

Motorways and the Mineralogy of Chromium Contaminated Land

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Environmental mineralogy [1, 2] has an important role to play in understanding the solid state speciation and geochemical behaviour of toxic metals in contaminated soils. For example, the implementation of the contaminated land provisions of Part IIA of the UK Environment act [3] now requires an approach based on risk assessment, where it is clear that total



Figure 1. Sampling COPR at Dukes Road, Glasgow.

metal determinations by chemical analysis alone are no longer sufficient. Our group (see references), initially funded under the NERC URGENT program, has applied a variety of mineralogical methods to chromate ore processing residue (COPR) which contaminates land around Glasgow, Scotland (Figure 1).

These methods are underpinned by use of the Chemical Database Service (CDS) databases in some very simple but important ways. These include calculation of X ray powder diffraction (XRPD) patterns to aid in phase identification, as a source of structure details for starting models for Rietveld

refinement of XRPD patterns and/or structure representation to illustrate mineralogical concepts of relevance to metal speciation, as well as a source of other basic crystallographic data.

Approximately 2.5 million tonnes of COPR, produced by a 'high lime process' have been used as fill at a network of sites in and around Glasgow [4]. The COPR is derived from a former chromium works at Rutherglen, which operated between 1830 and 1968. Large areas are heavily contaminated with alkaline (up to pH 12.3) waste, often of granular appearance (Figure 2) containing Cr(VI), a known carcinogen of significant mobility.



Figure 2. Granular looking COPR.

Using a combination of quantitative mineralogical analysis of XRPD data (Figure 3) by the Rietveld method and phase compositions obtained by electron microprobe analysis, it was shown previously (5) that chromium was present in at least five distinct phases, namely chromite, brownmillerite, ettringite, hydrocalumite and hydrogarnet. Along with other crystalline phases in COPR these were rationalised into three categories 1) unreacted chromite ore, 2) high temperature phases mainly brownmillerite and periclase produced during the high lime roasting process, and 3) low temperature phases, including brucite, calcite, aragonite, ettringite, hydrocalumite and hydrogarnet all produced by hydration and carbonation among other reactions of the COPR over the protracted period that it has been exposed to ambient conditions and to leaching at the disposal sites.

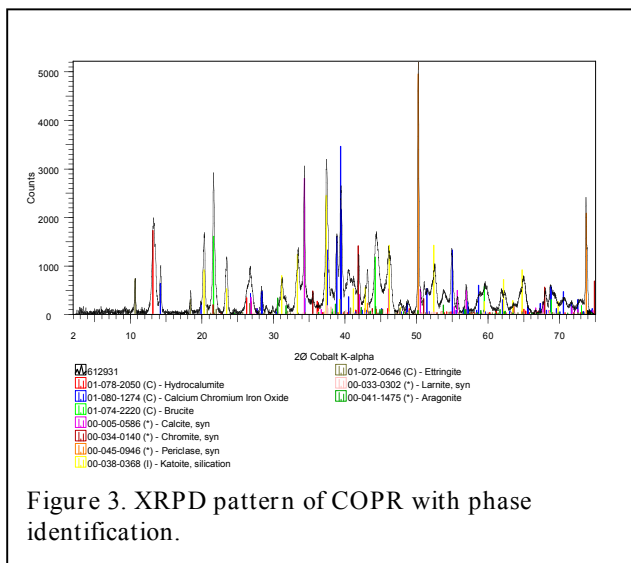


Figure 3. XRPD pattern of COPR with phase identification.

Unreacted chromite accounted for an average of about 6% by weight of COPR and along with brownmillerite which averaged around 14 wt. %, it was demonstrated [5] that these two phases host virtually all the of Cr (III) found in COPR. Hydrocalumite belongs to a group of phases known in the cement literature as AFm.

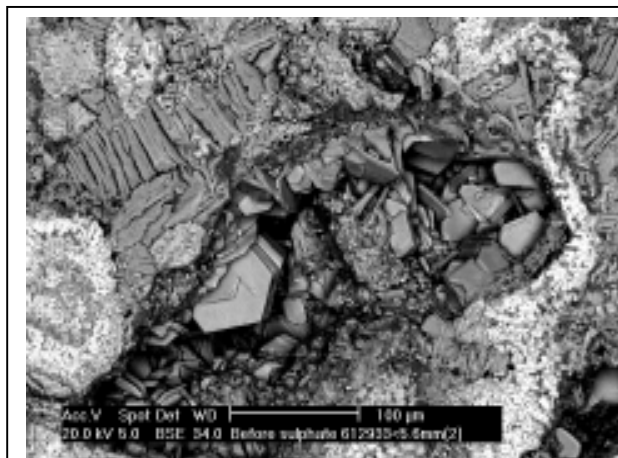


Figure 4. Back Scattered Electron image of hydrocalumite type phase (platy hexagonal habit) in COPR

The basic structure of these phases consists of layers of composition $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6 \bullet 2\text{H}_2\text{O}]^+$ the positive charge from which is balanced by interlayer anions; and they may occur in a range of hydration states. In COPR it was found that hydrocalumite is an important host for approximately half of its Cr(VI) content [5]; held in an exchangeable anionic form [6]. The most abundant crystalline phase in the COPR from Glasgow, however, is hydrogarnet (2030 wt. %)

and it was speculated [5] that most of the remaining Cr(VI) in COPR was structurally incorporated in hydrogarnet. The garnet structure consists of alternating corner sharing tetrahedra and octahedra. In classic rock forming garnets the tetrahedra are silica SiO_4^{4-} tetrahedra, whereas in hydrogarnet the tetrahedra are composed of four hydroxyls, $\text{H}_4\text{O}_4^{4-}$,

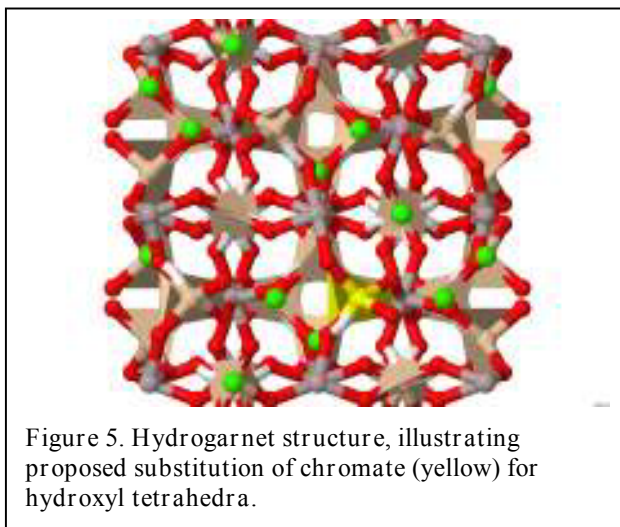


Figure 5. Hydrogarnet structure, illustrating proposed substitution of chromate (yellow) for hydroxyl tetrahedra.

although solid solutions with some silica tetrahedra are common (Figure 5). Octahedral sites in garnets are occupied by trivalent cations such as aluminum in 6 fold coordination. The cavities formed between the corner sharing tetrahedra and octahedra have the shape of distorted cubes and contain divalent cations, such as calcium in 8 fold coordination. As an example, the end member hydrogarnet, known by its mineralogical name of katoite, has an ideal formula unit of $\text{Ca}_3\text{Al}_2(\text{H}_4\text{O}_4)_3$ and there are eight such formula units per unit cell [7]. The capacity of hydrogarnet to host Cr(VI) by substitution of CrO_4^{2-} tetrahedra was subsequently confirmed by a combination of diffraction and spectroscopic methods [8]; an investigation supported throughout by access to the CDS. Although hydrogarnet is the most stable calcium aluminate phase at the high pH of COPR, it is likely to dissolve and release chromium if pH is lowered. The understanding gained from these environmental mineralogy investigations underpins attempts to find strategies and technologies for the remediation of these contaminated sites [9,10]. Many of these sites lie along the proposed course of the M74 motorway extension through Glasgow, which it is planned to build by 2010, at an estimated cost of £500 million [11], and effective methods to deal with chromium contamination will be needed.

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