

Trivalent Chromium: A Neglected Latent Contaminant

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As the 21st most abundant element in earth's crust, chromium has been extensively used in industrial activities such as paint pigments and leather tanning. As a consequence, there is a continual influx of chromium contaminants into the environment, thereby posing a serious environmental problem. Chromium exhibits a wide range of possible oxidation states, where trivalent chromium [Cr (III)] is most stable energetically, but Cr (III) and Cr (VI) are most commonly observed in aquatic environment. Cr (VI) species are of great environment concern due to their well-known toxicity, carcinogenic properties and high mobility in environmentally relevant media. Cr (III) is generally regarded as benign and even essential for human and animal, since trace amounts of Cr (III) is required for sugar and lipid metabolism. In this context, it is a common strategy in environmental remediation to reduce toxic Cr (VI) to Cr (III) by various redox reactions. Cr (III) is thought to be immobilized by precipitating into insoluble Cr (III) hydroxides [1].

Is it really the case that Cr (III) is completely safe in this remediation scheme? Recent investigations indicated that the environmental fate of Cr (III) species is far from being well understood. Cr (III) chemistry is dominated by the formation of stable hexacoordinate complexes with both inorganic and organic ligands. In the absence of organic ligands, hexaaquachromium (III) is the dominant Cr species under strongly acidic conditions. This inorganic Cr (III) complexes undergo hydrolysis at pH>4, leading to a rapid precipitation of multinuclear Cr (III) hydroxides at neutral pH. In contrast to its aqua complexes, Cr (III) is readily organically complexed with carboxylic acids and amino acids so as to make it remain soluble for a long time. Therefore, it is worthy to note that the description of Cr (III) insolubility at neutral pH is only correct for solutions without strong organic ligands that out compete H₂O for Cr (III) [2]. Formation of stable organo-Cr (III) complexes during Cr (VI) reduction can increase their environmental mobility and maintain Cr (III) solubility even at neutral pH.

These soluble Cr (III) complexes with small organic molecules are often neglected and indeed deserve careful investigations on their mobility and particularly their potential transformation to Cr (VI) in different environmental compartments. However, there is very limited knowledge about environmental oxidation of Cr (III) to Cr (VI) [1]. H₂O₂ is known to oxidize Cr (III) at pH>7, but reduces Cr (VI) at acidic pH. In soils, Mn (IV) oxides are regarded as the sole oxidant for Cr (III) transformation, however, it is no longer efficient if insoluble Cr (III) solid blocks the surface sites of Mn oxides. Currently there is increasing evidence that photo oxidation is an alternative pathway to convert Cr (VI) to Cr (III) [3-6]. Zhang et al. [3] first reported light-induced oxidation of Cr (III) by ·OH radicals resulting from photolysis of Fe(III)-OH species (especially Fe(OH)²⁺), suggesting its potential for an important oxidation pathway in atmospheric waters. Recently Wang et al. [4] observed that Cr (III) can be oxidized in Fe (III)-oxalate (Ox)-Cr (III) systems at pH 3.0, however, no Electron Spin Resonance (ESR) signal of Cr (V)-Ox was measured during Cr (III) oxidation. In contrast, as for Fe (III)-Ox-Cr (VI) solutions, formation and decay of Cr (V) species can be detected by ESR upon UV irradiation. This indicates that Cr (V) is an important intermediate for Cr (VI) reduction, but not the case for Cr (III) oxidation in irradiated Fe (III)-Ox-Cr (III) system. Wang et al. [4] proposed that Cr(IV)-Ox complexes were

formed during Cr(III) transformation, which were stable at acidic pH but would be decomposed under alkaline conditions, thus greatly enhancing the environmental risk of Cr (VI) release. The further investigation by Dai et al. [5] indicated that photo oxidation of Cr (III)-citrate (Cit) without Fe (III) also can transform Cr (III) to Cr (VI). Rates of Cr (III) oxidation were not sensitive to pH within the range of 7 to 9, but increased significantly at higher pH. Cr (II) was firstly generated by a Ligand-to-Metal-Charge-Transfer (LMCT) after excitation of photoactive [Cr (III)-Cit-OH]⁻ species, and then was oxidized to Cr (VI) via a multiple step pathway. Similar to natural systems, Cr (III) oxidation is also found in water treatment process such as chlorination. Rates of Cr (VI) formation from Cr (III) nitrate, Cr (III)-EDTA and Cr (III) hydroxide were rapid via chlorine oxidation, on the order of hours. It manifests the possibility of transformation of Cr (III) to Cr (VI) during chlorination of drinking water [7].

Therefore, it is urgent and critical to better understand the fate of soluble Cr (III) species and their release risk as latent Cr (VI) precursor. Due to the complicated nature of chromium chemistry, chemical kinetic modeling and quantum chemical calculations may be required as effective tools to predict the kinetics and intermediates of Cr (III) oxidation. Secondly, ESR is a powerful and highly sensitive spectroscopic method to reveal the underlying mechanism for Cr (III) transformation [8]. However, it should be emphasized here that only organo-Cr (V) or Cr (V)/peroxo, and Cr (III) in some cases are ESR-sensitive [4]. It is therefore expected that the advances in fundamental of Cr (III) chemistry from a viewpoint of chemical kinetics and theoretical calculations, will benefit the in-depth exploration of uncertain fate of Cr (III) in the environment.

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