



**University of California**

Agriculture and Natural Resources | California Institute for Water Resources

## **Minimizing Hexavalent Chromium in Californian Water: Understanding Hiding Reaction Pathways in Drinking Water and Reinventing Treatment Process**

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Project Summary

Chromium (VI), known as hexavalent chromium, is a highly toxic and soluble compound that has been widely observed in groundwater across California. It enters groundwater through improper industrial waste disposal as well as geological weathering of naturally occurring chromium-containing aquifer minerals. As a major drinking water supply in California, especially in vast inland areas, the presence of chromium (VI) in groundwater threatens source water quality and poses great public health risks. Current EPA drinking water standards are only applicable to total chromium, which can be present as chromium (VI) as well as the much less toxic form of chromium(III) that is even a nutrient at low concentrations. However, a new drinking water standard specific to chromium(VI) was recently proposed by the California Department of Public Health. The proposed low drinking water standard for chromium (VI) is estimated to pose great challenges to Californian water systems to upgrade treatment to meet the regulation.

Available water treatment technologies normally transform soluble chromium(VI) to particulate chromium(III) before removing the solids. Albeit that, these treatment processes are not efficient to achieve the low concentrations that will be required. Subsequently, in water distribution piping systems, residual chromium(III) and chromium(VI) can participate in multiple reactions that involve heterogeneous chemical oxidation, reduction, adsorption, and co-precipitation. However, these chemical processes that eventually impact chromium(VI) levels in finished drinking water are not understood yet. The primary objective of this research project is to advance the mechanistic understanding of chromium(VI) conversion and formation pathways from water resources to treated drinking water, specifically by residual disinfectants and corrosion scales in water distribution system. The project will evaluate chromium(VI) transformation mechanisms over a broad range of typical groundwater chemistry conditions in batch reactors in PI's laboratory. Analytical methods will track changes in both total chromium and chromium(VI) to the very low levels that are being considered for regulations.

The investigation will use advanced spectroscopic and electrochemical tools to identify the dominant reaction mechanisms that impact the occurrence of chromium(VI) in drinking water. Mass spectroscopic and UV spectroscopic measurements coupled with particle separation will provide insights into the oxidation state and molecular-scale coordination of chromium associated with various chemical processes in drinking water condition. *In situ* electrochemical detection of chromium transient species can be diagnostic of specific reaction mechanisms. A mathematical kinetics model for chromium(VI) formation via oxidation of Cr(III) oxidation by disinfectants will integrate the mechanistic insights and data from the laboratory-scale experiments to enable predictions of its occurrence over a broad range of water conditions. The research will enable the optimal design of treatment strategies and accurate prediction of treatment performance for chromium(VI) removal.

This project will provide scientific information that will help improve the removal of hexavalent chromium, a contaminant of critical Californian and national interest, from drinking water. The research will determine the influence of water chemistry on the reactions involved in the process, which will enable the design of effective strategies for the minimization of chromium(VI) occurrence for a broad range of drinking water sources. The research activities will determine reaction mechanisms of interest in water resources management as well as environmental science and engineering. The project's overall application of interfacial process characterization and electrochemistry tools will advance the overall infrastructure for resource management and water quality research. The educational components of the project will enhance student training and promote early student interest in water science.

## Research Program

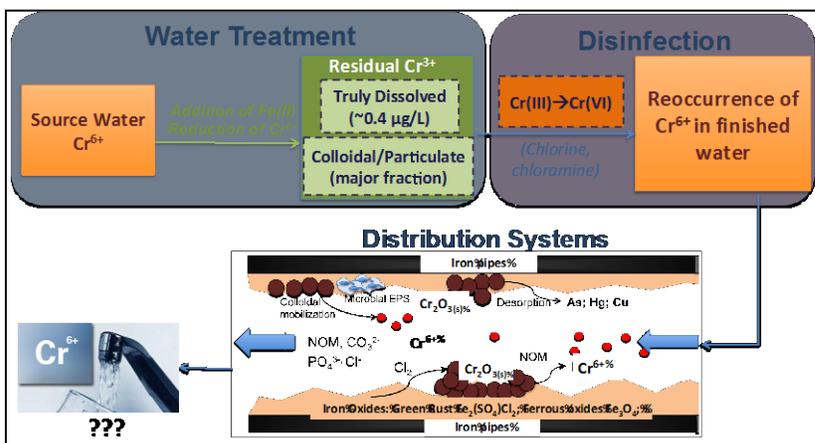
### **Background**

Hexavalent chromium, denoted as Cr(VI), is a highly toxic and soluble compound that has been widely observed in groundwater across California (i). Historically improper disposal of industrial wastes from processes such as tanneries, metal dipping, electroplating, and industrial process corrosion control water are responsible for anthropogenic sources of Cr(VI) in California (ii-iii). In addition, chromium is the 21<sup>st</sup> most abundant element found in the earth's crust (iv). Weathering of chromite (FeCr<sub>2</sub>O<sub>4</sub>) and other chromium-bearing minerals present in bedrock and aquifer will generate natural Cr(VI) in groundwater (v). Although chromium can be present in various oxidation states, only hexavalent chromium Cr(VI) and trivalent chromium Cr(III) are predominant in the aquatic environment. The mobility and toxicity of chromium in water largely depend on its oxidation state. Cr(VI) is a known carcinogen and mutagen if ingested, causing a variety of terminal illness including stomach cancer and DNA damage (vi), whereas Cr(III) is an essential nutrient at trace levels (vii).

Unfortunately, there is no current federal or state standard specific to the hexavalent chromium in groundwater or drinking water. Only total chromium is regulated at 100 µg/L at the deferral level by US EPA, while in California, the total chromium drinking water standard is 50 µg/L (viii). However, a new drinking water standard specific to Cr(VI) was recently proposed by the California Department of Public Health in August 2013 with a draft standard at 10 µg/L (ix). It is expected that a new regulation specific to Cr(VI) will be implemented soon in California.

Because groundwater is a major drinking water supply in California, the wide occurrence of hexavalent chromium in Californian groundwater has threatened water quality and posed great public health risks. A recent occurrence analysis of approximately 2500 water samples from California showed that more than 30% of the samples had hexavalent chromium level higher than 10 µg/L, the proposed new standard in California (viii). Most of those "hot spots" are located in areas where groundwater is a major drinking water source. In addition, newly collected data based on EPA's Third Unregulated Contaminant Monitoring Rule (UCMR3) showed that approximately 35% of source water samples taken from locations nationwide exceeded the proposed Californian standard (x). With a new standard on Cr(VI) is in the foreseen future, it is urgent for Californian water systems to find ways to remove Cr(VI) from groundwater source.

Available water treatment technologies apply different unit operations to transform soluble chromium(VI) in source groundwater to particulate chromium(III) before removing the solids (xi-xvi). Albeit that, these water treatment processes are not efficient to achieve low concentrations and result in the carry-over of residual non-toxic Cr(III) particles and colloids to water distribution system (Figure 1). The distribution system is a complex reactor where pipeline corrosion materials and residual disinfectants can impact the fate and transformation of chromium (xvii-xix). Of particular concern is the conversion of non-toxic residual Cr(III) to toxic Cr(VI) via oxidation processes by disinfectants, and redox chemical processes associated with corrosion scale surfaces on iron pipes (Figure 1).



**Figure 1.** A schematic illustration of hiding chromium redox pathways in drinking water distribution system after the water treatment processes which could contribute to the re-occurrence of Cr(VI) in finished drinking water.

Preliminary findings from the PI's laboratory – conducted using model Cr(III) solids that are typically found in drinking water treatment plant – suggested that chlorine as a residual disinfectant can oxidize Cr(III) and unintentionally produce hexavalent Cr(VI), resulting in deterioration of water quality (preliminary data shown in Section 3 Research Plans). No previous study has focused on the reactivity of particulate Cr(III) and its transformation to Cr(VI) in water distribution system. In addition, different water chemical parameters can affect the rate of conversion, including water pH, alkalinity, availability of iron oxides on internal piping surface, and the presence of soil humic substances introduced from groundwater (xx-xxv). Furthermore, the redox pathway between Cr(VI) and Cr(III) is hypothesized to be involved with intermediate chromium species that are short-lived but could impact the overall reaction rate. However, these chemical processes that eventually impact chromium(VI) levels in finished drinking water have not been explored yet, and the Californian's public health is at huge risk.

Considering the high toxicity of hexavalent chromium and the upcoming low drinking water standard in California, it is urgent and critical to determine the conversion and transformation pathways of chromium(VI) in the treatment and distribution systems and the water chemical conditions under which changes may occur. Accordingly, the objectives of this project are:

- Systematic investigate the nature of hexavalent chromium(VI) formation via trivalent chromium(III) oxidation by residual disinfectants in drinking water distribution system.
- Examine the effects of water chemical parameters on the rate of hexavalent chromium transition, including pH, alkalinity, organic carbon content and other anions.
- Explore the association of soluble chromium(VI) with corrosion scales in distribution system and related redox processes that stabilize chromium(VI).
- Detect intermediate chromium species during the redox pathways and identify the rate-limiting step using electrochemical analysis.

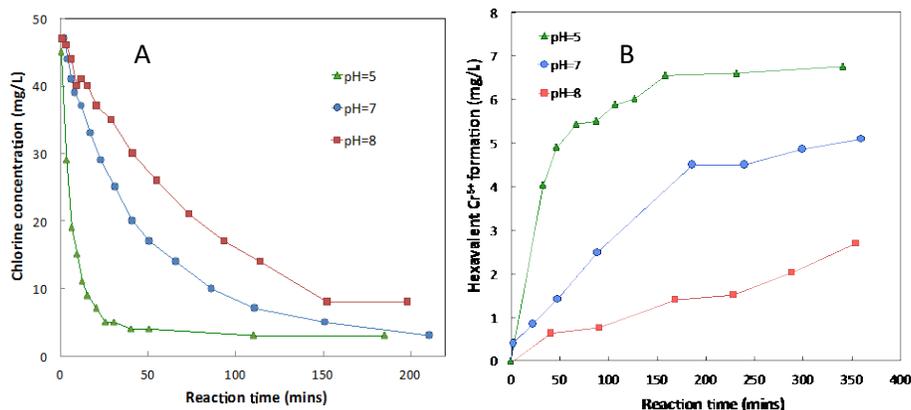
### Information Transfer/Outreach Program

**Task 1: investigate the formation of hexavalent chromium(VI) via oxidation of particulate trivalent chromium(III) in typical drinking water conditions.**

Hypotheses: In the presence of residual disinfectants, re-occurrence of Cr(VI) takes place via oxidation of Cr(III), but different disinfectants have distinct reactivities with respect to Cr(VI) generation and Cr(III) conversion.

**Approaches:** Experiments in this task will be conducted in a controlled batch reactor, using a systematic matrix approach with typical chromium(III) compounds found in drinking water. Specifically chromic hydroxide  $\text{Cr}(\text{OH})_3$  and chromite  $\text{FeCr}_2\text{O}_4$  will be employed as model Cr(III) compounds. These two solids have been identified as the thermodynamically most stable phases of Cr(III) compounds in water but no data are available on their reactivity and potentials to be converted to toxic Cr(VI). Because chlorine and chloramine are the two most commonly used disinfectants by water utilities, these two disinfectants will be applied in experiments for this task. In each batch oxidation test, an initial dosage of disinfection ranging from 2 to 50 mg/L as chlorine will be injected to the reactor to start the reaction. At pre-determined reaction interval, samples will be taken and filtered through 0.45- $\mu\text{m}$  filter.

The concentration of chromium(VI) in the filtrate will be analyzed by UV spectroscopic method, and the total chromium concentration will be analyzed by the start-of-the-art Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). These two spectroscopic measurements can differentiate Cr(VI) from Cr(III) in the filtered sample. The concentration of disinfectant will be quantified by standard DPD colorimetric method. Preliminary experiments confirmed that chlorine can quickly oxidize Cr(III) hydroxide solids to Cr(VI) following a first-order reaction kinetics (Figure 2).



**Figure 2.** Evidences of Cr(VI) regeneration via Cr(III) oxidation by chlorine. (A) Results showed that chlorine was consumed and the reaction rate decreased with increasing pH. (B) Formation of Cr(VI) from the same experiments.

Preliminary results in Figure 2 strongly suggested that reoccurrence of Cr(VI) is a big concern in drinking water using chlorine as the disinfectant. Even slightly amount of residual Cr(III) carried over from treatment process can be quickly converted to toxic Cr(VI) by chlorine under circumneutral pH condition and exceed the proposed California regulation. However, the reaction rates and conversion rates of Cr(III) to Cr(VI) remains to be systematically investigated at varying chlorine concentrations typically found in drinking water. In addition, the conversion of Cr(III) to Cr(VI) by another typical disinfectant (*i.e.*, chloramine) will be investigated in similar conditions to the chlorine experiments.

**Task 2: Examine impacts of typical water chemical parameters on chromium(VI) formation.**

**Hypotheses:** Typical water chemical parameters, including solution pH, alkalinity level, organic carbon content, and anion concentration (especially bromide) can impact the rate of Cr(VI) formation via oxidation of Cr(III) by disinfectants. Organic carbon levels, especially soil humic substances derived from groundwater origin, can also reduce Cr(VI) back to Cr(III).

**Approaches:** Experiments in this task will be conducted in the same batch reactor system established from Task 1. Both  $\text{Cr}(\text{OH})_3$  and  $\text{FeCr}_2\text{O}_4$  will be used as the model Cr(III) compounds. A series of experiments will be conducted with varying water chemical parameters. Specifically, the solution pH will range from 5 to 9

to cover all possible drinking water pH levels. Five level of alkalinity will be examined at 20, 50, 70, 100 and 150 mg/L as CaCO<sub>3</sub> when pH is fixed at 7.0. Another important chemical parameter to examine is bromide. First, bromide usually co-exist with chromium(VI) in groundwater basins of California. Second, bromide can be oxidized by disinfectant chlorine to form bromine and accelerate many oxidation processes. It has been observed that in bromide-containing water, the rate of oxidation of Mn(II) by chlorine was increased by more than two orders of magnitude (xxvi). It is hypothesized that bromide will also exhibit a catalytic effect on Cr(VI) reformation via Cr(III) oxidation. To investigate the effect of bromide, its level will be varied between 1 and 2 mg/L in oxidation experiments, which also represents typical bromide concentrations in groundwater.

To investigate the impact of organic carbon content, Suwannee River Humic Acids will be used as a model Natural Organic Matter. It was reported that humic substances can reduce Cr(VI) to Cr(III) and alleviate the re-occurrence issue of Cr(VI) in finished drinking water. However, this back reaction is a very slow process, with a half-life approximately 50 days in the presence of 100 mg C/L soil humic substances at pH 6 (xxvii). Interestingly, when trace amount of Fe(III) is present in the system, Fe(III)/Fe(II) redox couple acts as an electron transfer mediator (therefore as a redox catalyst) for the transition of Cr(VI) to Cr(III). As a result, the half-life of Cr(VI) is decreased by one order of magnitude in the presence of trace Fe(III). This implies that in the presence of chromite FeCr<sub>2</sub>O<sub>4</sub>, the impact of humic substances will be more prominent. Therefore, the impact of organic content will be conducted only with FeCr<sub>2</sub>O<sub>4</sub>.

***Task 3: Detect short-lived chromium intermediates during in the Cr(III)/Cr(VI) redox cycle.***

Hypothesis: Because the oxidation of Cr(III) to Cr(VI) involves the loss of three electrons. It is hypothesized that this overall redox reaction involves multiple one-electron transfer processes. Therefore, short-lived chromium intermediates, such as Cr(IV) and Cr(V) are generated. The nature of these intermediate species and their reactivities control the overall rate of Cr(VI) re-occurrence.

Approaches: To detect these short-lived intermediates, a novel electrochemical (EC) analytical method will be applied. The above discussion indicates that phenomena that involve formation of Cr(IV) and Cr(V) intermediates are critically important for the suppression of hexavalent formation in drinking water. The task will establish an EC protocol to quantify Cr(IV)/Cr(V) generation in drinking water conditions (i.e., circumneutral pHs, varying carbonate levels, presence of chlorine and naturally-generated organic species). The method of rotating ring disk electrode (RRDE) will be the preferred tool. The PI's group has strong experience in applying the advanced EC techniques for examination of metal redox reaction (xxviii). Tests will be conducted to optimize the EC system parameters, including ring/ disk potentials, potential scan rate, supporting electrolyte and electrode rotation rate.

Effects of complexing agents that conceivably can stabilize Cr(III) will also be examined. The formation of chromium intermediates will be examined based on the intensity and location of corresponding characteristic peaks in voltammograms. Cr(III) solutes such as Cr(ClO<sub>4</sub>)<sub>3</sub> will be used for Cr(IV) and Cr(V) generation in the EC optimization procedures at neutral pH, low carbonate and in the absence of chlorine. Gold or platinum will be used as the electrode material. It is expected that the completion of this task will gain insights into the fundamental redox reaction mechanisms associated with Cr(VI) and eventually develop management strategies to reduce its formation in drinking water.

## Notable Achievements

This project will provide scientific information that will help improve the removal of hexavalent chromium, a contaminant of critical Californian and national interest, from drinking water, especially by understanding the hiding reaction pathways in drinking water distribution system. The research will determine the influence of water chemistry on the reactions involved in the process, which will enable the design of effective strategies for the minimization of chromium(VI) occurrence for a broad range of drinking water chemical conditions typically in California. The research activities will determine reaction mechanisms of interest in water resources management as well as environmental science and engineering. The project's overall application of interfacial process characterization and electrochemistry tools will advance the overall infrastructure for resource management and water quality research. The educational components of the project will enhance student training and promote early student interest in water science.

## Student Support table

The outreach component of the proposed work addresses the need to integrate research and education. The plan involves engaging students from Riverside City College (RCC) and University of California, Riverside (UCR) in the growing field of environmental science and engineering. Both UCR and RCC are recognized as Hispanic Serving Institutions (UCR #OPEID-00131600), and this research project offers a good opportunity to involve students from underrepresented groups in locally relevant science and engineering research.

A mechanism exists by which eligible RCC students can apply to participate in research taking place in UCR labs. Additionally, the PI will present seminars on the work conducted in the lab at RCC, to which RCC students taking science and mathematics will be invited. One of the goals of this outreach effort is to increase the number of underrepresented individuals from RCC (a two-year institution) who transfer to UCR or other institutions to pursue a career in science and engineering. The PIs' experience in mentoring underrepresented individuals has taught them that the best way to encourage participation in the fields of science and engineering is by exposing young people to hands-on lab experience. This project will allow RCC students to participate in lab-based research, and hopefully instill them with a passion for science and engineering and the desire to pursue a career.

One PhD student from UCR's Department of Chemical and Environmental Engineering (CEE) will perform the main experimental work. UCR CEE undergraduate research assistants will have the opportunity to participate in research activities during the academic year and summer months for the duration of the project. We will collaborate with UCR Mentoring Summer Research Internship Program to recruit first-generation college students from socioeconomic disadvantaged backgrounds to participate in intensive summer research annually.

Results and techniques to be developed in this study will be integrated into the engineering curriculum at UCR (*e.g.*, Aquatic Chemistry and Advanced Water Treatment taught by the PI). Findings of the study will be disseminated to the professional community through publication in peer-reviewed journals, presentations at conferences and interactions with the general public in multiple events, including the UCR Engineering Discovery Day and other outreach activities at UC Riverside.

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