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Implications of mineral equilibrium on hexavalent chromium leaching from buried chrome ore spoils

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Chromite Ore Processing Residue (COPR) is the refuse from sodium dichromate production, which was a large industry in the United States during much of the Twentieth Century. Due to its granular form and high particle density, COPR frequently was as fill material in marsh areas. The production process involved blending chromite ore with unslaked lime and sodium carbonate, which when heated to approximately 1200˚C, converted trivalent chromium in the ore to hexavalent sodium chromate, which was separated from the residue by water leaching. However, some un-recouped hexavalent chromium remained in the residue at levels of approximately 5000 mg/kg, which often was the source of groundwater contamination.

Freshly produced COPR was composed of three mineral compounds: calcium ferrate (brownmillerite, $Ca_2Al_{1-x}Fe_xO_5)$, magnesium oxide (periclase, MgO), and hydrated lime (portlandite, $Ca(OH)_2)$, in order of decreasing abundance. Exposure to groundwater caused each of these compounds to undergo chemical reactions that produced hydration products that ranged from simple hydroxides to compounds having complex structures. Analysis of system thermodynamics shows that the reaction path initially involves the formation of metastable phases, which later become converted to stable solids.

Although the predominant element (other than oxygen) in COPR is iron, the chemistry of the hydration products is dominated aluminum, which is both mobile and reactive in alkaline conditions. At ambient temperatures aluminum tends to form a large number of hydrated compounds with other elements in the systems, including calcium, chromate, carbonate, sulfate, chloride, magnesium, and silicon. A particularly important group of compounds is aluminoferrite-mono (AFm), which are present in aluminous cements as well as in COPR. The literature reports the existence of chromate-bearing AFm phases when pH is >11.5 and aqueous concentrations of hexavalent chromium are elevated. A general form of chromate-bearing AFm phases is $Ca_4Al_2CrO_{10}\cdot nH_2O$, where $n$can be 9, 12, or 14. SEM, microprobe, and XRD analyses reveal that AFm is capable of forming solid solutions in which chromate may be replaced partially or completely by carbonate, hydroxide, and chloride ions. In addition, it is evident by these analytical tools that chromate may be contained in other phases besides AFm, including hydrogarnet (ideally $Ca_3Al_2(OH)_{12})$, which also exhibits a broad range of Fe(III) substitution for aluminum and some silica substitution for hydroxide (katoite series).

This paper will discuss the results of laboratory experiments using natural and synthetic materials, plus the application of thermodynamic modeling to understand phase equilibrium relationships in the COPR chemical system. The most important reactions from an environmental perspective are those that control chromate concentration in aqueous solution, since these directly impact leaching of chromate into groundwater. However, the geochemical behavior of the whole system must be understood to fully describe the behavior of chromate-bearing compounds. It is an objective of this research effort to define each of the mineral transformations that takes place during diagenesis, so that a complete picture of this complex process can be appreciated and potentially controlled.