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Environmental impact of toxic elements in red mud studied by fractionation and speciation procedures

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ABSTRACT

Aluminum (Al) is mostly produced from bauxite ore, which contains up to 70% of Al_2O_3 (alumina). Before alumina is refined to aluminum metal, it is purified by hot alkaline extraction. As a waste by-product red mud is formed. Due to its high alkalinity and large quantities, it represents a severe disposal problem. In Kidričevo (Slovenia), red mud was washed with water before disposal, and after drying, covered with soil. In Ajka (Hungary), the red mud slurry was collected directly in a containment structure, which burst caused a major accident in October 2010. In the present work the environmental impact of toxic elements in red mud from Kidričevo and Ajka were evaluated by applying a sequential extraction procedure and speciation analysis. The predominant red mud fraction was the insoluble residue; nevertheless, environmental concern was focused on the highly mobile water-soluble fraction of Al and Cr. Al in the water-soluble Ajka mud fraction was present exclusively in form of toxic $[Al(OH)_4]^-$, while Cr existed in its toxic hexavalent form. Comparative assessment to red mud from Kidričevo (Slovenia) with a lower alkalinity (pH 9) with that from Ajka demonstrated significantly lower Al solubility and the presence of only trace amounts of Cr(VI), confirming that disposal of neutralized mud is environmentally much more acceptable and carries a smaller risk of ecological accidents.

Since during the Ajka accident huge amounts of biologically available Al and moderate Cr(VI) concentrations were released into the terrestrial and aquatic environments, monitoring of Al and Cr(VI) set free during remedial actions at the contaminated site is essential. Particular care should be taken to minimize the risk of release of soluble Al species and Cr(VI) into water supplies and surface waters.

1. Introduction

Aluminum (Al) is ubiquitously present in the terrestrial environment, being the most abundant metal in the lithosphere, comprising about 8% of the Earth's crust (Ščančar and Milačič, 2006). Due to its low density, resistance to corrosion, high weight to strength ratio, and recycling-ability, Al is widely used in industry. Annual global primary production of metallic Al from ore in 2006 was around 34 million tons and recycled production around 16 million tons (http://www.world-aluminium.org/About+Aluminium/Story+of). Almost all metallic Al are produced from the bauxite ore, which contains from about 50% up to 70% of Al_2O_3 (alumina) (Shaheen et al., 2010). Before alumina is refined to metallic Al, it must be purified. For this purpose bauxite ore is extracted with hot NaOH solution by the Bayer process, which enables separation of pure alumina from other bauxite components. As a by-product of the Bayer processing red mud emerges from the alkaline digestion of bauxite. Metallic Al is further produced from alumina by the electrolytic process. The major residual constituents of red mud that are not dissolved during alkaline digestion are oxides of aluminum, iron and titanium, with minor to trace concentrations of rare earth and other elements (Szépvölgyi, 2011). Today about 90% of bauxite is processed by Bayer technology (Szépvölgyi, 2011; Liu et al., 2007). As a highly alkaline slurry (pH 10–12.5) with 15–30% solids, red mud represents a huge disposal problem. About 120 million tons of red mud are produced every year throughout the world, while the total bauxite residue disposed of amounts up to date is estimated to be about 3 billion tons (Szépvölgyi, 2011; Gräfe and Klauber, 2011). The cheapest method of disposal of red mud, but environmentally less acceptable, is a collection of the alkaline slurry (30 to 35% solid content) in land-based ponds without prior neutralization. More expensive is dry disposal of red mud after washing with water to lower the pH and formation of dry cake residue (more than 60% solid content) (Szépvölgyi, 2011; Gräfe et al., 2011). For storage of red mud large disposal areas are needed, so many investigations were oriented in evaluating the potential re-use of red mud as a secondary material in civil engineering (building materials) (Somlai et al., 2008), in the chemical industry (adsorbents, ceramic glazes, catalysts, pigments, polymers) and metallurgy (extraction of iron and titanium oxides, vanadium, rare earth elements) (Szépvölgyi, 2011). After appropriate neutralization, red mud can be used for remediation of sites with contaminated soil for reducing

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metal solubility and bioavailability (Brunori et al., 2005; Santona et al., 2006; Gray et al., 2006; Lee et al., 2011). Nevertheless, due to the huge amounts of bauxite residue, disposal of red mud is the most common practice worldwide, despite its potentially hazardous environmental impact.

In Ajka, Hungary, the red mud slurry was collected directly in a containment slurry pond, which burst caused a major accident in October 2010 (Szépvölgyi, 2011). After this ecological disaster, some investigations were carried out to estimate its environmental impact. Gelencsér et al. (2011) characterized the resulting dust and evaluated its potential health effects. Studies were also performed on trace metal bioavailability and plant toxicity in red mud contaminated soils. Foliar diagnostics suggested that Na salinity, not trace metal contamination, decreased barley yields in red mud amended soils (Ruyters et al., 2011). It is surprising that in the latter research Al as the major pollutant in the Ajka accident was not considered, and that no attempt was made to understand the present and future impact of Al on the affected environments.

In order to evaluate the partitioning of elements between highly and sparingly mobile fractions in waste materials, contaminated sediments and soils, different sequential extraction procedures have been developed and applied (Rauret et al., 1999; Janoš et al., 2010; Tessier et al., 1979; Ščančar et al., 2001a; Ščančar et al., 2001b; Paganelli et al., 2004; Ghosh et al., 2011). Nowadays, the BCR three-step sequential extraction procedure is commonly used (Rauret et al., 1999; Janoš et al., 2010). As an alternative Tessier's sequential extraction procedure and its modifications (Tessier et al., 1979; Ščančar et al., 2001a; Ščančar et al., 2001b; Paganelli et al., 2004; Ghosh et al., 2011) are still applied. The procedures based on Tessier's extraction scheme enable the study of the partitioning of elements even in highly alkaline samples (Ščančar et al., 2001a; Ščančar et al., 2001b; Paganelli et al., 2004; Ghosh et al., 2011), whereas the BCR scheme is not capable of such investigations (Ščančar et al., 2001a; Ščančar et al., 2001b).

The aim of the present work was to assess the environmental impacts of Al and other toxic elements in the highly alkaline red mud (pH 12) from Ajka (Hungary) that was collected in a land-based pond without prior neutralization, and which burst caused one of the worst cases of industrial pollution in recent history. For this purpose a modified Tessier's sequential extraction procedure was applied to estimate the partitioning of elements between easily and sparingly soluble mud fractions. In addition, chemical speciation of Al and Cr was performed in the highly mobile water-soluble red mud fraction. Comparative assessment with red mud from Kidričevo (Slovenia) of lower alkalinity (pH 9) that was washed with water before disposal, and after drying covered with soil, was also performed to demonstrate that by combination of fractionation and speciation analytical procedures it is possible to evaluate the environmental impacts of different red mud disposal practices.

Table 1
Determination of elements in Quality Control Material for Surface Water Analysis SPS-SW1 by ICP-MS. Results represent the mean ± variation of duplicate samples.

Element	Certified value ($\mu g\ L^{-1}$)	Determined value ($\mu g\ L^{-1}$)
Cd	0.50 ± 0.01	0.49 ± 0.01
Cr	2.00 ± 0.02	2.06 ± 0.05
Se	2.00 ± 0.02	2.00 ± 0.02
Pb	5.0 ± 0.1	4.99 ± 0.04
Ni	10.0 ± 0.1	10.1 ± 0.1
Mn	10.0 ± 0.1	10.3 ± 0.1
As	10.0 ± 0.1	10.2 ± 0.1
Mo	10.0 ± 0.1	9.9 ± 0.1
Fe	20 ± 1	21 ± 1
Cu	20 ± 1	20.7 ± 0.4
Zn	20 ± 1	22 ± 1
Al	50 ± 1	49 ± 1

2. Materials and methods

2.1. Apparatus

Total concentrations of elements in red mud and in the phases of the sequential extraction procedure were determined by inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent (Tokyo, Japan) 7700× ICP-MS, by flame atomic absorption spectrometry (FAAS) on a Varian (Mulgrove, Victoria, Australia) Spectra AA 110 atomic absorption spectrometer, and by electrothermal atomic absorption spectrometry (ETAAS) on a Hitachi (Tokyo, Japan) Z-8270 polarized Zeeman atomic absorption spectrometer. Al and Cr speciation was performed by fast protein liquid chromatography (FPLC) with ICP-MS detection. The chromatographic system consisted of an Agilent (Tokyo, Japan) series 1200 quaternary pump equipped with a Rheodyne model 7725i (Cotati, Ca, USA) injector using an 0.05 mL injection loop. For separation of Al and Cr species a strong anion-exchange FPLC Mono Q column HR 5/5 (Pharmacia, Uppsala, Sweden) was used. The outlet of the chromatographic column was directly connected to the ICP-MS instrument. A CEM Corporation (Matthews, NC, USA) CEM MARS 5 Microwave Acceleration Reaction System was used for digestion of red mud. Mechanical shaking of samples was performed on a Vibromix 40 elliptical (Tehtnica, Železniki, Slovenia) orbital shaker. Samples were centrifuged on a Hettich Universal 320 Centrifuge (Hettich GmbH & Co. KG, Tuttlingen, Germany). A WTW (Weilheim, Germany) 330 pH meter was employed to determine pH. An AE 163 analytical balance from Mettler (Zürich, Switzerland), was used for all weighing.

2.2. Reagents

Merck (Darmstadt, Germany) suprapur acids and Milli-Q water (Direct-Q 5 Ultrapure water system, Millipore Watertown, MA, USA) were used for the preparation of samples and standard solutions. All other reagents were of analytical reagent grade.

Stock IV CertiPUR ICP Multi Element Standard Solution containing $1000\ mg\ L^{-1} \pm 10\ mg\ L^{-1}$ element concentrations in $1\ mol\ L^{-1}$ HNO_3 was obtained from Merck. For preparation of the standard solutions used in the speciation procedure Cr(VI) solution (K_2CrO_4 in water) containing $1.000 \pm 0.002\ g\ L^{-1}$ of CrO_4^{2-} and $Al(NO_3)_3 \cdot 9H_2O$ salt were purchased from Merck.

Sartorius (Goetingen, Germany) 0.45 μm cellulose nitrate membrane filters of 25 mm diameter were used in the filtration procedure.

The certified reference material bauxite ore B.C.S. No. 395 Bauxite obtained from the Bureau of Analysed Samples Ltd. (Middlesbrough, England), SPS-SW1 Quality Control Material for Surface Water Analysis purchased from SPS Spectrapure Standards AS (Oslo, Norway) and certified reference material CRM 545, Cr(VI) in welding dust, obtained from the Community Bureau of Reference (BCR, Geel, Belgium) were used to check the accuracy of the analytical procedures.

Table 2
Determination of elements in B.C.S. No. 395 bauxite certified material by ICP-MS, ETAAS and FAAS. Results represent the mean ± variation of duplicate samples.

Element	Certified value ($mg\ kg^{-1}$)	Determined value ($mg\ kg^{-1}$)	Analytical technique used for analysis
Al	277,000 ± (n.a.)	277,000 ± 15,000	ETAAS
Fe	113,000 ± (n.a.)	120,000 ± 6000	FAAS
Cr	453 ± 29	437 ± 22	ICP-MS
Cu	21 ± 3	20 ± 1	ICP-MS
Mn	42 ± 5	39 ± 2	ICP-MS
Ni	34 ± 8	32 ± 2	ICP-MS
Pb	28 ± 5	29 ± 2	ICP-MS
Zn	43 ± 7	41 ± 2	ICP-MS

n.a. — not applicable.