (RMS). In 2007, the annual production of red mud was estimated at 119 million tonnes and the global inventory had risen to 2.6 billion tonnes (Power et al., 2009). In China, there were nearly 30 million tonnes of red mud produced in 2009, with only 4% of them being utilized. Furthermore, the total quantity of red mud in China was over 200 million tonnes as of 2009 (MIIT and MOST, 2010). The treatment and utilization of red mud is of environmental and economic significance.

Mixing red mud with other additives for building materials, such as ceramics, cement and clay bricks, are thought to be a potential of utilization for red mud in bulk. However, the natural radioactive elements (such as uranium and thorium) from bauxite ore transfer to red mud and restrict the use of red mud as building materials or additives. More than 80% of thorium and uranium in the bauxite is concentrated in the red mud (Adams and Richardson, 1960). Red mud from Shandong, China, was reported to not meet the regulations of Chinese safety limits for radioactivity of main materials or internal materials for buildings (Zhao et al., 2009). Red mud in Hungary was limited in building materials (bricks) to less than 15%; otherwise, brick production would contain enhanced levels of natural radioactivity (Somlai et al., 2008).

The chemical composition of red mud is important for industrial applications (Atasoy, 2005). Guizhou is one of the biggest alumina industrial provinces in China and produces more than 1.2 million tonnes of red mud per year. It is essential to know the main chemical composition and trace element composition of Guizhou red mud for comprehensive utilization. Therefore, the objective of this study was to characterize and radiologically examine different types of red mud from Guizhou.

Materials and methods

Materials

Red mud samples from three companies in Guizhou, China, were examined in this study. The samples from Guizhou Enterprise of China Aluminum Co., Ltd (GZHE) were slurry and fresh, and included BRM and RMS. Samples from Kaili Aluminum Plant (KLAP) and Pingba Aluminum Plant (PBAP) were both produced by the Bayer process. The homogeneous solid samples had

---

[1] Laboratory for Study of the Earth's Interior and Geofluids, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, Guizhou, PR China
[2] Graduate University of Chinese Academy of Sciences, Beijing, PR China
[3] State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, Guizhou, PR China

Corresponding author:
Ning Wang, Laboratory for Study of the Earth's Interior and Geofluids, Institute of Geochemistry, Chinese Academy of Sciences, 46 Guanshui Road, Guiyang City, Guizhou 55002, PR China
Email: nwangig@163.com

Table 1. Main chemical composition of Guizhou red mud samples

Samples		Chemical composition (wt %)									
		Al_2O_3	SiO_2	Fe_2O_3	CaO	TiO_2	Na_2O	K_2O	MgO	L.O.I.	Total
BRM	KLAP	33.20	16.68	8.24	19.59	4.33	16.23	0.61	0.71	1.71	101.30
	PBAP	20.04	14.32	15.99	20.03	5.45	9.15	1.96	0.87	12.33	100.14
	GZHE-01	27.25	15.69	7.74	21.49	4.83	15.41	2.84	1.72	3.83	100.80
	GZHE-02	27.45	15.86	7.23	21.58	4.93	15.94	2.89	1.44	3.53	100.85
RMS	GZHE-01	10.84	20.41	9.06	34.29	4.10	5.29	1.22	1.18	14.05	100.44
	GZHE-02	7.37	20.61	9.22	37.52	4.02	4.84	1.10	1.39	14.60	100.67

BRM, Bayer red mud; RMS, red mud from sintering alumina process; KLAP, Kaili Aluminum Plant; PBAP, Pingba Aluminum Plant; GZHE, Guizhou Enterprise of China Aluminum Co., Ltd; L.O.I, loss on ignition.

to be ground and milled to a smaller size before characterization and radiological examinations.

Analytical methods

The main chemical composition and trace element composition of red mud samples were determined using X-ray fluorescence spectroscope (XRF) and quadrupole inductively coupled plasma mass spectrometer (ICP-MS) respectively. A back-scattered electron image was obtained by Shimadzu EPMA-1600 (Shimadzu Corporation, Japan) electron probe micro-analyzer (EPMA) at an accelerating voltage of 25 kV and a beam current of 4.5 nA, and energy-dispersive X-ray spectroscopy analysis was carried out by Genesis EDAX. The analyses of XRF, ICP-MS and EPMA were performed at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (IGCAS).

Gamma spectroscopy is a non-destructive analytical technique used for measuring and calculating the activity of natural and artificial radioisotopes in solid and liquid samples of various types. A multi-channel gamma spectrometry (Canberra S-100) with a high purity germanium (HPGe) detector was used. The experiment on the activity concentration of natural radionuclides was executed at State Key Laboratory of Environmental Geochemistry, IGCAS.

Results and discussion

Main chemical composition

The red mud samples consisted mainly of Al_2O_3, SiO_2, Fe_2O_3, CaO, TiO_2, Na_2O, K_2O and MgO (Table 1). RMS contained higher CaO, but BRM contained higher Na_2O and Al_2O_3. This was because the sintering alumina process added more limestone but less NaOH (or Na_2CO_3) than the Bayer process. The aluminum recovery from the bauxite ore in the Bayer process was lower than that in the sintering alumina process, so Bayer red mud usually contained more Al_2O_3 than red mud from sintering alumina process. Red mud from Guizhou had higher concentrations of CaO, K_2O and MgO than those from other countries (Table 2), but had lower concentrations of Fe_2O_3, of which the content was usually less than 10%, except the sample from PBAP, which contained 15.99% Fe_2O_3.

Trace element composition

The number of trace elements that was detected in red mud by ICP-MS was about 50 (Table 3). With the exhaustion of many natural resources, some rare elements, such as gallium, scandium, yttrium and the lanthanides, in red mud could be a potential future resource if the extraction of these elements can be economically viable (Ochsenkühn-Petropulu et al., 1996). Trace metals in red mud may exceed regulatory levels in certain circumstances (Gräfe et al., 2010). The toxicity characteristic leaching procedure test for chromium, copper, zinc, lead, cadmium, mercury and manganese indicated that red mud from Shandong was not hazardous (Zhao et al., 2009). However, red mud could vary in the leaching potential because of the occurrence states and the amounts of toxic heavy metals contained. Threats to human health and living organisms from toxic heavy elements in red mud could still exist.

The dominant source of natural radioactivity in red mud is based on the presence of thorium and uranium (Akinci and Artir, 2008). In this study, the thorium and uranium content in Guizhou

Table 2. Chemical composition of red mud (RM) from different countries

Components (wt%)	Al_2O_3	SiO_2	Fe_2O_3	CaO	TiO_2	Na_2O	K_2O	MgO	L.O.I.	Other	References
Spanish RM	20.20	7.50	47.85	6.22	9.91	8.40	0.11	0.33	–	–	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	Tsakiridis, et al. (2004)
Greek RM	17.04	7.79	44.34	11.64	5.12	3.17	0.07	0.57	9.77	–	Pontikes, et al. (2007)
Italian RM	20.00	11.60	35.20	6.70	9.20	7.50	–	0.40	7.30	2.10	Sglavo, et al. (2000)
Birac RM	14.14	11.53	48.50	3.96	5.42	7.50	0.06	0.05	7.25	0.61	Cablik (2007)

L.O.I., loss on ignition.

Table 3. Trace element composition of Guizhou red mud samples

Samples (μg g^{-1})	Li	Be	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As
KLAP-BRM	28.2	3.73	53.2	654	514	6.18	31.5	31.9	33.3	85.7	3.20	13.7
PBAP-BRM	53.2	4.94	88.5	316	322	26.2	79.3	159	56.2	56.2	8.84	40.3
GZHE-BRM	43.2	7.22	82.0	494	388	14.8	51.4	91.2	56.1	42.5	5.51	10.7
GZHE-RMS	162	9.41	74.7	332	345	23.7	77.3	107	110	27.9	5.36	26.1

	Rb	Sr	Y	Zr	Nb	Mo	Ag	Cd	In	Sn	Sb	Cs
KLAP-BRM	8.53	333	71.9	2050	93.3	8.57	1.36	0.499	0.398	–	5.50	1.33
PBAP-BRM	26.4	1180	216	1650	135	4.12	2.06	1.05	0.530	–	5.52	2.57
GZHE-BRM	23.1	1024	129	1290	97.2	13.2	2.07	0.805	0.466	24.6	1.97	1.59
GZHE-RMS	28.7	1054	152	1330	107	8.13	2.65	0.618	0.468	17.7	3.15	2.48

	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er
KLAP-BRM	124	40.1	88.8	9.47	34.0	8.17	1.94	9.11	1.83	11.6	2.59	8.37
PBAP-BRM	1380	365	714	76.2	281	56.0	10.2	45.4	7.27	38.6	7.61	23.1
GZHE-BRM	187	199	390	44.2	156	29.4	5.34	23.6	3.86	21.4	4.84	13.4
GZHE-RMS	297	260	529	57.9	214	39.6	7.72	36.5	5.12	29.5	5.99	17.9

	Tm	Yb	Lu	Hf	Ta	W	Tl	Pb	Bi	Th	U
KLAP-BRM	1.31	9.56	1.50	50.0	5.45	24.0	0.129	47.4	1.88	98.5	17.1
PBAP-BRM	3.44	22.0	3.22	41.0	7.96	24.1	0.354	272	4.53	176	44.1
GZHE-BRM	1.97	13.0	1.98	35.9	7.20	18.6	0.161	93.7	2.74	99.9	26.1
GZHE-RMS	2.52	16.9	2.50	39.7	9.11	8.42	0.0894	92.7	1.39	121	34.9

KLAP-BRM, Kaili Aluminum Plant-Bayer red mud; PBAP-BRM, Pingba Aluminum Plant-Bayer red mud; GZHE-BRM, Guizhou Enterprise of China Aluminum Co., Ltd-Bayer red mud; GZHE-RMS, Guizhou Enterprise of China Aluminum Co., Ltd-red mud from sintering alumina process.

red mud was 98.5–176 μg g^{-1} and 17.1–44.1 μg g^{-1}, respectively, which is about 10 times higher than their abundance in the continental lithosphere in China (7.15 μg g^{-1} and 2.43 μg g^{-1} respectively) (Li and Ni, 1997). Red mud from Guizhou may emit ionizing radiation above natural background level owing to the high concentration of thorium and uranium, and members of their decay chains. Red mud is a valuable industry by-product that has the potential to be re-used in construction; however, its natural radioactivity has to be addressed.

Morphological characteristics

The particles of red mud were aggregated, with many different constituents existing as very fine particles. The main mineral compositions of BRM from GZHE were aluminosilicates (Figure 1). The mineral composition of red mud depends on the mineral composition of the source material—bauxite ore. Bauxite is a multiphase ore that may contain, according to some references, more than 100 minerals (Cablik, 2007). The mineral composition of red

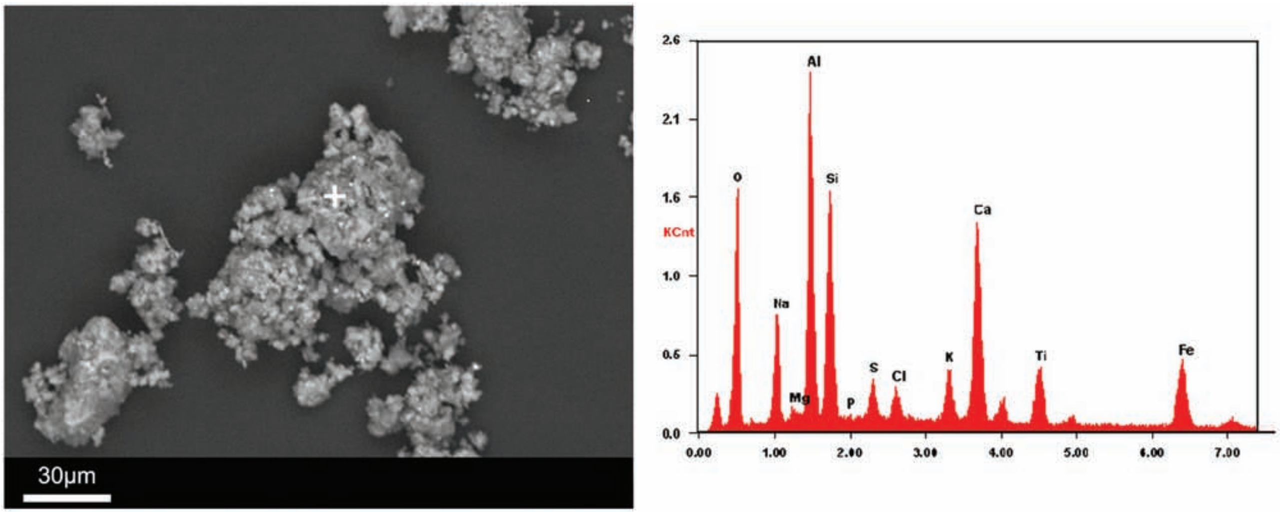

Figure 1. Back-scattered electron micrograph and energy-dispersive X-ray spectroscopy analysis of the particles of Bayer red mud (BRM) from Guizhou Enterprise of China Aluminum Co., Ltd (GZHE).

mud is complex. It is difficult to determine the minerals or amorphous phases hosting radioactive elements.

Gamma spectroscopy results

Rocks minerals and building materials contain various amounts of natural radioactive nuclides [also referred to as naturally occurring radioactive material (NORM)], mainly including ^{238}U, ^{232}Th, ^{40}K (Kovler, 2009; Somlai et al., 2008). In the uranium series, the decay chain segment starting from radium (^{226}Ra) is radiologically the most important and, therefore, reference is often made to radium instead of uranium (Kovler, 2009). The activity safety limits value for building materials can be calculated in China using equations (1) and (2):

$$I_{Ra} = \frac{C_{Ra}}{200} \tag{1}$$

$$I_{\gamma} = \frac{C_{Ra}}{370} + \frac{C_{Th}}{260} + \frac{C_K}{4200} \tag{2}$$

where C_{Ra}, C_{Th} and C_k are the radium, thorium and potassium activity concentrations (Bq kg^{-1}) in building material, I_{Ra} and I_{γ} are the internal and external exposure indices respectively (AQISQ and SAC, 2010). For main building materials, the values of I_{Ra} and I_{γ} must be less than 1.0.

Activity concentrations in Guizhou red mud samples determined by gamma spectroscopy are given in Table 4. I_{Ra} and I_{γ} 1.1–2.4 and 2.3–3.5 respectively. According to Chinese National Standards (AQISQ and SAC, 2010), none of the red mud samples could be used as main building materials without limit.

Calculation of restrictions in construction

Guizhou red mud cannot be used as a main building material directly, but can be used as building material additive within a safety limit. Red mud mixed with bauxite, lime, fly ash and gypsum are suitable for bricks, tiles and cement with a good bonding capacity (Somlai et al., 2008). When supposing that the other ingredients mixed in the main building materials have no radiological effect, the amounts of the red mud from Guizhou can be estimated. The ratio of red mud added in main building materials can be calculated using equations (3) and (4):

$$\frac{f_s \cdot C_{Ra} + (1-f_s)\cdot C_{Ra}^{'}}{200} \le 1.0 \tag{3}$$

$$\frac{f_s \cdot C_{Ra} + (1-f_s)\cdot C_{Ra}^{'}}{370} + \frac{f_s \cdot C_{Th} + (1-f_s)\cdot C_{Th}^{'}}{260} + \frac{f_s \cdot C_K + (1-f_s)\cdot C_K^{'}}{4200} \le 1.0 \tag{4}$$

where f_s is the ratio of red mud in the building products; C_{Ra}, C_{Th} and C_k are the radium, thorium and potassium activity concentrations (Bq kg^{-1}) of red mud; and C'_{Ra}, C'_{Th} and C'_k are the radium, thorium and potassium activity concentrations (Bq kg^{-1}) of other materials, except in red mud in building products (AQISQ and SAC, 2010).

Based on the above, for main building material production in China, 28–44% of Guizhou red mud can be used. If a greater mixing ratio is used, the criteria $I_{Ra} \le 1.0$, $I_{\gamma} \le 1.0$ would not be complied with.

The more red mud that is added to main building materials, the more the cost will be reduced for construction companies. According current Chinese policy, if industrial waste, such as red mud, was utilized in a product at a rate of >30%, the product can enjoy preferential tax policies. However, in case of amounts exceeding 30% in building materials, the limits for the value of I_{Ra} or I_{γ} would not be complied with. Therefore, construction companies have no positive attitude toward using red mud as building material additive.

Table 4. Activity concentration of natural radionuclides in Guizhou red mud samples and their calculated internal exposure indices and external exposure indices

		Specific activity (Bq kg^{-1})			I_{Ra}	I_{γ}
		^{226}Ra	^{232}Th	^{40}K		
BRM	KLAP	225.3 ± 7%	422.2 ± 10%	163.8 ± 9%	1.1	2.3
	PBAP	477.8 ± 5%	555.3 ± 10%	400.9 ± 8%	2.4	3.5
	GZHE-01	350.4 ± 6%	414.0 ± 10%	583.0 ± 8%	1.8	2.7
	GZHE-02	369.9 ± 6%	437.2 ± 10%	505.0 ± 8%	1.8	2.8
RMS	GZHE-01	427.7 ± 6%	521.0 ± 10%	160.1 ± 9%	2.1	3.2
	GZHE-02	388.8 ± 6%	468.0 ± 10%	405.2 ± 9%	1.9	2.9
	GZHE-03	424.0 ± 6%	462.9 ± 10%	237.5 ± 9%	2.1	3.0
	GZHE-04	322.7 ± 6%	369.3 ± 10%	225.7 ± 8%	1.6	2.3
	GZHE-05	416.9 ± 6%	421.4 ± 10%	395.5 ± 8%	2.1	2.8
	GZHE-06	439.1 ± 6%	472.2 ± 10%	262.4 ± 9%	2.2	3.1

BRM, Bayer red mud; RMS, red mud from sintering aluminum process; KLAP, Kaili Aluminum Plant; PBAP, Pingba Aluminum Plant; GZHE, Guizhou Enterprise of China Aluminum Co., Ltd.

Conclusions

The results of the study show that the main chemical components of Guizhou red mud were CaO, Al_2O_3, SiO_2, Fe_2O_3, TiO_2, and Na_2O, together with minor components, such as K_2O and MgO. There were no differences in the types of chemical composition, but significant differences in the amounts of different chemicals between BRM and RMS were found. The concentrations of Fe_2O_3 detected in Guizhou red mud were much lower than those from other countries. It also contained complex trace elements of which some elements may be economically valuable, whereas others could be hazardous to environment.

Gamma spectrometric analysis showed that the I_{Ra} and I_γ values of Guizhou red mud were 1.1–2.4 and 2.3–3.5 respectively. According to Chinese National Standards, Guizhou red mud was added to main building material production at a maximum of 28–44 wt%. It is reasonable to check the ingredients or the product from a radiological aspect in all cases.

Funding

This research work related to this article was financially supported by Guizhou Provincial Science and Technology Foundation (No.J [2012] 2329).

References

Adams JAS and Richardson KA (1960) Radioactivity of aluminum metal. *Economic Geology* 55; 1060–1063.

Akinci A and Artir R (2008) Characterization of trace elements and radionuclides and their risk assessment in red mud. *Materials Characterization* 59: 417–421.

AQSIQ (General Administration of Quality Supervision, Inspection and Quarantine of P.R.C.) and SAC (Standardization Administration of P.R.C.) (eds) (2010) *Limits of Radionuclide in Building Materials GB 6566-2010*. Beijing: AQSIQ and SAC, pp. 1–3.

Atasoy A (2005) An investigation on characterization and thermal analysis of the Aughinish red mud. *Journal of Thermal Analysis and Calorimetry* 81: 357–361.

Cablik V (2007) Characterization and applications of red mud from bauxite processing. *Gospodarka Surowcami Mineralnymi* 23: 27–38.

Gräfe M, Landers M, Tappero R, Klauber C, Hutomo G, Gan B, et al. (2010) Chemistry of trace and heavy metals in bauxite residues (red mud) from Western Australia. In: *2010 19th World Congress of Soil Science, Soil Solutions for a Changing World*, pp. 3–5. 1-6 August 2010, Brisbane, Australia. Warragul, Victoria, Australia: Australian Society of Soil Science Incorporated.

Kovler K (2009) Radiological constraints of using building materials and industrial by-products in construction. *Construction and Building Materials* 23: 246–253.

Li T and Ni S (1997) Element abundances of the continental lithosphere in China. *Geology and Prospecting* 33: 31–37 [in Chinese].

MIIT (Ministry of industry and information technology of P.R.C.) and MOST (Ministry of science and technology of P.R.C.) (eds) (2010) Chinese guidelines for comprehensive utilization of red mud. Available at: http://www.miit.gov.cn/n11293472/n11293832/n12843926/13509788.html (accessed 8 October 2011.)

Ochsenkühn-Petropulu M, Lyberopulub T, Ochsenkühn KM and Parissakis G. (1996) Recovery of lanthanides and yttrium from red mud by selective leaching. *Analytica Chimica Acta* 319: 249–254.

Pascual J, Corpas F, López-Beceiro J, Benítez-Guerrero M and Artiaga R. (2009) Thermal characterization of a Spanish red mud. *Journal of Thermal Analysis and Calorimetry* 96: 407–412.

Pontikes Y, Nikolopoulos P and Angelopoulos GN (2007) Thermal behaviour of clay mixtures with bauxite residue for the production of heavy-clay ceramics. *Journal of the European Ceramic Society* 27: 1645–1649.

Power G, Gräfe M and Klauber C (2009) Review of current bauxite residue management, disposal and storage: practices, engineering and science. DMR-3608, pp. 3-4. Waterford, WA, Australia: CSIRO-Minerals.

Sglavo VM, Campostrini R, Maurina S, Carturan G, Monagheddu M, Budroni G and Cocco G (2000). Bauxite 'red mud' in the ceramic industry. Part 1: thermal behaviour. *Journal of the European Ceramic Society* 20: 235–244.

Somlai J, Jobbágy V, Kovács J, Tarján S and Kovács T (2008) Radiological aspects of the usability of red mud as building material additive. *Journal of Hazardous Materials* 150: 541–545.

Tsakiridis PE, Agatzini-Leonardou S and Oustadakis P (2004) Red mud addition in the raw meal for the production of Portland cement clinker. *Journal of Hazardous Materials* 116: 103–110.

Zhao Y, Wang J, Liu C, Luan Z, Wei N and Liang Z (2009) Characterization and risk assessment of red mud derived from the sintering alumina process. *Fresenius Environmental Bulletin* 18: 989–993.