PROBABILITY OF SOIL ENVIRONMENT CONTAMINATION BY CHROMIUM COMPOUNDS IN UNDERGROUND CP SYSTEMS UTILIZING HIGH-SILICON CHROMIUM CAST IRON ANODES

Dr. J. A. Jakobs
Corrosion Consultant

ABSTRACT: Theoretical considerations relating to formation of toxic chromium compounds, supported by a review of scientific studies and practical investigation reports, lead to better understanding of the formation mechanism of toxic chromium compounds as well as the chemistry of chromium immobilization within soils. No evidence was found supporting the expectation that chromium compounds diffuse unrestricted to soil or groundwater in the neighborhood of high-silicon chromium cast iron anode CP groundbeds. Chromium ions released to soil as corrosion products of this type of anodes are very unlikely to be oxidized to Cr(VI) due to Fe(II) ions presence, and all chromium compounds developed in the anodic process are expected, and in known cases were found, retained in the close vicinity of the groundbeds.

INTRODUCTION

Chromium metal is extensively used in ferrous alloys, mostly due its resistance to ordinary corrosive agents. Chromium forms a variety of chemical compounds and may occur in several oxidation states, chiefly II, III and VI.

<u>Chromium Compounds</u>

Cr metal dissolves in non-oxidizing mineral acids, like HCl and H_2SO_4, but not in oxidizing acids (HNO_3; aqua regia) which passivate the metal.

Cr(II); divalent; several compounds of Cr^{2+} (chromous ion) are known and these are strong reducing agents. Stable chromous compounds and complexes are used for industrial purposes.

Cr(III); trivalent; it is the most stable and important oxidation state of chromium, particularly in its aqueous chemistry; compounds like: $Cr_2(SO_4).xH_2O$; $CrCl_3.xH_2O$ are soluble in water to varying degree. Many Cr(III) complex combinations, also with organic substances, are known and practically utilized. Trivalent chromium is relatively immobile in the aquatic system due to its rather low water solubility, in certain cases resulting in retaining chromium in solid phase as colloids or precipitants.

Cr(VI); hexavalent; it is chromium highest oxidation state with very strong oxidizing properties. The basic oxide of this group is CrO_3, readily soluble in water. In alkaline water solutions Cr(VI) exists as chromate ion, CrO_4^{2-}. A decrease in pH results in creation of dichromate ions: $2CrO_4^{2-} + 2H^+ = Cr_2O_7^{2-} + H_2O$. Cr(VI) compounds are highly soluble in water and can be transported over a great distance before they are reduced back to the trivalent state. Hexavalent chromium compounds are poisonous, carcinogenic and skin irritants.

Chromium ions of valences Cr(I), Cr(IV), Cr(V) have no stable water solution chemistry and primarily exist as transients intermediates between Cr(VI) and Cr(III) and appear in solid form (ref.1, 2).

Redox potential of chromium compounds

Chromium appears in wide range of oxidation states.
Oxidation - reduction potentials for some chemical reactions of Cr compounds are shown in Table 1 (ref. 3). The standard hydrogen electrode potential has been added as reference.

Table 1

Reaction	Redox potential E (volts)	Notes
$Cr^{2+} + 2e = Cr$	- 0.91	
$Cr^{3+} + e = Cr^{2+}$	- 0.41	Several Cr(II) compounds are strong reducing agents.
$Cr^{3+} + 3e = Cr$	- 0.74	Cr(III) is a stable oxidation state chromium compound in aqueous chemistry.
$Cr_2O_7^{2-} + 14H^+ + 6e = = 2Cr^{3+} + 7H_2O$	1.23	Acid solutions of dichromate $(Cr_2O_7^{2-})$ are very strong oxidants.
$2H^+ + 2e = H_2$	0.0000	Standard hydrogen electrode

Note: These potential values apply to open 'circuit systems', i.e. when there is no current drained or applied from outside.

STUDIES AND INVESTIGATIONS

Chromium compounds in the hexavalent oxidation state have been placed on the Environment Canada list (ref.12) of toxic substances. Hence, the interest in the environmental impact of CP groundbeds involving anodes containing chromium and releasing chromium ions into the ground and, possibly, groundwater while generating current for cathodic protection purpose.

1. Extensive studies of the chemical transformation of chromium in natural water have been undertaken in recent years, including a model study conducted in the USA (ref. 4). In the study simulations were implemented to examine the effect of 11 chemicals and environmental parameters on the redox cycle between trivalent [Cr(III)] and hexavalent [Cr(VI)] chromium. Very strict model parameters, covering a range of chemical and environmental conditions encountered in typical natural water, were applied over pH range 4-9.

    It has been found that natural water serves as a reductive environment for chromium under typical conditions, since the common oxidants of Cr(III), like hydroxyl radical and manganese [Mn(III), Mn(IV)] do not convert chromium to Cr(VI) at significant rate. At the same time, other constituents of natural water, such as S(IV) at lower pH (<5), and Fe(II) at pH~6 become the predominant reductants of Cr(VI). At higher pH (>8), and in the presence of dissolved oxygen, reduction by Fe(II) is suppressed due to oxidation of Fe(II) by oxygen.

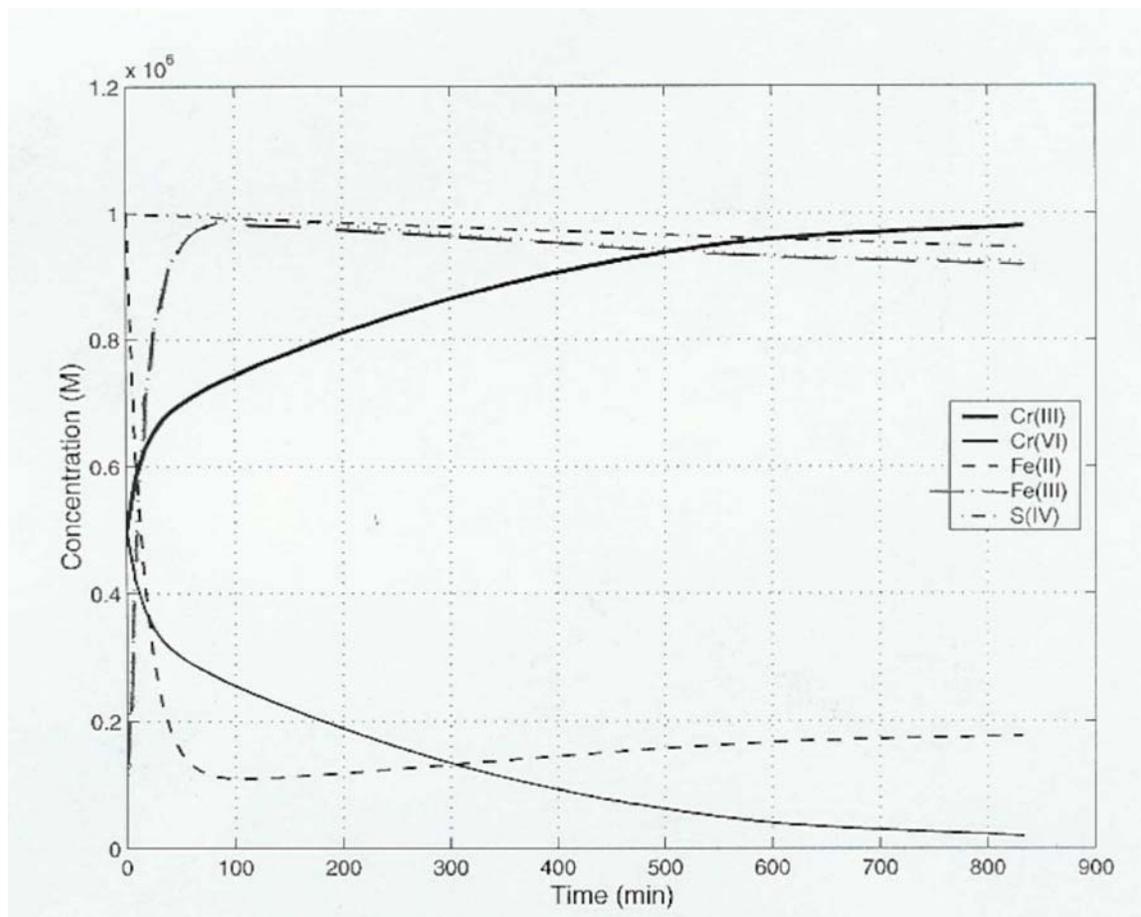   Important findings of the study are presented graphically in Fig. 1

Figure1. Modeling under assumed typical conditions (pH7).

It is noticeable in Figure 1 that significant changes, in both - trivalent and hexavalent chromium concentration, occurred when the level of Fe(II) was high, indicating the importance of this metal ion in Cr(VI) reduction.

It is also worth noting that the concentration profiles of Cr(III) and Cr(VI) are symmetrical to each other; it should be stressed that equal initial concentration of Cr(III) and Cr(VI) were used in the model study shown on the graph.

Other factors affecting the redox transformation of chromium, determined in this study, can be summarized as follows:

- Dissolved oxygen in natural waters can effect the redox cycle of chromium since it is a major sink (absorber) for Fe(II) at neutral to alkaline pH. It was found, however, that the effect of dissolved oxygen at various concentrations had been rather insignificant, most likely due to slow consumption of Fe(II) by dissolved oxygen in moderately acidic conditions of pH up to 7. At this range of pH, Fe(II) in the presence of Cr(VI), was predominantly oxidized in the reaction with Cr(VI).

- The pH 4 - 5 range favors formation of Cr(III) as a result of reduction activity of sulfite ions [S(IV)] if present in water. At higher range of pH, up to neutral, the reduction activity of Fe(II) becomes important as indicated above. With further increase of pH (8-9 range), the role of Fe(II) in reducing Cr(VI) gradually diminishes.

- Substances such as hydrogen peroxide (H_2O_2) and hydroxyl radical (OH+), if present in water in higher concentrations, are strong oxidants able to oxidize Cr(III) to Cr(VI). When, however, the reducing ions like [Fe(II), S(IV)] are also present in sufficient quantity in the water at pH 4-7, they effectively 'neutralize' the oxidants in their role in chromium redoxy chemistry.

- Fe(II) was found to be predominant reductant of Cr(VI) under, so called, default modeling conditions of the study at water pH 6 - 7. It rapidly reacted with Cr(VI) and reduced it to lower oxidation level. At pH higher than 8, dissolved oxygen easily oxidizes Fe(II), resulting in substantial decreases of Cr(III) formation.

2. A laboratory test and field investigations were carried out in Calgary (ref. 5) to identify possible problems of soil and groundwater contamination by toxic chromium ions and other chemical compounds generated in CP groundbeds by high-silicon chromium cast iron anodes.

   While the results and conclusions of the laboratory tests of this investigation are not easily transferable into actual field conditions, the results of field investigations are of interest.
   During field investigations three shallow anode groundbeds were excavated and samples of soil collected from several spots around the anodes in the string. The excavated grounbeds varied in time of operation from eleven (11) months to nineteen (19) years. Location of the soil sampling differed at each groundbed; the samples were taken in some cases at close vicinity of the anodes and in other cases further away, over the range of 0.5 to a few meters.

None of the soil samples taken from the grounbed depth, at a distance of approximately 2 meters, show the metal ion concentration in excess of applicable environmental guidelines. Chromium concentration declined sharply within short distance, indicating that chromium compounds were immobilized within 1 to 2 meters from the anodes. Water samples taken from boreholes were acidic, rich in ferric sulfate. Chlorine gas presence was perceptible. There was, however, practically no indication of water contamination by species generated by current discharging anodes at a distance of a few meters from the anode beds.

3. An interesting laboratory investigation was carried out in Denmark (ref.6) for the purpose of finding an effective method of chromium removal from the groundwater heavily contaminated with various industrial chromium Cr(VI) containing effluents. The cleaning process involved a redox reaction between chromium ions and iron Fe(II). The process was carried out by forcing water contaminated with Cr(VI) through an iron filings filter (no details on the composition of the filings were given). The iron filings were contained within the organic glass column equipped with sampling gates on the column sides. The arrangement allow for testing both the flow and the fillings along the column length. The pH of contaminated water was adjusted to 4 upstream of the filter.

    It has been found that the procedure was effective in removing chromium from the contaminated water almost entirely (below 3 µg/L). The redox reaction between chromium and iron Fe(II) leads to conversion of chromium from hazardous and mobile hexavalent [Cr(VI)] to trivalent [Cr(III)] which is immobile, less harmful and retains in the iron filter. It was also determined that the iron filings capacity of chromium removal gradually declines with the amount of chromium put through the filter (the filings being oxidized). For continuous effective chromium removal, the iron filing of the filter must be periodically replaced. The significance of pH level in the process of chromium removal has been confirmed.

4. Most soils and associated groundwater contains certain amounts of dissolved inorganic compounds (salts) which dissociate releasing ions, primarily chlorides (Cl^-) and sulfates ($SO_4^=$). When current is applied to an   anode in a CP installation, the anode is polarized and the process of electrolysis of water begins. The chloride and/or sulfate ions migrate to the anode surface yielding chlorine gas when Cl^- ion is discharged; oxygen plus sulfuric acid   when $SO_4^=$ ions are discharged in the anodic process. In case of low concentration of chloride and sulfate ions, oxidation of water may take place at certain potential levels, with the release of hydrogen (H^+) ions. In consequence, during the anodic electrolysis, the anode and the surrounding are exposed to low pH and, often, to strong oxidants (ref. 7,8).

Redox potential considerations indicate that the likelihood of forming certain compounds depends on the respective oxidation-reduction potential (E) values that apply.

If an inert electrode is anodically polarized in an electrolyte containing chromium compounds specified in Table 1, first - chromium Cr(III) is expected to be generated, then hydrogen ions would be released; oxidation of chromium to hexavalent [Cr(VI)] state would require further significant voltage increase.

When current is applied in field conditions to high-silicon chromium cast iron anodes in a typical anode groundbed the reactions are different, being affected by various parameters including anode metallurgical content, anode surface profile developing in the process and the catalytic interaction between compounds released in the anodic process to the anolyte. This phenomenon in general terms is called polarization.

The most important constituents and factors affecting the behavior of Cr ions in corrosion deposits and fluids present in the anode vicinity would be iron ions [Fe(II)] and pH of the environment.

SUMMARY AND CONCLUSIONS

This review of the basic and other available sources of information leads to formulation of the following summary and conclusions.

During anodic reaction the anode material gradually deteriorates releasing ions of metals originally cast in the body. Predominantly iron and chromium ions are being released in this process, since ~ 85% of the anode material consists of these two metals; iron~ 80% and chromium 3.25 to 5.0 %.

Electrochemical reactions associated with current discharge create low pH of the environment around anodes in the groundbed.

Electrochemical and chemical reactions favor formation of trivalent [Cr(III)] and, likely, divalent [Cr(II)] chromium compounds in the anode vicinity. These compounds are relatively immobile and insoluble, tending to precipitate or be captured close to the anode.

There is little probability of chromium Cr(III) ions oxidation to hexavalent state even if the electrolysis of water or discharge of sulfate ions are involved in creating oxidizing environment in the anode vicinity. Transformation of Cr(III) to Cr(VI) requires pH of no less than 8. This higher value of pH is unlikely to be reached in normally acidic environment surrounding the anodes.

Findings of the tests and investigations reviewed for this summary, reveal a rapid decline in the presence of chromium compounds in a rather short distance from the anodes in CP groundbeds. It is evident that redox potentials of chromium compounds and chemistry of the environment (low pH), favor formation of trivalent chromium [Cr(III)] in the anode surrounding. Immobilization of chromium in the areas adjacent to anodes appears to be independent on the operation time of the grounbed, within the time frame of a few months to several years.

The special role of Fe(II) ions, discharging along Cr ions during the anodic process of deterioration of high-silicon chromium anodes, should be recognized and acknowledged.

Both, the extensive and thorough scientific study and more practically oriented investigations indicate that ions of iron Fe(II) are not only strong reducing agents of chromium Cr(VI) but also are very effective 'absorbing filters' retarding chromium migration to the ground or groundwater environment, in the vicinity of CP groundbeds.

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