

Project title: Should calcium aluminates be used to remediate hexavalent chromium-contaminated sites?

Supervisors:

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Project background

Chromium (Cr) occurs naturally in both trivalent and hexavalent oxidation states. Cr(III) is an essential nutrient, whereas Cr(VI) is toxic, carcinogenic and mutagenic and readily forms the highly soluble and environmentally mobile anion, CrO_4^{2-} . Past disposal of chromite ore processing residue (COPR), the byproduct of Cr(VI) production for use in dyes, chrome plating etc., presents a significant environmental hazard as concentrations of $\leq 1\%$ Cr(VI) w/w can be anticipated. Field studies (fig. 1) have shown Cr(VI) in calcium aluminate phases such as ettringite (fig. 2), hydrocalumite and hydrogarnet continue to emerge at the soil surface and leach into both ground and surface waters even 5 decades after waste emplacement. There is, however, a growing interest in the use of calcium aluminates to immobilise Cr(VI) and thus remediate Cr(VI)-contaminated sites. To address the question of slow release vs long-term immobilisation, this PhD will undertake more controlled laboratory studies into the formation of Cr(VI)-containing calcium aluminates to characterise the effects of pH, time and temperature on their formation and subsequent stability. Real time studies of the effects of the formed solid phases under different flow conditions will also be monitored.

Mapping the results from the laboratory studies to those obtained from previous projects on the natural field samples, will allow a more definitive understanding on how these phases form and what impact they have on the long-term mobility of Cr(VI) in the environment.



Figure 1 Yellow/green Cr(VI)-containing phases emerging at the surface of a COPR-contaminated site

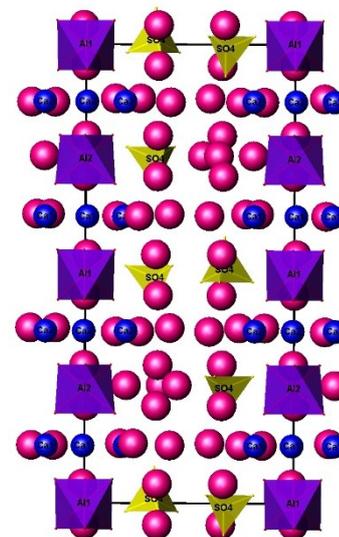


Figure 2 Crystal structure of ettringite; Cr^{3+} can substitute for Al^{3+} (purple) or $(\text{CrO}_4)^{2-}$ can substitute for $(\text{SO}_4)^{2-}$ (yellow)

Key research questions

1. What phases form in the system Ca-Al-Cr-S-O- H_2O under the pH conditions found at COPR-contaminated sites?
2. How well do the phases formed under laboratory conditions correlate with those present in fresh and weathered COPR in the field?
3. What are the structure-composition-property relationships of the different formed phases?

Methodology

Year 1 of the PhD will consist of studying the formation of phases with targeted compositions as identified to be present in the solid COPR samples (REF Thomas 2001). This will include formation of ettringite $\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$ and its chromium analogue $\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{CrO}_4)_3 \cdot 26\text{H}_2\text{O}$ and monitoring solid solution formation between these 2 phases, i.e. $\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_{3-x}(\text{CrO}_4)_x \cdot 26\text{H}_2\text{O}$. The hydrocalumite $[\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 2\text{H}_2\text{O}]_2(\text{SO}_4)_{1-x}(\text{CrO}_4)_x$ system and hydrogarnet ($\text{Ca}_3\text{Al}_{2-x}\text{Cr}_x(\text{OH})_{12}$) system will also be studied. Characterisation of the formed phases will be carried out using Powder X ray Diffraction (PXRD), Infrared spectroscopy (IR), Thermogravimetric Analysis (TGA), Inductively Coupled Optical Emission Spectroscopy (ICP-OES) and Scanning Electron Microscopy SEM. Full structural characterisation will be carried out through Rietveld refinement of PXRD data. **Year 2** will use the data collected on the synthetic phases to link to that found from the field samples to establish possible formation pathways of these phases. Stability of the synthetic samples will be monitored under different conditions of pH, time and temperature this will allow the structure-composition-property relationships to be established. With these data a more meaningful understanding of the likely degradation of the phases under different conditions and their potential to release Cr(VI) into the environment will be established. Alongside this, development of a flow cell for use with the in-house powder X ray diffractometers will be carried out and tested for use in the final year. **Year 3** will focus on use of the flow cell to monitor the structural integrity of the phases produced and their degradation pathways. Applications to the Diamond Light Source will also be made during year 2 and at the start of year 3 to carry out *in situ* high resolution powder diffraction studies using advanced synchrotron techniques.

Training: A comprehensive training programme will be provided comprising both specialist scientific training and generic transferable and professional skills. The project provides high level training in: (i) materials synthesis; (ii) sample characterisation using Powder X ray Diffraction, Infrared Spectroscopy, Thermogravimetric Analysis and Scanning Electron Microscopy; (iii) structural characterisation of Powder X ray Diffraction data; (iv) development of flow cell for use with in-house x ray diffractometers

Requirements: An excellent first degree in BSc Environmental Chemistry, Environmental Science, Geoscience, Earth Science, Environmental Engineering, MChem or related discipline. Candidates should have strong skills in the laboratory and in experimental design, enjoy fieldwork and hold a driving licence.

Further reading

S.Hillier, M.J. Roe, J.S. Geelhoed, A.R. Fraser, J.G. Farmer and E. Paterson 2003. Role of quantitative mineralogical analysis in the investigation of sites contaminated by chromite ore processing residue. *The Science of the Total Environment*, **308**, 195-210

R.P. Thomas, S.J. Hillier, M.J. Roe, J.S. Geelhoed, M.C. Graham, E. Paterson and J.G. Farmer 2001. Analytical Characterisation of Solid- and Solution-Phase Chromium Species at COPR-Contaminated Sites, *Environ. Geochem. and Health*, **23**, 195-199

S. Hillier, D.G. Lumsden, R. Brydson and E. Paterson 2007. Hydrogarnet: A Host Phase for Cr(VI) in Chromite Ore Processing Residue and Other High pH Wastes, *Environ. Sci. Technol.* **41**, 1921-1927

R.L. Norman, S.E. Dann, S.C. Hogg, C.A. Kirk 2013. Synthesis and structural characterisation of new ettringite and thaumasite type phases: $\text{Ca}_6[\text{Ga}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_6[\text{M}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2(\text{SO}_4)_2(\text{CO}_3)_2$, M=Mn, Sn, *Solid State Sci.*, **25**, 110-117

Project summary: This project will establish the structure-composition-property-relationship of chromium-containing calcium aluminate phases, through combined laboratory and field studies to assess their impact on the long-term mobility of Cr(VI) in the environment.

The application procedures is outlined at: <http://e3dtp.geos.ed.ac.uk/apply.html>

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