# The Use of Reduction, Coagulation and Filtration for the Removal of Hexavalent Chromium in Groundwater—Ferrous Reagent Concerns for Drinking Water Applications

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**ABSTRACT:** The purpose of this paper is to provide a comparative evaluation of the use of bulk ferrous [Fe(II)] and in-situ generated stannous [Sn(II)] reagents for the removal of hexavalent chromium [Cr(VI)] to meet California's regulatory standard for this contaminant. Title 22 identifies reduction-coagulation-filtration (RCF) using either bulk ferrous chloride or the in-situ electrolytic generation of stannous as a Best Available Technology for treating Cr(VI) and ensuring compliance with the MCL.

### INTRODUCTION

In October 2024, the amendment to California Title 22 Social Security Division 4. Environmental Health Chapter 15. Domestic Water Quality and Monitoring Regulations Article 2 came into effect and obliges municipalities with levels higher than 10 parts-per-billion (ppb) of Cr(VI) in their groundwater supplies to treat water to below this limit to afford consumers access to safe drinking water. This regulation will impact approximately 500 wells operated by around 300 municipalities that supply water to five million households. The amendment states explicitly the conditions that a Cr(VI) treatment system must satisfy for approval. These include:

"The proposed method for complying with the chromium (hexavalent) MCL; if a new or modified treatment process is proposed, the Hexavalent Chromium MCL Compliance Plan shall include a pilot study adequate to demonstrate that the new or modified treatment process will result in compliance with the chromium (hexavalent) MCL"

"A description of procedures used to determine chemical dose rates sufficient to ensure the treatment process is operating as designed"

Title 22 identifies three Best Available Technologies for treating Cr(VI) and ensuring compliance with the MCL: ion exchange, reverse osmosis and reduction-coagulation-filtration (RCF) using either bulk ferrous chloride or the in-situ electrolytic generation of stannous. While municipalities are not mandated to adopt a BAT to comply with the Cr(VI) regulation, any proposed treatment system must meet the requirements specified by Title 22 for approval.

In the State Water Resources Control Board's (SWRCB) Standardized Regulatory Impact Assessment (SRIA), December 2022, the following was stated about RCF and ion exchange, including Weak Base Anion (WBA) and Strong Base Anion (SBA): "At the proposed MCL of 10 ug/L, RCF [Reduction, Coagulation and Filtration] is calculated to be the least expensive treatment for all but 11 sources. WBA treatment was chosen for the remaining 11 sources, and SBA treatment was never the least expensive option for any source at the proposed MCL". p.p.13-14<sup>1</sup>

The RCF process is based on the controlled dosing of a reducing agent to convert Cr(VI) to trivalent chromium [Cr(III)] sufficiently to reduce the concentration of Cr(VI) to below 10 ppb. Following this reduction, the resulting coagulant, which includes Cr(III) and any excess reducing agent, is removed by filtration.

Two chemical reducing agents can achieve this goal: electrolytically generated Sn(II), which is produced on-site and on-demand, and Fe(II), which is supplied to the site as a bulk chemical in the form of ferrous sulfate.

While the use of Fe(II) for Cr(VI) treatment has been characterized as an RCF process, in practice, it is a Reduction-Coagulation-*Oxidation*-Filtration process (RCOF) that requires an additional treatment step to oxidize excess Fe(II) and ensure it can be removed in the subsequent filtration phase because Fe(II) cannot be allowed to pass into drinking water supplies. It is important to note that the Fe(II) reduction-filtration (RF) process has not been identified as a BAT and the only documented demonstration of the process fails to meet the standards set by Title 22.

Over the past eight years, a number of RCF/RCOF demonstrations were conducted to assess the performance of both reducing agents.<sup>2,3,4</sup>

#### THE SCOPE AND DESIGN OF DEMONSTRATIONS

For demonstrations to satisfy the criteria for Title 22 approval, a system that is representative of a full-scale system must be evaluated under typical field conditions (e.g., stop-run, a range of ambient conditions, a range of Cr(VI) levels and reagent dosing rates, failure modes, etc.). RCF/RCOF demonstrations include a contactor vessel of sufficient size to ensure that there is enough time for the reduction process, during which Cr(VI) is converted to Cr(III) prior to filtration. This also allows any excess reducing agent to be oxidized (converted into insoluble filterable form) so that it can be removed during the filtration process, thereby avoiding the risk of it carrying over and contaminating drinking water supplies.

# REDOX REACTIONS—Sn(II) AND Fe(II)

The redox reactions that take place between Cr(VI) species and both reductants (ferrous and stannous) are shown in the equations below:

$$3Fe(OH)2 + CrO42 + 4H2O \rightarrow 3Fe(OH)3 + Cr(OH)3 + 2OH - (E1 = 0.43 V) (1)$$

$$3Sn2+ 2CrO42- 4H2O \rightarrow 2Cr(OH)3 + 3SnO2 + 2H+$$
  
(E2 = 0.64 V) (2)

The stoichiometric and thermodynamic characteristics of the ferrous reaction are less favorable than the stannous reaction. The reagent/chromate stoichiometric ratio is 3:1 for a ferrous reagent and 1.5:1 for a stannous reagent. Also, the stannous reagent has a higher reduction driving force (E2 > E1) in the Cr(VI) reduction process. And finally, the kinetics of the Sn(II)/Cr(VI) redox reaction is faster than the Fe(II)/Cr(VI) one.

# PERFORMANCE COMPARISON—Sn(II) AND Fe(II)

The reduction potential of stannous and its process characteristics are more favorable than ferrous. The consequences of using a ferrous reagent for designing and operating full-scale Cr(VI) treatment systems are significant.

#### The Reduction Phase

- When using Fe(II), a significantly larger contactor vessel is necessary to allow sufficient time—approximately 15 minutes—for the reduction process to occur. In contrast, only about three minutes is required when using Sn(II). This difference has important implications for capital costs and space requirements. Additionally, much higher molar ratios (or reagent doses) of Fe(II) compared to Sn(II) are required to treat equivalent amounts of Cr(VI) in water. This very significant disadvantage of Fe(II) leads to increased chemical demand, more frequent backwashing and much higher waste generation. In fact, up to 10 times more Fe(II) may be required to achieve the same treatment goals as Sn(II).
- 2. The reducing power of Fe(II) is highly dependent on pH levels.<sup>5</sup> To achieve Cr(VI) removal to less than 5 ppb, the pH of the water may need to be adjusted and maintained within a very narrow range of 7.3–8.1.<sup>5</sup> However, in many wells, water pH often exceeds this range, and is coupled with high water alkalinity. Consequently, maintaining tight pH control will require large amounts of acid to be dosed for pH adjustment. In contrast, the redox potential Sn(II) reagent is unaffected and remains stable across a broad pH range of 6–12.<sup>3</sup>

- 3. Because Fe(II) is not a selective reagent, its reducing power can be adversely affected by multiple water matrix interferences such as total organic carbon (TOC), phosphates and more. This may necessitate additional overdosing of the reagent to overcome specific water matrix effects. By contrast, the Sn(II) reagent is highly selective to Cr(VI) and practically unaffected by the water's matrix composition.
- 4. Fe(II) can reduce Cr(VI) to 3-5 ppb, which is low enough to meet the current MCL of 10 ppb. However, this solution is not future-proof against a probable lowering of the MCL to a level closer to the Public Health Goal of 0.2 ppb. By contrast, Sn(II) can reduce Cr(VI) to non-detect levels, providing municipalities with a future-proof solution safe-guarded against future reductions in the MCL. Moreover, for utilities that operate multiple wells and have the capacity to blend their production, there is an opportunity to achieve non-detect levels of Cr(VI) from one well and blend that with untreated water from other wells to produce a blended stream below 10 ppb. This approach, only available with Sn(II), offers an opportunity for significant capital savings that are not attainable with Fe(II).
- 5. Because of the Fe(II) redox thermodynamic and kinetic limitations mentioned, spontaneous oxidation of Fe(II) excess into filterable Fe(III) form in the contactor cannot occur and an additional Fe(II) oxidation step is necessary.<sup>5</sup>

#### The Coagulation Phase

To achieve the treatment goals for Cr(VI), a high excess of Fe(II) over Cr(VI) may be needed, with ratios up to 75:1.<sup>5</sup> A major challenge during the reduction phase is that any unreacted soluble Fe(II) must be converted into an insoluble form of Fe(III) so it can be effectively coagulated and removed in the subsequent filtration stage. There are two significant consequences of this process:

1. To prevent iron carry-over into drinking water supplies, it is essential that the water leaving the contactor is oxidized using air or chlorine to ensure complete Fe(II) oxidation and better iron removal.<sup>5</sup> The kinetics of Fe(II) oxidation by aeration is slow and the process is energy-intensive, requires significant hardware intensive, and introduces increased latency in the system. Additionally, the oxidation rate is pH dependent, which may necessitate additional adjustments and controls. Using chlorine can shorten the oxidation time for Fe(II); however, it introduces the risk of Cr(III) reoxidation back to toxic Cr(VI), which the treatment process is designed to remove. This step is also reagent-intensive and needs to be performed in a separate vessel, increasing the overall system complexity, latency, and footprint. Consequently, the Fe(II) oxidation stepwhether using air or chlorine-becomes another potential failure point. If Fe(II) is overdosed to compensate for its slower kinetics, the risk of Fe(II) carry-over increases. This situation leads to higher costs due to the increased use of reagents and oxidants, as well as greater sludge production, which ultimately results in elevated waste handling and disposal costs. In contrast, the stronger kinetics of Sn(II) ensure that complete oxidation of the reagent occurs in the contactor. Sn(II) dosing is tightly controlled to meet

the stoichiometric requirement to reduce Cr(VI) to below the MCL, or non-detect if required. As a result, the volume of sludge generated by Sn(II) is up to 10 times lower than that produced by Fe(II). Additionally, it is worth noting that the sludge produced from Sn(II) has beneficial reuse applications.

2. The oxidation of Fe(II) to Fe(III) results in the formation of colloidal ferric hydroxide particles, which need to be coagulated into filterable size floc to be captured by media filters. The coagulation of Fe(III) hydroxide is seriously compromised by the presence of silica in the groundwater, even at relatively low concentrations.<sup>5</sup> Silica is present in many wells impacted by elevated Cr(VI) levels that require treatment. To address the negative impact by silica, high doses of polymer are necessary with various complications. Unlike problematic Fe(II) oxidation/coagulation, excess Sn(II) is rapidly oxidized into insoluble Sn(IV) within the contactor vessel. This process creates larger floc particles which are removed reliably by media filtration.<sup>3</sup> Most groundwater wells operate on a stop-run basis; therefore when a complex, multi-stage RCOF treatment system based on Fe(II) is restarted, the initial water produced will not meet compliance standards and must be discarded to sewage until the system has stabilized. Numerous demonstrations<sup>2</sup>,<sup>3</sup> have confirmed the rapid reduction of Cr(VI) by Sn(II) ensures a quick stabilization of the system after startup, thereby eliminating the need to waste water.

#### The Filtration Phase

Under well-controlled conditions, the coagulated Cr(VI) treatment by-products [Sn(IV)/Cr(III) or Fe (II)/Cr(III)] are captured by the filtration process, and then the clean treated water will move to the disinfection stage before being supplied to consumers.

At appropriate intervals, the filters will require backwashing which involves recycling some of the treated water. The backwash is collected and stored in a backwash tank prior to discharge.

There are notable differences in how this backwash water is treated depending on the reducing agent used in the system. In the case of Fe(II), the filtered particulate settles far more slowly compared to a Sn(II) based system. This difference has two important consequences:

- 1. The backwash water (BWW) from the Fe(II) based system has high turbidity. As a result, the backwash water in the Fe(II) system must be discharged into sewage, representing a water loss of  $3-5\%^6$  of the total volume through the entire treatment process.
- In addition, wells that are not connected to a sewage system will incur the cost of providing sewage disposal or will be unable to use Fe(II), as noted<sup>5</sup>:

"It should be explicitly stated the viability of Fe(II)-RCF/Sn(II)-RF as a cost-effective Cr(VI) treatment technology is dependent on sewer discharge access and rates,

# and the alternative of onsite BWW storage and management could add approximately **10%–30%** to annualized costs based on the complexity of the equipment selected."

The backwash water from the Sn(II) based system settles quickly in the backwash tank. This backwash water does not need to be wasted; instead, it can be returned to the head of the treatment process. Additionally, the sludge can be drawn off from the bottom of the backwash tank and dewatered, including air evaporation. This dewatered sludge can be beneficially used in other water treatment processes.

### Chemical Properties and Delivery Mechanisms

Sn(II) is produced on-site and on-demand through the electrolysis of food-grade tin using low-power electricity. Additionally, Sn(II) is non-toxic. The stannous reagent generated by this process is dosed according to the required treatment level. This dosage can be minimized to a point where Cr(VI) is undetectable, with only a slight increase in Sn(II) dosing and operating costs.

Fe(II) is commonly provided as a bulk chemical in the form of ferrous sulfate. This reagent is highly corrosive, requiring careful handling and appropriate safety measures to protect both personnel and the environment. Facilities that store Fe(II) are at risk of corrosion. Additionally, Fe(II) functions most effectively within a narrow pH range, which may require pH adjustment of the water before treatment with this reagent. This adjustment can lead to increased costs and serves as another potential point of failure. The complexity and size of a Fe(II) based RCOF system reflect the weaker reducing power of Fe(II), as illustrated in the system's design depicted in Figure 1 from a 2017 study.<sup>7</sup>



Figure 1- Fe(II) Based System RCOF Process Flow Diagram

The authors of this study<sup>7</sup> concluded the disadvantages of Fe(II) include:

- Fairly complex process to operate and maintain
- Larger footprint
- Handling and storage of chemicals
- Significant waste stream
- Solids dewatering and disposal
- Needs higher-skilled operators and constant operator attention

Blute's study<sup>5</sup> identifies additional problems with the use of Fe(II):

"An issue encountered in RCF demonstration-testing that required significant troubleshooting was bacterial growth in the treatment system. Because Glendale was serving the treated RCF effluent to customers, CDPH mandated frequent monitoring of heterotrophic plate count bacteria and total coliforms, with triggers in place to divert the water if the values exceeded set thresholds. An examination of components in the treatment process revealed that the polymer was the primary source of bacteria for the RCF system, possibly because a small amount remained in the tank when the solution was refilled each day and high outdoor temperatures contributed to growth. The lack of chlorination in the process allowed bacteria to proliferate. Additional testing is under way with the use of chlorine for ferrous oxidation, which may help minimize bacterial growth." <sup>S p.p. E169</sup>

The implications of this conclusion are higher operating costs and additional process complexity which led Blute to observe:

"The primary observation noted by operations staff regarding the RCF process is the significantly greater operational attention required compared with the WBA system. The 100-gpm RCF system is estimated to have required ~ 5–6 h/d for routine operation and monitoring, plus the additional time needed to trouble-shoot, replace malfunctioning equipment parts, and address simultaneous compliance issues."  $5^{p.p. E169}$ 

By contrast, the on-site electrolytic Sn(II) generation system has a far smaller footprint, is fully automated, and requires minimal supervision. It produces a significantly smaller waste stream that can be repurposed for beneficial uses. Additionally, reusing backwash water eliminates water loss and the need for sewage disposal.

### RCF COST COMPARISON-Sn(II) AND Fe(II)

There are a number of publicly available costing of Fe(II) systems. In the case of Fe(II) based RCOF, a 2016 study<sup>8</sup> indicated that treating six wells at the City of Watsonville would cost \$20 million and \$750,000 annually to operate. A 2017 study by Hazen and Sawyer and Corona<sup>9</sup> and cited again by Corona in  $2024^{10}$  calculated that the capital cost of the Fe(II) RCOF treatment systems required to treat four wells for the City of Coachella would be \$22.5M and annual O&M between \$0.9-1.2M. The Corona study<sup>4</sup> makes two claims:

"...the savings on reduction contactors makes the two systems [Fe (II) and Sn(II)] competitive over 20 years."

and:

# "Based on feasibility level annualized cost estimates, the cost of Fe(II)-RCF has likely decreased substantially since 2013/2014, and although Sn(II)-RF (sic) can be considered as an alternative to Fe(II) RC, this study did not reveal advantages."

The claims are unwarranted and do not bear scrutiny. This study fails to cite an earlier comparative analysis of Cr(VI) treatment technology costs published by the California State Water Resources Control Board in 2022<sup>1</sup> which provides a comparison of the capital costs of RCOF and RCF systems based on Fe(II) and Sn(II) reagents. For a design flow of 100 gallons per minute (gpm) the Fe(II) based system was reported to cost \$1.4M compared to \$730,000 for a Sn(II) based system. For a flow of 250 gpm, the Fe(II) RCOF system was reported to have a capital cost of \$2.1M which is 40% higher than the actual cost of a Sn(II) system being installed in California during 2025 with this flow rate. This notable cost differential between the two technologies, Fe(II) and Sn(II), is maintained for larger systems.

When looking at the equipment and annual O&M costs of the RCOF and RCF processes to address Cr6 contamination at the City of Banning, CA M12 Cluster, the Sn(II) system remains the most affordable and cost-effective option (Table 1).

Table 1- Cost Comparison for RCOF and RCF

2,800 GPM	RCOF*	RCF**
Design Flow	Bulk Ferrous	On-site Generated
C	Reagent	Stannous Reagent
Equipment	\$4.162M	\$2.2M
Annual O&M	\$0.527M	\$0.276M
*Hazen and Sawyer 2022, ** N2W Engineering 2025		

It should be noted that the costs of Fe(II) RCOF process do not include continuous monitoring of treated water quality to ensure the system is operating, whereas the on-site generated Sn(II) RCF-based system includes this real-time monitoring cost.

# THE REDUCTION-FILTRATION PROCESS FAILS TO MEET TITLE 22 REQUIREMENTS

To reduce the capital costs associated with the Fe(II) process, which has several inherent drawbacks due to the ineluctable kinetics of its chemistry, a proposal<sup>4</sup> has been made to significantly decrease the size of the contactor where the dosing of the reagent occurs to reduce Cr(VI) to Cr(III) and oxidize excess Fe(II). By doing so, the contact time is dramatically reduced from 15 minutes to just one minute. However, this approach contradicts previous studies and is not supported by the redox chemistry of Fe(II) and Cr(III).

One major issue is that a dramatic overdosing of Fe(II) has been used [with a ratio of 167:1 Fe(II) to Cr(VI)] compared to the stoichiometric ratio of 3:1. This excessive dosing was necessary to compensate for the reduced size of the contactor and the limited time available for the reduction reaction to occur. Even though the study was conducted under favorable raw water conditions (with Cr(VI) levels under 12 ppb and low silica levels) and with lenient treatment goals, the treatment performance was found to be unstable, resulting in limited removal of Cr(VI) and multiple excursions of iron levels.

Moreover, the short contact times used in the filters, along with the virtually absent time allowed for Fe(II) oxidation and coagulation, prevent an adequate response from the treatment system to multiple process factors (such as reagent doses and pH control). This significantly decreases the controllability and stability of the process. Overall, the limitations imposed by eliminating the contactor have led to unpredictable and potentially catastrophic effects on treatment performance.

In summary, this RF treatment approach—characterized by multiple shortcuts and a disregard for the limitations of the treatment reagents—poses considerable risks and goes against "good engineering" practices that prioritize safety and reliability in treatment processes. While this may reduce capital costs by \$100,000 to \$150,000 (approximately 5% of the system costs), any such savings will likely be offset by higher chemical treatment costs and increased sludge production. More importantly, there are serious doubts about whether this system can meet the requirements of Title 22. Furthermore, the authors<sup>4</sup> have made an unsupported claim that the system will be less expensive than a Sn(II) based system without providing any evidence.

In practical terms, the proposed RF system involves eliminating the contactor and dosing Fe(II) directly onto the filters where the reduction process is intended to occur. The challenges of using Fe(II) with a contactor in an RCOF process still exist with this proposed RF process; however, they are far more acute. Untreated water must be held in the filter for an extended time period for the reduction process to occur. When water supplies resume from the well, the latency of the treatment process will result in inadequately treated water being released from the filter. To accelerate treatment, Fe(II) can be overdosed; however, to avoid unused Fe(II) entering the drinking water system, chlorine will need to be added to the filter to re-oxidize Cr(III) in the filter to Cr(VI) which the process was designed to remove in the first place.

In reviewing the demonstration report conducted by Gorman et al.<sup>4</sup>, we conclude that it fails to satisfy the requirements of Title 22. The demonstration failed to adequately show that the new or modified treatment process will result in compliance with the Cr(VI) MCL because the demonstration was not subjected to typical field conditions where a well may not operate for a few hours to days. In addition, it lacks a description of procedures used to determine chemical dosing rates of Fe(II), chlorine and polymer are sufficient to ensure the treatment process is operating as designed.

# CONCLUSION

The intrinsic chemical properties of Sn(II) and Fe(II) determine that electrolytically generated Sn(II) is a far more powerful and effective reagent than Fe(II) for treating Cr(VI). An added advantage of Sn(II) is that it can be produced on-site and on-demand, eliminating the challenges associated with handling a corrosive and toxic bulk chemical reagent.

While the use of Fe(II) for Cr(VI) treatment has been characterized as an RCF process, it is an RCOF process that requires an additional treatment step to 'oxidize' excess Fe(II). Based on publicly available costings for Fe(II) based RCOF systems, the lifetime costs of a Sn (II) based RCF system are considerably lower (40%). The use of Sn(II) provides municipalities with the opportunity to reduce Cr(VI) to non-detectable levels. This reduction allows them to implement blending as a treatment strategy and future-proof their water systems against stricter MCLs.

# AUTHOR

**Vladimir Dozortsev**, PhD. is the Senior Product Manager for AMS. Dr. Dozortsev holds PhDs in Chemistry and Chemical Engineering. He is the author and co-author on numerous patents related to voltammetry-based analysis of trace metals and the in-situ generation and use of ferrous, ferrate and stannous for water and wastewater remediation. He has published widely in these fields and his work has greatly influenced the development of cost-effective and environmentally sustainable solutions to analyze and treat contaminants. Dr. Dozortsev is the recipient of the 2025 AWWA Water Science & Research Division Best Paper Award.

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