

Long-term behaviour of contaminant metals in red mud.

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Abstract (199 words)

The catastrophic failure of the bauxite residue dam at the Ajka alumina plant on the 4th October 2010 resulted in the release of around 1 million m³ of caustic metalliferous red mud slurry. The accident was unprecedented in terms of scale and the type of material released. The red mud surged downstream, caused over 150 injuries, destroyed homes and claimed 10 lives. Over 100 km of rivers and 40 km² of land were also affected. In the weeks following the spill there was much concern regarding the potential leaching of toxic contaminants, especially arsenic, chromium and vanadium, which are present at high concentrations in the red mud. Therefore, we used a combination of traditional geochemical methods, electron microscopy and X-ray absorption spectroscopy techniques to characterise the occurrence of arsenic, chromium and vanadium within the red mud and predict their environmental behaviour. Our findings show that chromium in red mud is effectively trapped in iron oxide nanoparticles and is very resistant to future remobilisation. Arsenic and vanadium, however, exist as more easily solubilised arsenate and vanadate species. In particular, vanadate was poorly retained under environmental conditions and the red mud could be a significant source of toxic vanadium to waters.

Main Text (990 words)

Up to 120 million tonnes of bauxite residue (red mud) are produced annually during Al-extraction via the Bayer process [1]. To date no large scale after use for red mud has been found and most is still stored in land based repositories. Red mud typically contains minerals that survive high pH treatment during Bayer processing (such as iron oxides, quartz and titanium dioxide) and characteristic neoformed minerals (such as sodium aluminosilicates and calcium carbonate/aluminate). Red mud also contains sodium hydroxide that dissolves to produce highly alkaline leachate in which several oxyanionic forming trace elements are very soluble. At Ajka, water in the alkaline (pH 13) red mud suspension (Fig. 1) had elevated concentrations of metals and metalloids such as Al (650 ppm), As, V, and Mo (4 - 6 ppm) and the red mud itself has elevated concentrations of As, V, Cr, Co and Ni (100-1000 ppm) [2].

The red mud spill at Ajka was the first large-scale uncontrolled release of this material into a terrestrial environment; therefore, there was little information available on the likely long-term consequences of red mud addition to ecosystems. Initial investigations focused on the dispersion and transport of red mud in the environment [2], assessing the risk to humans caused by red mud derived dusts [3] and the short term effects of red mud on plant growth [4]. However the likely long-term behaviour and potential bioavailability of toxic trace elements found in the red mud remained a key uncertainty with respect to remediation plans. Traditional geochemical methods could easily describe the distribution of red mud in the environment, but without detailed information on the exact speciation of metals present in the red mud it was very difficult to predict the likely long-term harm. This created the key knowledge gap that required synchrotron based spectroscopy methods. Three of the potential most harmful elements present in elevated concentrations (As, Cr, and V) were accessible to X-ray absorption spectroscopy analysis at Diamond beamline I18 (despite the very complex nature of red mud samples) and, therefore, became the focus of our investigations.

Chromium commonly exists in two forms in the environment, toxic Cr^{6+} and relatively safe Cr^{3+} . The lack of the pre-edge peak characteristic of Cr^{6+} at 5993 eV in Cr K-edge XANES spectra collected from red mud samples (Fig. 2) confirms that Cr in red mud is predominately present as Cr^{3+} . When the Cr spectra from red mud were compared in detail with spectra collected from a Cr-substituted hematite standard there was also a very close match. This was supported by TEM analysis that found that Cr was indeed associated with the hematite particles present (Fig 3). Cr^{3+} can easily substitute for Fe^{3+} in hematite and the high pH, high temperature reaction conditions present in the Bayer process will certainly promote this process. Once incorporated into hematite Cr^{3+} is expected to be particularly stable as hematite is very insoluble under practically all environment conditions and environmental oxidation rates for Cr^{3+} are also very slow. Therefore there is very little possibility for red mud deposits to leach toxic Cr^{6+} in future.

Arsenic also exists in two common valence states under environmental conditions, As^{5+} and As^{3+} . Both are very toxic, but the greater solubility of As^{3+} species makes the reduced forms of particular concern. Arsenic in red mud, however, is largely present as As^{5+} (Fig. 2). EXAFS analysis of red mud samples further revealed that the As^{5+} was present as arsenate, either in simple inorganic arsenate phases or in inner sphere absorption complexes associated with Fe or Al oxides (Fig. 4). Arsenic solubility, therefore, is expected to be controlled by the interplay of dissolution and adsorption reactions. Dissolution of arsenate bearing phases may result in release of As^{5+} to solution, but under the circumneutral conditions that characterise most areas affected by the red mud spill, arsenate will readily adsorb to surfaces and be retained in solids. Ultimately adsorption processes should limit the leaching of As from red mud deposits; but adsorbed arsenate is potentially susceptible to anion exchange or bioreduction reactions that may lead to future remobilisation of As from the red mud.

Vanadium is found in multiple oxidation states in natural materials, with V^{4+} and V^{5+} being the most common. It is also more difficult to separate different oxidation states using V K-edge XANES analysis as there is considerable overlap in the spectral features present. Nevertheless, the spectra

collected from red mud samples are most similar to standards with vanadate (V^{5+}) present sorbed to minerals (Fig. 2). This result was augmented by TEM analysis that found that V was associated with the mineral hydrogarnet present in the red mud. Hydrogarnet is a high pH phase that forms during Bayer processing and is unstable at lower pH; thus under circumneutral pH is not be expected to be a stable long term host for and its dissolution may release V solution. In addition (and in contrast to As), V was very poorly removed from solution during neutralisation experiments; a result that mirrored water sample data recovered from red mud affected rivers treated with acid to lower pH [2]. This higher solubility is due to the lower sorption of vanadate to minerals at circumneutral pH. Therefore we expect V to more readily leach from red mud under the environmental conditions found at affected sites.

Our study highlights the importance of elemental specific X-ray absorption spectroscopy data in understanding the environmental behaviour of pollutants. In addition, this work benefited from rapid access to the I18 beamline at Diamond allowing us to respond quickly to unpredicted events such as the red mud spill at Ajka. Our results predict that leaving large volumes of red mud *in situ* would most likely be inadvisable with respect to the potential leaching of toxic metals such as V. These findings have been disseminated to the Hungarian authorities and support the approach they have taken in recovering much of the released red mud, despite the high costs involved.

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Figure 1. Red mud slurry continued drained from the breached Ajka dam (into rapidly constructed containment lagoons) for several weeks after the spill.

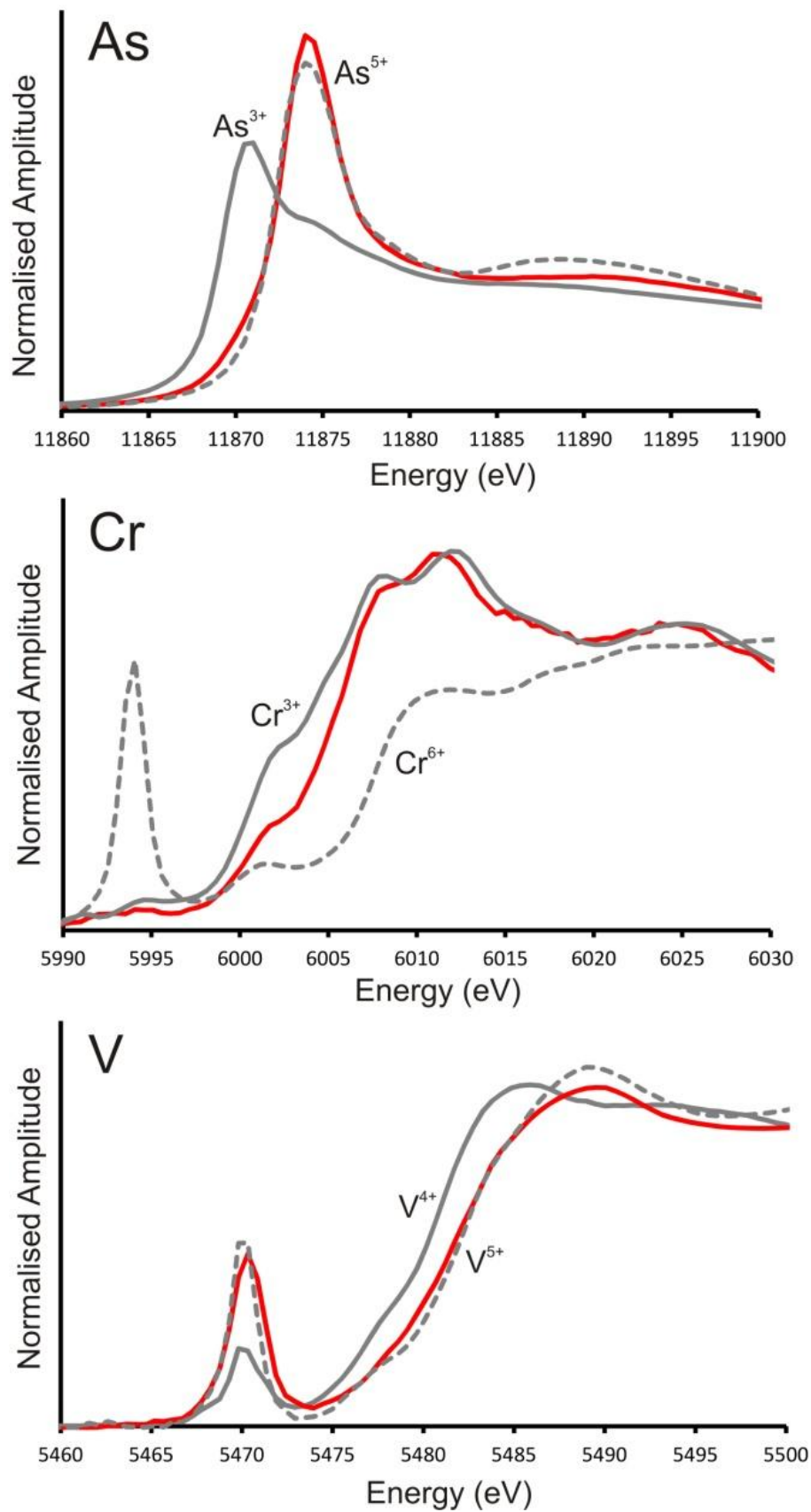


Figure 2. Comparison of the As, Cr and V K-edge XANES spectra collected from a sample of Ajka red mud (red lines) and spectra collected from standards (grey / dashed lines).

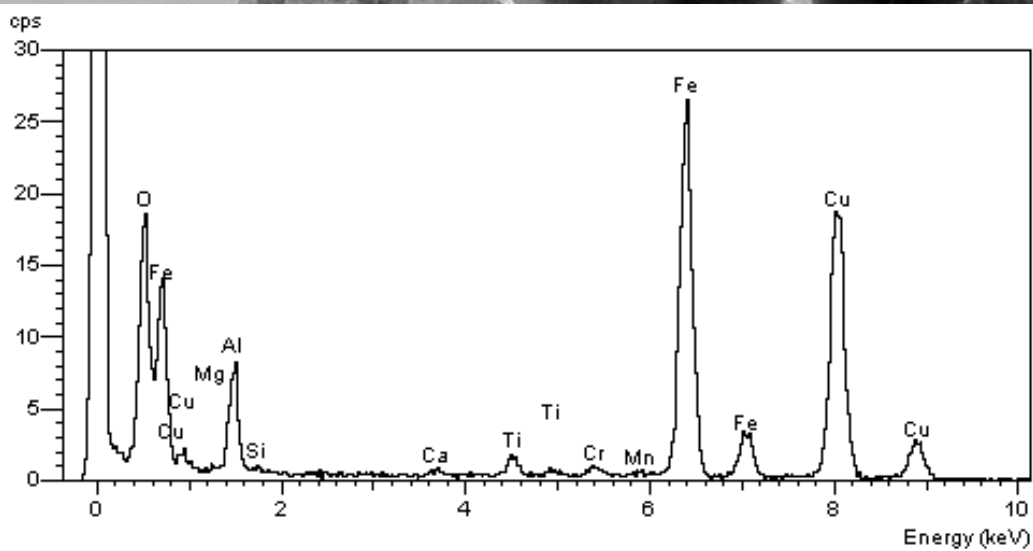
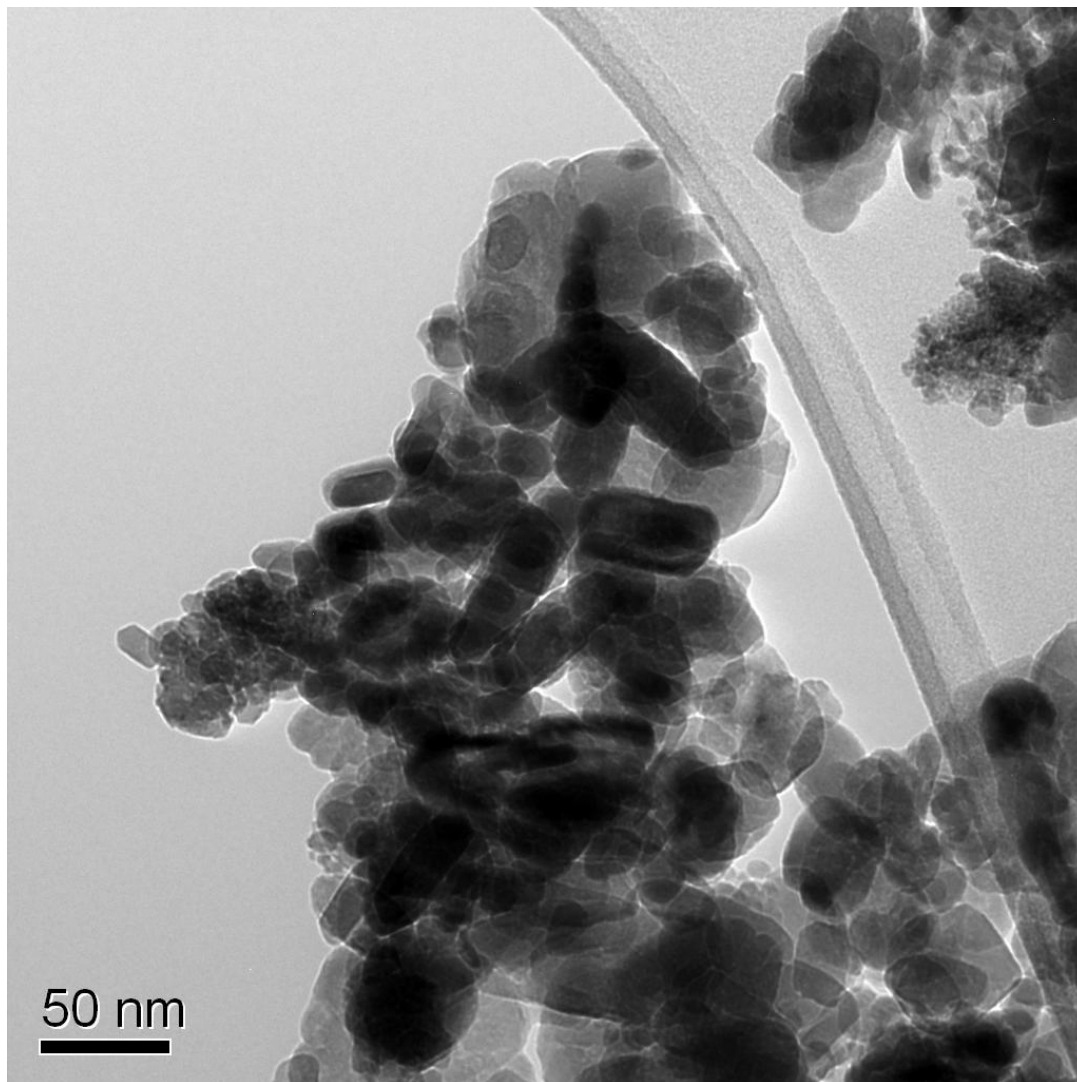
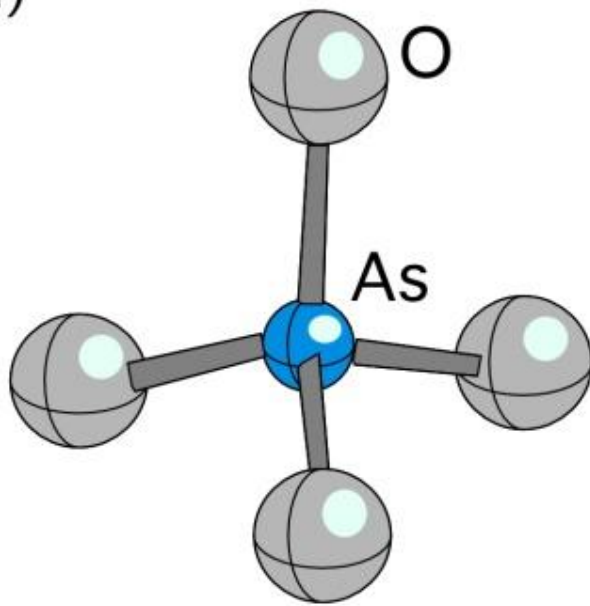


Figure 3. TEM image of hematite nanoparticles in red mud (identified by selected area diffraction) and an energy dispersive X-ray spectrum showing the trace elements associated with these particles (the presence of Cu is due to the TEM support grid).

a)



b)

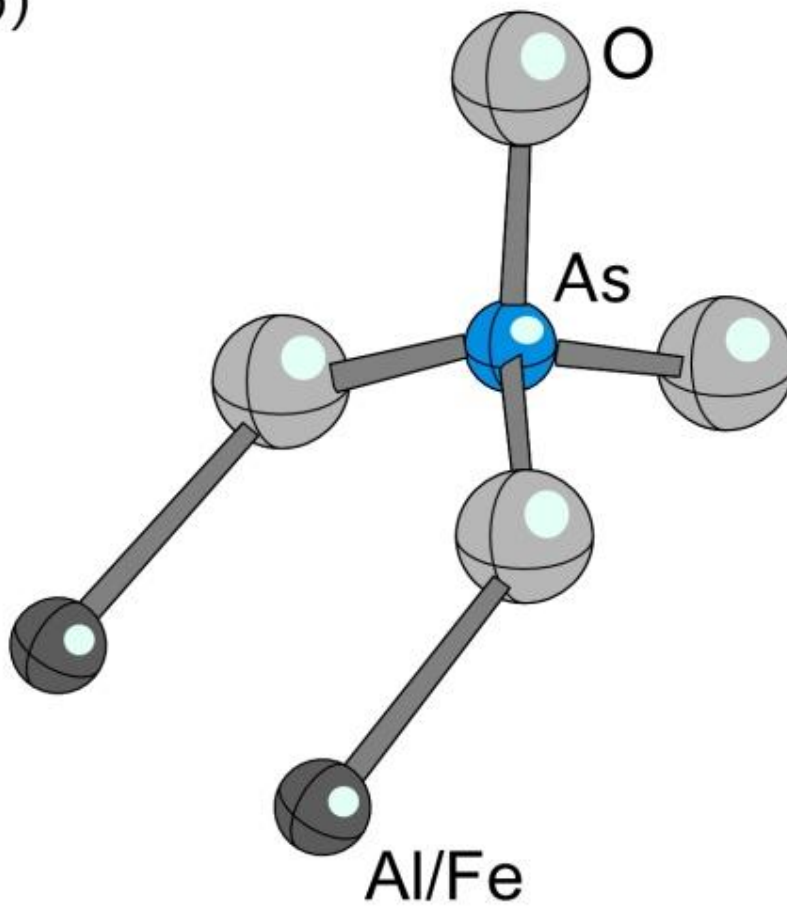


Figure 4. Simple molecule clusters required to model the As EXAFS data collected from red mud samples. (As = arsenic; O = oxygen; Al = aluminium; Fe = iron).

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