Appendix 6.3-E

Chromium Speciation in Mine Produced Dust

TECHNICAL MEMO

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1. Introduction

Chromium occurs in natural environments in two oxidation states: trivalent [Cr(III)] and hexavalent [Cr(VI)]. Elemental chromium [Cr(0)] is rarely found in nature (Motzer, 2004). Chromium(III) occurs as insoluble Cr(III) oxide (Cr_2O_3) and Cr(III) hydroxide ($Cr(OH)_3$); it can also occur as soluble Cr(III) hydroxide cations: $CrOH^{2+}$ and $Cr(OH)_2^{+}$. Cr(VI) generally occurs as soluble chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) anions (Motzer, 2004).

Relative to Cr(III), Cr(VI) has a high oxidizing potential, high solubility, and ease of permeation of biological membranes which make Cr(VI) more toxic than Cr(III) (CCME, 1999a; ATSDR, 2008). The understanding that the oxidation state of Cr greatly affects the toxicity of this metal is reflected in the BC working water quality guidelines for the protection of aquatic life (BC MoE,2015) which are specific to Cr(III) (8.9 µg/L) and Cr(VI) (1 µg/L). In contrast, other metals do not have BC or CCME guidelines that are specific to the oxidation state, except for the BC working guideline for Sb(III).

Water quality modeling for the Ajax Project predicts that Cr levels in waterbodies adjacent to the Project may increase above background concentrations, primarily due to dust generated during mine construction and operation. Water quality modeling generated predictions for total Cr. In order to relate the modeled Cr concentration to potential impacts to aquatic life, it is necessary to estimate the oxidation state of Cr that organisms may be exposed to. Since dust from the mine will be generated from blasting, excavating, transporting, and processing of mine rock, the oxidation state of Cr in dust from the mine will largely be determined by the oxidation state of rocks and soils at the mine site. This memo summarizes information available in literature regarding expected chromium speciation in mine generated dust and waterbodies receiving dust fall.

2. Chromium in Rocks and Soils

Crustal rocks on the earth contain on average 140 ppm of Cr. (Jacobs and Testa, 2004). The Cr concentration of different rocks is variable, with the highest concentrations reported for

ultramafic igneous rocks and their metamorphosed equivalents (2000 ppm on average). Mafic (basalts) and felsic (granites) have lower aveage Cr concentrations: 220 & 20 ppm, respectively (Motzer, 2004). Sedimentary rocks generally have Cr concentrations less than the crustal average.

The major Cr ore mineral is chromite, a magnesium–iron–chromium–aluminum oxide, $[(Mg,Fe^{2+})(Al,Cr,Fe^{3+})_2O_4]$ in which the chromic oxide content varies from approximately 15% to 65% owing to isomorphous substitution of Cr for Fe or Al. Chromium in chromite is present as Cr(III). Cr(VI)-bearing minerals are known to exist, but are rare relative to the Cr(III) proportion of total crustal Cr in rocks (CCME, 1999b; Motzer, 2004). Cr(VI) minerals may occur due to hyrothermal alteration of the source rock. For example, hydrothermal alteration of ultramafic rock, including serpentinite, could mobilize relatively insoluble Cr(III) minerals by altering them into different mineral species. Cr(III) may also be oxidized to Cr(VI) by Mn(IV) oxide (MnO_2) (Motzer, 2004).

As in rocks, chromium exists in two oxidation states (Cr(III) and Cr(VI)) in soils. Chromium in soils is naturally present mostly as insoluble Cr(III) hydroxide ($Cr(OH)_3$), or as Cr(III) sorbed to soil components (Bartlett and Kimble, 1976, cited in Stanin, 2004). Chromium also occurs naturally as a component of soils as chromite, a relatively insoluble Cr(III) mineral (Schmidt, 1984 cited in Stanin, 2004).

3. Chromium in Air

Worldwide, most atmospheric Cr source emissions are from wind-borne soil particles (62.4%) and volcanoes (34.67%) with the remaining emissions from sea salt spray, forest fires, and biogenic sources (Papp, 1994, cited in Jacobs and Testa, 2004). In 1986, the California Air Resources Board estimated that the ambient population-weighted annual Cr concentration ranged from 8.9 ng/m3 to 17.8 ng/m3. They also estimated that Cr(VI) comprised 3% to 8% of the reported ambient Cr in air; this occurred in the form of respirable particles with a median diameter of approximately 1.5 μm to 1.9 μm (CARB, 1986 cited in Jacobs and Testa, 2004). The low proportion of Cr(VI) in air is consistent with the findings that soil is the primary source of Cr in air, and that ambient Cr derived from soil particles are primarily composed of Cr(III) compounds (Jacobs and Testa, 2004; Stanin, 2004).

For aerosol particles, which have a longer residence time in air than particles derived from soil and rocks, it is expected that most of the total Cr will be present as Cr(III) since atmospheric conditions favor the reduction of Cr(VI) to Cr(III). This is the likely case because of the presence and concentrations of reducing agents in the air (e.g. V^{2+}, Fe^{2+}, H_2S, HSO_3^-, NO_2^-, and organic materials) as well as the acidity of the atmosphere. Cr(VI) can be reduced rapidly in the atmosphere based on theoretical (Seigneur and Constantinou, 1995) and experimental

(Grohse et al., 1988) studies. Estimates of atmospheric half-life for Cr(VI) reduction to Cr(III) range from 16 h to 4.8 days (Grohse et al., 1988; Kimbrough et al., 1999). The few materials capable of oxidizing Cr(III) to Cr(VI) in the atmosphere, such as ozone, occur in concentrations too low to produce measurable conversions in the atmosphere. (Motzer, 2004).

4. Solubility of Particulate Chromium

The two oxidation states of Cr that occur in the natural environment have very different mobility in the environment owing to different solubility and adsorption characteristics. Cr(III), *e.g.*. $Cr(OH)_3$, tends to be immobile because it is a cation that is sorbed to negatively charged surfaces in the bedrock or aquifer material (Calder, 1988; McClean and Bledsoe, 1992; both cited in Steinpress et al., 2004). Cr(III) species that are water soluble do not occur naturally and are unstable in the environment (Kimborough et al. 1999). Cr(VI) is an oxyanion (e.g., $HCrO_4^-$ or CrO_4^{2-}) and is more mobile in groundwater because of higher solubility and low adsorption to aquifer materials (Calder, 1988). Cr(VI) that is not adsorbed or reduced to Cr(III) remains highly mobile within the soil profile (CCME, 1999b).

Therefore if particulates containing Cr(VI) enter aquatic environments it is reasonable to assume that they will dissolve. It is estimated that 70 – 90% of total Cr in filtered (<0.45 µm) surface waters is present as Cr(VI) (CCME, 1999a). The most common forms of dissolved Cr in natural waters are the Cr(VI) ions CrO_4^{2-}(chromate), $HCrO_4^-$(hydrogen chromate), and $Cr_2O_7^{2-}$(dichromate) (Kotas and Stasicka, 2000). The primary source of Cr(VI) in surface waters is from anthropogenic sources, mainly pulp and paper mills, cement and fertilizer plants, textile mills, power plants, chlor-alkali plants, and petrochemical industries.. (CCME, 1999a).

Oxidation of any Cr(III) present in surface water to Cr(VI) by dissolved oxygen is unlikely because this process is slow, requiring several months at pH typical of surface waters (slightly acidic to basic). The slow oxidation kinetics of Cr(III) enable it to be involved in other faster reactions (sorption or precipitation) that will bring it out of solution (Stanin, 2004).

5. Implications for the Ajax Project

The Ajax deposit is an alkalic copper-gold porphyry, which has undergone albite and potassium-feldspar alteration as well as propylitic and serpentinite alteration. The dominant mine rock lithologies are the Iron Mask hybrid (diorite-gabbroic), mafic volcanic and picrite units, which contain several potentially Cr-bearing minerals (rutile, magnetite, actinolite, biotite, chlorite, clinopyroxene, epidote, serpentine, diopside and olivine) that comprise up to 84 wt.% in the Iron Mask hybrid samples and up to 100 wt.% in the picrite samples (Lorax, 2015). In particular, the picrite and mafic volcanic mine rock lithologies contain elevated

concentrations of Cr (90th percentile values of 836 ppm and 457 ppm, respectively) when compared to crustal averages (~140 ppm).

Given the geology and mineralogy of the Ajax deposit, the propensity of Cr(III) as a substitute in silicate minerals that dominate the mine rock lithologies of the Ajax deposit, and that Cr(VI) comprises a relatively small proportion of total Cr in rocks, it is expected that Cr in airborne particles produced during construction and operation phases of the Ajax Mine will be present primarily, if not exclusively, as Cr(III). Similarly, Cr in dust from roads will be present as Cr(III) given that Cr(III) is the predominant form of Cr in soils.

Cr(III) is highly insoluble in sediment and soils, therefore it is expected that only a small proportion of Cr in airborne particles generated by mine activities will dissolve in adjacent surface waters. The potential for oxidation of Cr(III) to Cr(VI) in particulates entering surface waters is unlikely due to the slow nature of oxidation kinetics at pH levels typical of surface waters, therefore, the potential for mobilization of Cr through transformation of Cr(III) to the more soluble Cr(VI) is low.

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