Chemistry of trace and heavy metals in bauxite residues (red mud) from Western Australia

Markus Gräfe[A], Matthew Landers[A], Ryan Tappero[B], Craig Klauber[A], Grace Hutomo[A], Bee Gan[A], Alton Grabsch[A], Peter Austin[A], and Ian Davies[A]

[A]CSIRO-Processing Scie nce & Engineering, Australian Minerals Research Centre, 7 Conlon Street, Waterford – WA, 6122, Australia.
[B]Beamline X-27A, National Synchrotron Light Source, Brookhaven National Laboratory, 75 Brookhaven, Bldg. 725B, Upton – New York, 11973-5000 USA.

Introduction

Bauxite residue is a mineral slurry left behind after extracting alumina from bauxitic ores using the Bayer process. Bauxite residues are strongly alkaline, have a high salt content and electrical conductivity (EC) dominated by sodium (Na^+), and its constituent particles are compacted upon drying imparting a high bulk density. By the year 2000, the alumina industry had produced circa 2 billion tons (Bt) of bauxite residue and is estimated to reach the 4 Bt mark at its current production rate by 2015 (Power *et al.* 2009). Amongst refiners and stakeholders of alumina refineries, it is well accepted that continued production of alumina is dependent upon a reliable, long-term disposal system for bauxite residues. Therefore, significant efforts have been undertaken over the past 25 years to find suitable utilization options, other than storage. In particular, utilization as a soil amendment or conversion into soil are high priority as they would enable a high-tonnage end-use outside of existing bauxite residue disposal areas (Klauber and Gräfe 2009).

For many bauxite residues, trace metals can be of concern and may exceed regulatory levels in certain circumstances (Goldstein and Reimers 1999; Anon 2000; Kutle *et al.* 2004). Some bauxite residues may emit ionising radiation above natural background rates due to the presence of naturally occurring radioactive materials (NORMs): ^{238}U and/or $^{228,\,230,\,232}Th$ and members of their decay chains (Bardossy and Aleva 1990; Pinnock 1991; von Philipsborn and Kuhnast 1992; Wong and Ho 1993; McPharlin *et al.* 1994; Cooper *et al.* 1995; Somlai *et al.* 2008). Little is known about the speciation of various metals and NORMs in bauxite residues, particularly with regard to pH neutralisation and the accompanying changes in the mineral and solution phases (Patel *et al.* 1986; Goldstein and Reimers 1999; Kutle *et al.* 2004). Potentially toxic metals and NORMs arise via the original bauxite, therefore, bauxite residues from different bauxitic ores are likely to vary in type and concentration of respective metal species. Thus, any single study is limited in its scope to the origin of the bauxite and the processing conditions at a particular alumina refinery. In this study, we are investigating bauxite residue from an alumina refiner processing Darling Range (Western Australia) bauxite in a low temperature (~ 145^{o}C) digest.

Aims and Objectives

The aim of this study is to provide a comprehensive description of the speciation of potentially toxic metals and NORMs and their mineralogical settings. To achieve this, the objectives are to determine the mineralogy of untreated and treated bauxite residues employing a suite of techniques including quantitative X-ray diffraction, optical microscopy, QEMScan (quantitative evaluation of mineralogy by scanning electron microscopy) and TEM. A synchrotron-based X-ray microprobe (X27A, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York) is used to overcome detection limits using the conventional techniques and to determine the chemical speciation of various metals and NORMS using X-ray absorption fine structure (μXAFS) spectroscopy at the micrometer scale. In this study we will show results of untreated bauxite residues from dust development experiments probed at three depths in drained and non-drained residue drying configurations.

Results from conventional laboratory analyses

The untreated bauxite residue, expressed as oxide wt %, were composed of primarily iron (56 wt %), aluminium (15 wt %), sodium (3.8 wt %), titanium (4.5 wt %), silica (5.0 wt %) and calcium (1.25 wt %). The potentially harmful metals in these samples are, *inter alia*, V (1270 mg/kg), Cr (615 mg/kg), Ga (90 mg/kg), As (35 mg/kg), Th (30 mg/kg) and U (3 mg/kg). Quantitative X-ray diffraction analysis (Figure 1) revealed that the samples are circa 50 % X-ray amorphous. The crystalline constituents are composed of up to 80% goethite and hematite, some quartz (3-5 wt%), rutile/anatase and ilmenite (1-2 wt %) and many minor phases remnant from the original bauxite ore (e.g., mica, boehmite) and some newly formed under the conditions of the Bayer process (e.g., natroalunite, noselite). Upon contact with water, these solids will impart a pH of circa 12.8.

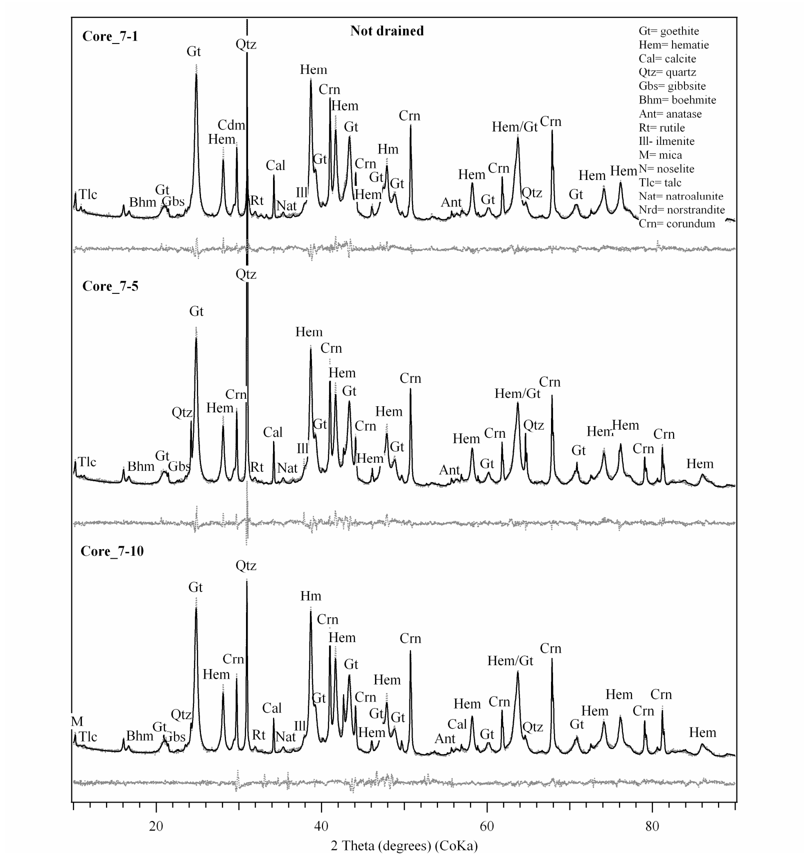
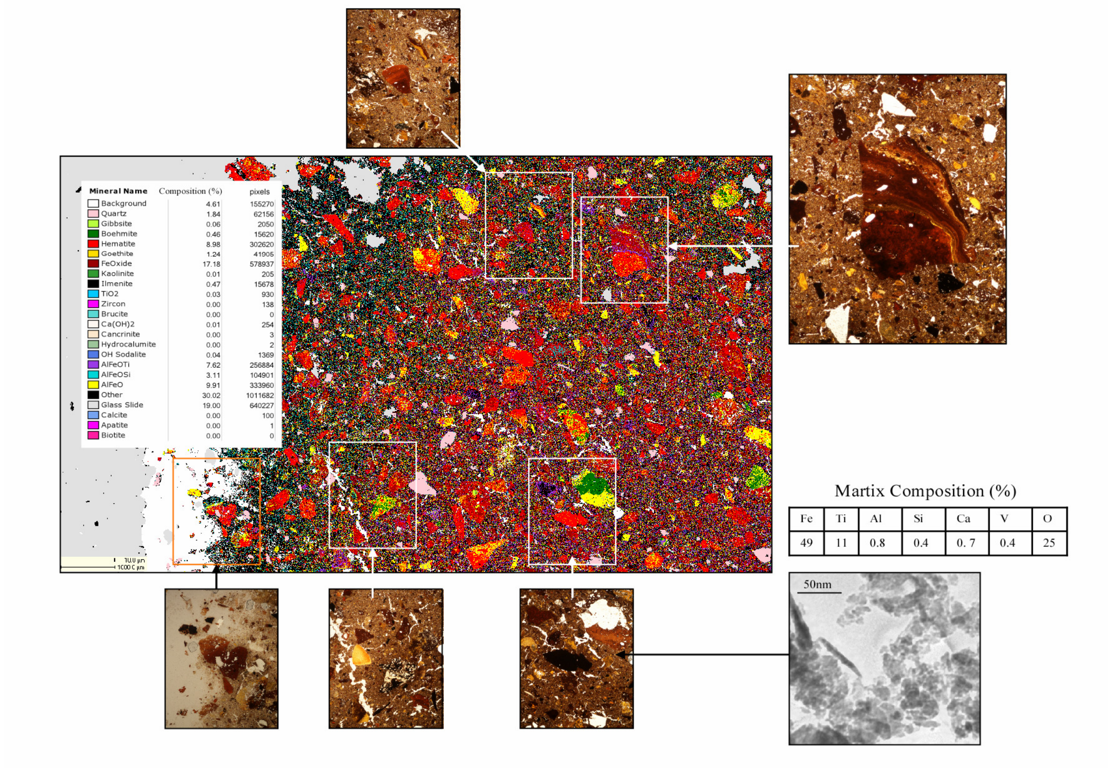


Figure 1. Quantitative X-ray diffraction analysis of core segments 7-1, 7-5 and 7-10 using the Rietveld method. Corundum was used as internal standard (~10 wt %). On average, each sample contained approximately 50 wt % X-ray amorphous phases. Of the 50 % X-ray crystalline material, 40-50% is goethite and 20-30 % is hematite. Both Fe-oxide phases display displacement of XRD reflections to higher degree 2 theta values indicating isomorphous substitution of Fe by a smaller cation in the octahedral cavity. The remaining phases are present at less than 5 wt %.

QEMScan and optical microscopy analyses of the micron size fraction show intimate associations of Fe, Al and Ti oxide particles existing as adjacent layers to each other, which are easily identifiable with an optical microscope (Figure 2). The QEMScan analysis suggests that these layers are composed of hematite, goethite, boehmite, and un-identifiable AlFeTi and AlFeTiSi rich oxides. These particles are remnants from the undissolved bauxite ore, while the sub-micron particles cement these larger particles into massive, hard agglomerates. Transmission electron microscopy with EDS and selected area electron diffraction (SAED) revealed that the cementing agents are between 5 and 20 nm in size, do not diffract, and are composed primarily of Fe with minor elemental contents of Al, Ti, Si, Ca and V.



Mineral Name	Composition (%)	pixels
☐ Background	4.61	155270
Quartz	1.84	62156
Gibbsite	0.06	2050
Boehmite	0.46	15620
🟥 Hematite	8.98	302620
Goethite	1.24	41905
FeOxide	17.18	578937
Kaolinite	0.01	205
■ Ilmenite	0.47	15678
TiO2	0.03	930
Zircon	0.00	138
Brucite	0.00	0
Ca(OH)2	0.01	254
Cancrinite	0.00	3
Hydrocalumite	0.00	2
OH Sodalite	0.04	1369
AlFeOTi	7.62	256884
AlFeOSi	3.11	104901
🟨 AlFeO	9.91	333960
■ Other	30.02	1011682
Glass Slide	19.00	640227
Calcite	0.00	100
Apatite	0.00	1
Biotite	0.00	0

Martix Composition (%)

Fe	Ti	Al	Si	Ca	V	O
49	11	0.8	0.4	0. 7	0.4	25

Figure 2. QEMScan and optical microscopy analyses of a 10-μm thin section from core 7-1 (0-2 cm, undrained and not treated) show close geochemical association of Fe, Al and Ti. The sub-micron particles as shown in the TEM image in the bottom right show particles of 5-20 nm in size composed primarily of Fe and some Ti, Si, Ca and V.

Further data collected from the X-ray microprobe X27A at the National Synchrotron Light Source will be shown focusing on the speciation of trace and heavy metals, and NORMs. To the best of our knowledge, this work represents the first X-ray microprobe work on bauxite residues (Gräfe *et al.* 2009).

References

Anon (2000) Australian and New Zealand guidelines for fresh and marine water quality. *In* Australian and New Zealand Environment and Conservation Council, Agriculture and Resource Management Council of Australia and New Zealand Eds.), Vol. 1. Australian and New Zealand Environment and Conservation Council, Canberra.

Bardossy G, Aleva GJJ (1990) Lateritic Bauxites. Elsevier, Amsterdam.

Cooper MB, Clarke PC, Robertson W, McPharlin IR, Jeffrey RC (1995) An investigation of radionuclide uptake into food crops grown in soils treated with bauxite mining residues. *J. Radioanal. Nucl. Chem.* **194**, 379-387.

Goldstein GL, Reimers RS (1999) Trace element partitioning and bioavailability in red mud synthetic freshwater sentiment. In 'Light Metals' (Eckert, CE), pp. 19-24. TMS, San Diego.

Gräfe M, Power G, Klauber C (2009) Literature review of bauxite residue alkalinity and associated chemistry. DMR-3610, pp. 1-49. CSIRO-Minerals, Waterford.

Klauber C, Gräfe M (2009) Review of Bauxite Residue Re-use Options DMR-3609, pp. 1-181. CSIRO-Minerals, Waterford, WA.

Kutle A, Nad K, Obhodas J, Orescanin V, Valkovic V (2004) Assessment of environmental condition in the waste disposal site of an ex-alumina plant near Obrovac, Croatia. *X-ray Spectr.* **33**, 39-45.

McPharlin IR, Jeffrey RC, Toussaint LF, Cooper MB (1994) Phosphorus, nitrogen and radionuclide retention and leaching from a Joel Sand amended with red mud/ gypsum. *Comm. Soil Sci. Plant Anal.* **25**, 2925-2944.

Patel CB, Jain VK, Pandey GS (1986) Micro-pollutants in red mud waste of aluminum pant. *Intern. J. Environ. Anal. Chem.* **25**, 269-274.

Pinnock WR (1991) Measurements of radioactivity and Jamaican building materials and gamma dose equivalents in a prototype red mud house. *Health Phys.* **61**, 647-651.

Power G, Gräfe M, Klauber C (2009) Review of Current Bauxite Residue Management, Disposal and Storage: Practices, Engineering and Science. DMR-3608, pp. 44. CSIRO-Minerals, Waterford.

Somlai J, Jobbagy V, Kovacs J, Tarjan S, Kovacs T (2008) Radiological aspects of the usability of red mud as building material additive. *J. Haz. Mat.* **150**, 541-545.

von Philipsborn H, Kuhnast E (1992) Gamma-spectrometric characterization of industrially used African and Australian bauxites and their red mud tailings. *Rad. Protect. Dosim.* **45,** 741-744.

Wong JWC, Ho GE (1993) Use of waste gypsum in the revegetation on red mud deposits-A greenhouse study. *Waste Manag. Res.* **11,** 249-256.