Hexavalent Chromium Treatment and Compliance Study By SafeGuard$^{\text{TM}}$ H2O Pilot System at the City of Banning, CA

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Table of Contents

Abbreviations

ACH	Aluminum Chlorohydrate
AMS	Aqua Metrology Systems, Ltd
BAT	Best Available Technology
Cr(III)	Trivalent Chromium
Cr(T)	Total Chromium
Cr(VI)	Hexavalent Chromium
DDW	Division of Drinking Water
GPM	Gallons per Minute
HLR	Hydraulic Load Rate
HMI	Human Machine Interface
IX	Ion Exchange
MG	MetalGuard^{TM}
MCL	Maximum Contaminant Level
MDR	Molar Dose Ratio
PLC	Programmable Logic Controller
PPB	Parts per Billion
PSI	Pounds per Square Inch
PSIG	Pounds per Square Inch - Gauge
RCF	Recution/Coagulation/Filtration
RG	Reagent Generator
RO	Reverse Osmosis
SG-H2O	SafeGuard^{TM} H2O
SWRCB	State Water Resource Control Board

Section 1 - Introduction

1.0 Background

Hexavalent chromium (Cr(VI)) is a common drinking water contaminant that impacts over 7,000 drinking water sources across the state.[1] Chromium is a naturally occurring element that is abundant in rock and soil. It is commonly present in two forms, Cr(III) and Cr(VI). While Cr(III) is an essential nutrient for humans, Cr(VI) is a potential carcinogen and highly mobile in water. Cr(VI) can occur naturally through erosions of rocks and soils. It can also come from anthropogenic sources and activities such as electroplating, the textile industry, pigment manufacture, cooling water blowdown, corrosion control, etc.

To address the health and safety concerns regarding Cr(VI) in drinking water, the Office of Environmental Health and Hazard Assessments (OEHHA) has established a Cr(VI) Public Health Goal (PHG) of 0.02 µg/L based on cancer risk since 2011. The PHG serves as a non-regulatory health basis for the State Water Resource Control Board (SWRCB) to establish drinking water standards, known as the Maximum Contaminant Levels (MCLs) that the public water systems must comply with. The MCLs are set as close to PHG as technologically and economically feasible. Currently, California implements an MCL for total chromium (Cr(T)), a combination of Cr(III) and Cr(VI), at 50 µg/L. In April of 2022, a Cr(VI) MCL Administrative Draft was released with a proposed MCL for Cr(VI) at 10 µg/L, and a compliance schedule from two to four years for systems with different numbers of connections. [2] Cost-effective and reliable technologies will be crucial to help the water agencies and the government to achieve stringent safe drinking water goals.

The SWRCB has suggested the three Best Available Technologies (BATs) for Cr(VI) treatment, namely reduction/coagulation/filtration (RCF), ion exchange (IX), and reverse osmosis (RO). The RCF process works by chemically reducing the Cr(IV) to Cr(III), which is a less soluble species of chromium that can be precipitated and removed by the subsequent coagulation and filtration steps. Stannous chloride ($SnCl_2$) is one of the common chemical reductants that can convert Cr(VI) to Cr(III) in water. It has been used in drinking water systems as a corrosion inhibitor. The chemical has also achieved NSF/ANSI 60 certification from Underwriters Laboratories Inc., one of the major certifying bodies in the U.S.

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[1] Hexavalent Chromium in Drinking Water Source: Sampling Results, State Water Resource Control Board, https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Chromium6sampling.html

[2] Chromium-6 Drinking Water MCL, State Water Resource Control Board, https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Chromium6.html

Traditional RCF systems usually implement chemical injection systems that dose stannous solution to the raw water. This method has its disadvantages. Stannous chloride undergoes hydrolysis in solution and precipitates. The solutions usually need to be stored with chemical preservatives (e.g., acid) and thus become highly acidic and hazardous. The acidic environment can slow down the hydrolysis but doesn't prevent it entirely. In addition to hydrolysis, the stock solution is also subject to oxidation by dissolved oxygen from the environment and slowly loses reductive efficacy.[3] As a result, the stock solutions usually have a limited shelf-life and need to be replaced frequently. Furthermore, at higher concentrations, e.g., 50%, the solution is temperature sensitive and becomes semi-solid at about 50 °F. In a full-scale demonstration project, electrical heaters were installed at the chemical enclosure to maintain the temperature which adds significant energy consumption.[4] If a dilute solution is used, the cost associated with shipping and handling will increase significantly. Thus, a reliable method that can utilize a solid or elemental form of stannous or tin for chemical dosing could drastically reduce the costs and circumvent the risks associated with the handling of the solution. The technology will have a great competitive advantage over traditional RCFs and help water agencies and the government achieve safe drinking water goals.

The technology being tested in this pilot study from Aqua Metrology Systems (AMS), the SafeGuard™ H2O (SG-H2O), is designed to utilize the electrolytic process coupled with real-time water quality monitoring to achieve onsite stannous generation and optimized dosing. The fully automated SG-H2O system uses a certified precursor and an in-situ electrolytic generator to create a non-toxic stannous reagent onsite and on demand. Accompanying the SG-H2O is the MetalGuard™ (MG) analyzer which is a fully automated online trace metals analyzer capable of providing real-time, multi-stream analysis for a range of trace metal contaminants. Because the system can be fully controlled, monitored, and optimized remotely, the presence of personnel on site for supervision is minimized, further reducing operating costs. It is an innovative RCF process that could overcome the limitations associated with the current traditional RCFs. The pilot testing was conducted with the primary objective of obtaining conditional acceptance from the CSWRCB Division of Drinking Water (DDW) for use of the SG-H2O technology by public drinking water systems for Cr(VI) treatment, by validating the effectiveness of the technology in treating the Cr(VI) and total chromium (Cr(T)) to below the current and the proposed MCLs in drinking water sources.

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[3] Kennedy, Anthony M.; Korak, Julie A.; Flint, Leah C.; Hoffman, Catherine M.; Arias-Paic, Miguel (2018). Pilot-Scale Removal of Total and Hexavalent Chromium From Groundwater Using Stannous Chloride. Journal - American Water Works Association, 110(4), E29–E42.

[4] Corona Environmental Consulting, LLC, "Coachella Valley Water District: Improvement District 8: Full-scale Stannous Chloride Demonstration Results, Technical Memorandum," http://www.cvwd.org/DocumentCenter/View/4203/CVWD-Improvement-District-8-Full-Scale-Stannous-Chloride-Demonstration-Results

The pilot test was performed on-site at Facility Well C2, located in the City of Banning, California, from June 2022 to September 2022. Well C2 is one of nine groundwater production wells operated by the City of Banning impacted by Chromium (VI). With a nominal production capacity of approximately 1,100 gpm, facility well C2 is a part of 40 percent of the City's total nominal production capacity impacted.

1.1 Hexavalent Chromium Regulatory History

Drinking water quality in California is regulated by the SWRCB DDW or designated County local primacy agencies. DDW is required to set and enforce drinking water standards that are at least as stringent as those set by the U.S. Environmental Protection Agency (USEPA), but may also set more stringent standards that apply to California only. The key points below highlight the main chromium-related regulatory milestones in California.

- The USEPA adapted the MCL for Cr(T), a combination of Cr(III) and Cr(VI), at 100 µg/L in 1991, with no separate MCLs for Cr(VI). California adopts an MCL for Cr(T) of 50 µg/L.
- In 2011, the California OEHHA established the PHG of Cr(VI) at 0.02 µg/L.
- In August 2013, California adopted the MCL for Cr(VI) at 10 µg/L.
- In 2017, the Superior Court of Sacramento County invalidated the Cr(VI) MCL, due to its economic feasibility in certain areas. The SWRCB worked on a rule to revise and implement a new MCL for Cr(VI).
- In April of 2022, the SWRCB DDW released an administrative draft with a proposed MCL for Cr(VI) that remains at 10 µg/L, and the Staff Report to illustrate its economic feasibility.[5]
- Currently, California enforces the drinking water MCL for Cr(T) at 50 µg/L. The formal rulemaking for the 10 µg/L Cr(VI) MCL will begin later in 2022 after receipt and consideration of comments on the administrative draft.

1.2 Pilot Study Goals and Objectives

The primary goals of the pilot study are:

1. Evaluating an innovative RCF technology SG-H2O, which utilizes onsite stannous generation, real-time continuous online Cr measurement, coupled with coagulation and filtration, to treat Cr(VI) and Cr(T) in the drinking water sources to meet the current and future MCLs;

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[5] SWRCB DDW, Proposed Hexavalent Chromium MCL Staff Report, https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/chromium6/proposed-hexavalent-chromium-mcl-staff-report.pdf

2. Providing the SWRCB DDW with the data the information from the pilot study to obtain regulatory approval by the DDW for use of this technology by public drinking water systems for Cr(VI) and Cr(T) treatment.

Specifically, the detailed objectives are determined for the pilot system to achieve the primary goals:

- Conversion of influent Cr(VI), at levels typically between 14 and 17 µg/L, to Cr(III) with no more than 5 µg/L residual Cr(VI) remaining.
- Residual Cr(T) in the treated water of no greater than 10 µg/L
- Residual tin in the treated water of no greater than 50 µg/L

In addition to the above objectives, the pilot system also underwent a series of challenge tests simulating potential failure conditions that could occur during treatment, including water, electrical, and chemical failures. The pilot system's performance and resilience under these failure conditions are evaluated. These secondary performance goals serve to evaluate the implemented safety features to provide a secure and risk-free environment.

1.3 Pilot Study Scope

The scope of this demonstration pilot focused on the safe, reliable reduction of Cr(VI) to Cr(III) using the SG-H2O onsite stannous generation system. Removal of the resulting Cr(III) and tin from the treated water is ensured by the addition of aluminum chlorohydrate (ACH) and using pressurized media filters to decrease the chance of re-oxidation of trivalent chromium back to hexavalent chromium in the water distribution system. ACH coagulant is added to the treated water flow upstream of the media filter to enhance the coagulation of particulates and minimize the treatment process by-products level in the effluent.

A 3-GPM pilot system, including the SG-H2O stannous generation system, the MG online trace metal analyzer, the ACH coagulation system, and the media filtration system, is installed onsite at the City of Banning's Facility Well C2. The pilot testing was conducted from June to September 2022. Cr(VI), Cr(III), and tin concentrations in the feed, effluent, and stream after the SG-H2O contactor and before the pressurized media filter were analyzed to evaluate the effectiveness of the Cr(VI) reduction and removal. As noted above, in addition to the normal operation, the pilot system was also subjected to various abnormal operational conditions, such as electrical, chemical, and water failures, and the result is summarized in this document for the system's reliance under challenging conditions.

Section 2 – Description of Technology

2.1 Pilot System Description

2.1.1 SafeGuard™ H2O Pilot Unit

The SG-H2O system utilizes an electrolytic process to generate a stannous reagent on-demand, in-situ within a side stream of the water being treated. The stannous ion produced by the process reacts with certain metals, such as Cr(VI), in the source water to reduce them into lower oxidation states to be separated by downstream processes.

The SG-H2O system consists of seven key components:

1. Stannous reagent generator (RG)
2. Galvanostat and control system
3. Real-time (Cr(VI)) monitoring system (MG analyzer)
4. Generator conditioning solution feed system
5. Contactor vessel
6. Sand media filter
7. ACH coagulant dosing system

A Process flow diagram of the pilot system is presented in Figure 2-1.

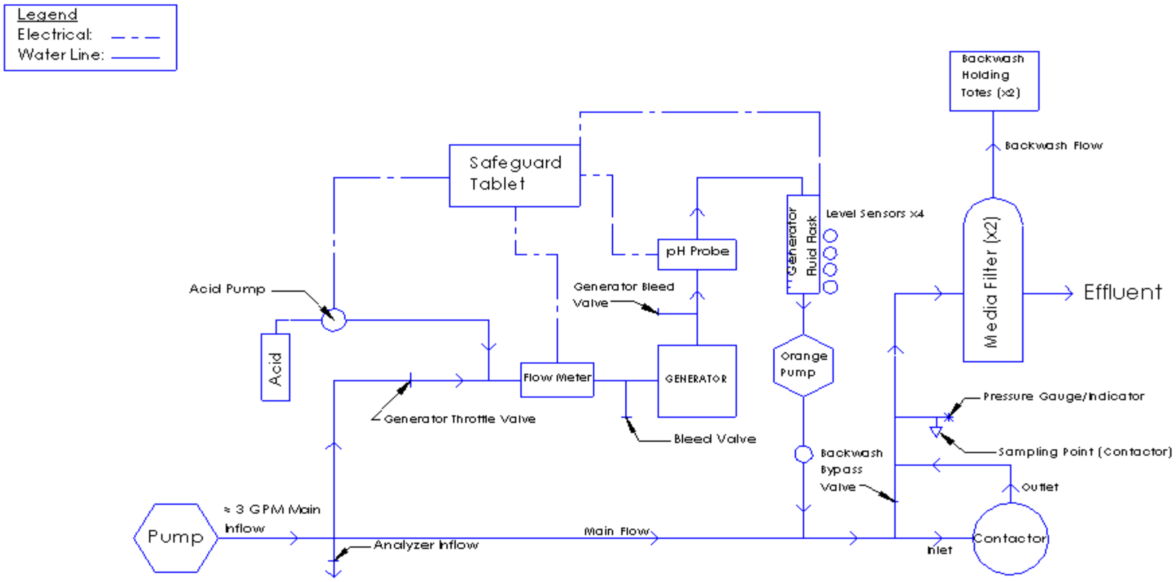


Figure 2-1 Cr Treatment Pilot Process Flow Diagram

The reagent generator (RG) is a proprietary electrolytic cell (electrolyzer) capable of releasing stannous ions into solution on demand based on applied current.

The stannous reagent is released into the water as a result of the controlled dissolution of the tin anode located within the RG (reaction 1)

$$Sn^0 + 2e- \rightarrow Sn^{2+} \text{ ....(1)}$$

The amount of tin released into the water is a function of the current applied to the RG by the galvanostat. Stannous ions introduced into the water react with Cr(VI) and reduce it to Cr(III) (reaction 2):

$$2CrO4^{2-} + 3Sn^{2+} + 4H_2O \rightarrow 2Cr(OH)_3\ (s) + 3SnO_2\ (s) + 2H^+ \text{ …………(2)}$$

The conversion of Cr(VI) to Cr(III) is thermodynamically favorable and, with sufficient time, will proceed to near completion. A tank to provide the necessary contact time (up to five minutes) is considered to be an integral part of the SG-H2O system.

The RG is controlled and monitored by the galvanostat, which maintains a constant current regardless of load. The galvanostat also incorporates a programmable logic controller (PLC) that provides all control and monitoring functions for the complete SG-H2O system. For process monitoring and feedback, the SG-H2O system utilizes AMS's MG fully automated online Cr(VI) analyzer to provide continuous feedback to the galvanostat to optimize stannous generation and Cr(VI) removal. A more detailed description of the MG analyzer is provided in Section 2.2.
The performance of the RG is sensitive to the following water quality conditions:

1. The chloride level within the reagent generation stream should be reliably above 500 mg/L. Higher levels of chloride facilitate the release of soluble stannous tin from the electrode (reaction 1) and the stabilization of resulted stannous ions in the reagent solution;

2. The pH within the reagent generation stream should be maintained within the range of 1-2 to avoid the formation of insoluble tin species that inhibit the release of stannous ions from the electrodes (electrode passivation).

In our test, the targeted stannous dose was around 0.3 mg/L based on the desired target of under 1 µg/L Cr(VI) in the effluent. Based on second Faraday's law and stannous generation efficiency at pH ~ 2 (pH in generator flow), the formula below (3) presents a method of calculating RG dose concentration:

$$C = 29\ I/Q \qquad (3)$$

Where:

- C = stannous concentration (mg/L)
- Coefficient = 29
- I = generation current (A)
- Q = treated water flow rate (L/min)

If site-specific bench scale testing indicates that any of these water parameters would adversely impact treatment performance, the system will incorporate a conditioning solution feed system (4M HCl generator solution) to adjust the water quality in the generation stream. It should be noted that the full primary stream of water will not need to be chemically adjusted.

The pilot unit is identical to the full-scale SG-H2O system except for size. The unit is designed to treat up to 3 gpm, of which up to 150 mL/minute is bypassed into the stannous generation stream. The water was taken from the above-ground Well C2 discharge manifold upstream from the City's sodium hypochlorite injection point. A backflow preventer was installed downstream of the manifold tie-in to protect against possible contamination of the well water by the pilot unit due to the backflow. A junction with separate hoses for the main treatment and stannous generation streams was provided downstream from the pressure regulator with each supply hose equipped with a gate or ball valve for manual flow regulation. The flow rate was verified and corrected weekly by comparing the flow meters on the pilot system to the volumes of water collected in a graduated cylinder over a set period of time. The treated water stream after stannous dosing will flow into an unbaffled contactor providing approximately 4 minutes of nominal contact time and then pass through the sand media filter. Filtration to remove insoluble Cr(III) and tin is provided by the regular sand filter (HLR 5-6 gpm/ft^2). Water is then diverted out of the filter to two on-site holding totes to be reprocessed back into the pilot system, or eventually removed for proper wastewater disposal.

Photos of the SG-H2O pilot system and the stannous reagent generator are presented in Figure 2-2 and Figure 2-3.

Figure 2-2 SG-H2O Pilot System

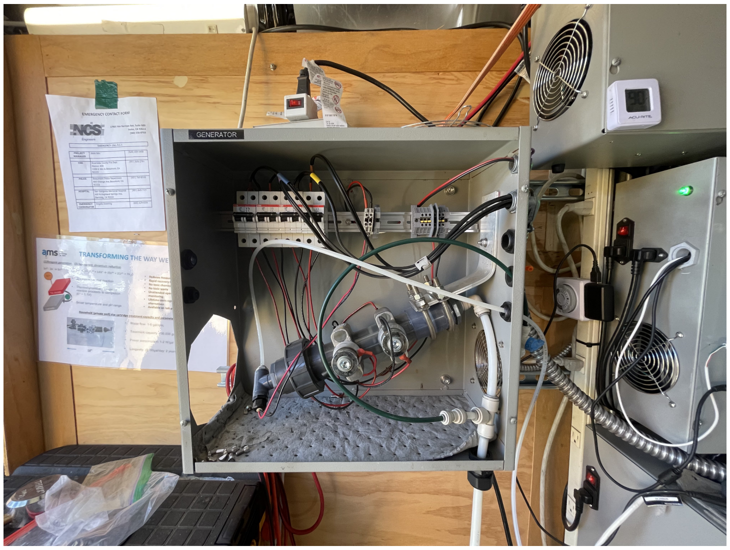


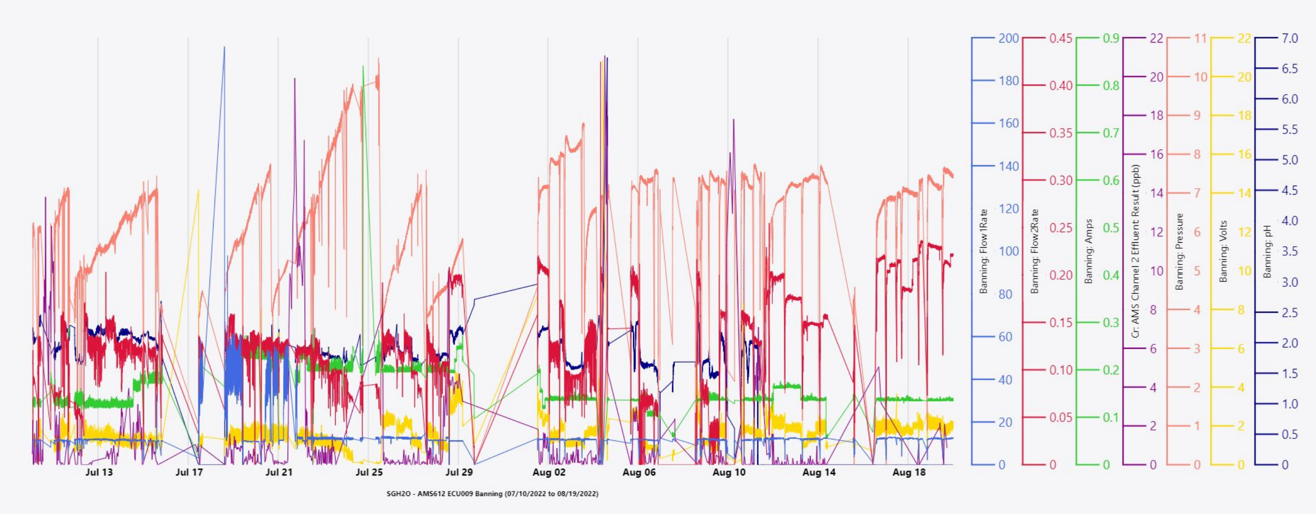
Figure 2-3 Stannous Reagent Generator in the SG-H2O Pilot Unit

2.1.2 MetalGuard™ Analyzer

The MetalGuard delivers accurate and reliable results (up to 1 µg/L or ± 15%, whichever is higher) with a typical measurement time of fewer than 30 minutes. The system also allows for manually collected samples to be analyzed by swapping internal sample bottles. Figure 2-4 presents the internal sample bottles inside the MG pilot.

Figure 2-4 Internal Sampling Bottles

Measurements and data taken are automatically compiled, stored, and accessible through the front panel and via the internal database. Remote access to the measurement data is available over email, via the Cloud, via a memory stick, or an optional 4-20 mA connection. Figure 2-5 presents the generated monitoring data plots of the pilot unit.



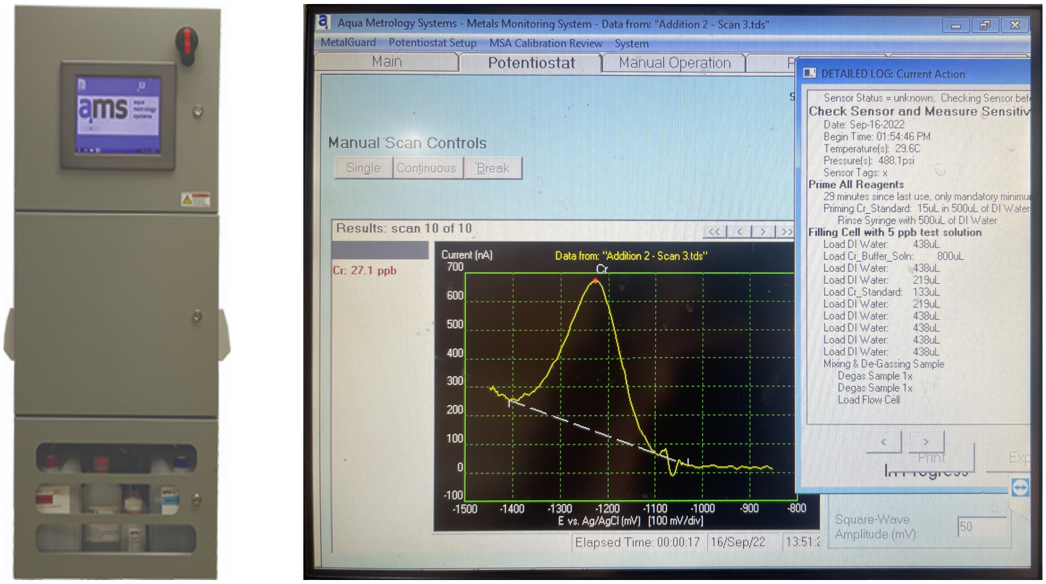
SGH2O - AMS612 ECU009 Banning (07/10/2022 to 08/19/2022)

Figure 2-5 Compilation of Data Stored by MG

The control loop utilized by the SG-H2O system implements the MG monitor to confirm that Cr(VI) levels have been decreased to the treatment objective. If Cr(VI) levels in the treated water rise, the MG provides feedback to the galvanostat that results in an increase in current to the RG, which in turn results in a greater release of stannous ions. The treated stream, after re-introduction of the generation stream, will pass into a contactor/reactor to provide sufficient time for near-full conversion of Cr(VI) into Cr(III) to occur. The sample stream for the MG is taken from both the raw water and sand filter effluent.

The system controller is designed to respond to a wide range of contingency conditions and generate appropriate alarm notifications and actions. The following alarms are built into the standard system:

1. Loss of power;
2. High and Low treated water Cr(VI);
3. Electrode replacement notification and automatic shutdown.



Cr: 27.1 ppb

```
    Sensor Status = unknown,  Checking Sensor bef
Check Sensor and Measure Sensitiv
    Date: Sep-16-2022
    Begin Time: 01:54:46 PM
    Temperature(s):  29.6C
    Pressure(s):  488.1psi
    Sensor Tags: x
Prime All Reagents
    29 minutes since last use, only mandatory minimu
    Priming Cr_Standard:  15uL in 500uL of DI Water
        Rinse Syringe with 500uL of DI Water
Filling Cell with 5 ppb test solution
    Load DI Water:        438uL
    Load Cr_Buffer_Soln:        800uL
    Load DI Water:        438uL
    Load DI Water:        219uL
    Load Cr_Standard:     133uL
    Load DI Water:        219uL
    Load DI Water:        438uL
    Load DI Water:        438uL
    Load DI Water:        438uL
    Load DI Water:        438uL
    Mixing & De-Gassing Sample
        Degas Sample 1x
        Degas Sample 1x
        Load Flow Cell
```

Figure 2-6 MG Unit and HMI

2.2 Pilot System Operation

System Start-Up

With a consistent flow of water, the SG-H2O and most accompanying components were able to be remotely started. Integrated software allowed for a one-button push-to-start, and for pre-loaded chemical flow rates to begin immediately and automatically when the system is turned on.

System start-up was initiated by the following steps:

1. Check if the well is operating;

2. Monitor media life, chemical levels, and DI water levels for replacement;
3. Engage the Pump + Valve switch which simultaneously initiates feed water flow, acid pump, acid injection, ultrasonics, and the RG;
4. Adjust the generator throttle valve to set the generator flow at the desired level (approximately 150mL/min);
5. Monitor filter pressure;
6. Monitor the main flow rate, pH, galvanostat, and Cr(VI) levels to ensure that the system is stable

Backwash Procedure

The backwash procedure was initiated once every 7 days or when filter pressure reached 6-8 psi (whichever came first). Backwash was conducted manually through the complete shutdown of the system and flow path adjustments.

1. System Shut-off:
    - The influent pump is stopped, the flow path into the generator is closed and the contactor is bypassed.

2. Idle Time:
    - The backwash water drain valve is opened to drain the water from the media sand filter. After draining, the drain valve is closed.

3. Pump + Valve switch is turned on:
    - The pump is turned on to supply a steady stream of water into the backwash inlet of the media filter unit. The media sand filter backwash sludge is diverted from the backwash outlet into one of two 275-gallon totes for proper disposal on pilot test completion.

4. Return to normal operation:
    - Valves are returned to their original positions for normal operation

Remote Monitoring

The operation of the SG-H2O is supported remotely with 24/7 factory monitoring to ensure prompt identification and remediation of any operational issues. A reduction of on-site personnel allows for minimal downtime while instantly optimizing performance. Figure 2-7 presents the HMI control panel for the remote monitoring and control of the SG-H2O pilot system.

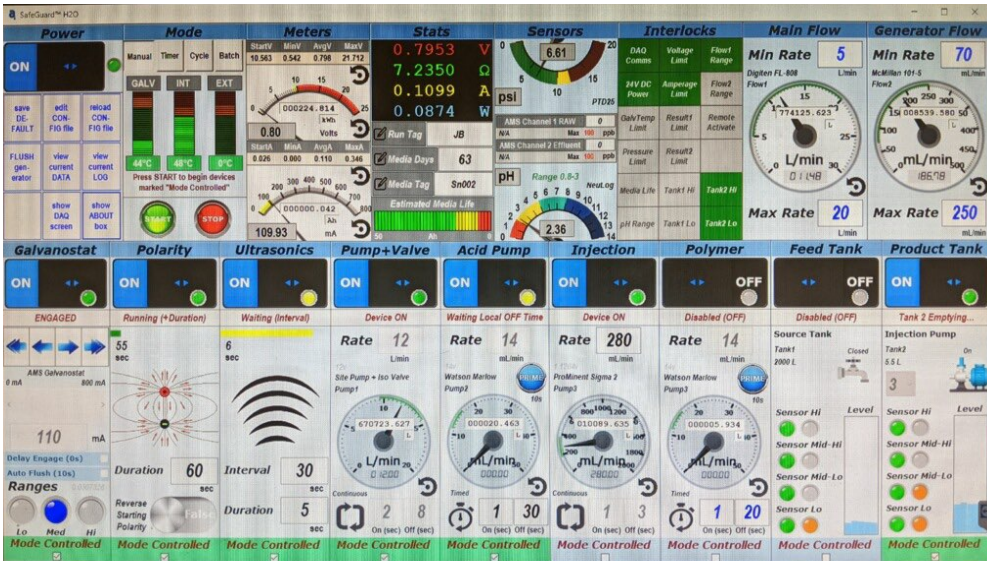


Figure 2-7 SG-H2O Pilot System HMI

Operational data, such as main flow rate, generator flow rate, generator plate health, pressure, pH, ultrasonics period, and galvanostat current was measured continuously and automatically stored in an off-site storage center.

Key operation parameters and control methods of the SafeGuard™ H2O pilot system are summarized in Table 2-1

Table 2-1 SafeGuard™ H2O Key Operation Parameters and Control Methods

Parameters	Control Method	Operation Range
Influent Flow	Fixed	Up to 3 gpm, approximately 11.5 L/min
Generator Flow Rate	Manually adjusted by manipulation of valve based on flow meter reading	Approximately 150 ml/min
Acid Pump Rate	Adjusted remotely through HMI	14 ml/min with a one-second injection interval every 30 seconds
Ultrasonics	Adjusted remotely through HMI	5-second vibration duration every 30 seconds
Polarity	Adjusted remotely through HMI	60-second oscillation interval for each plate
Galvanostat	Adjusted remotely through HMI	110 mA
Backwash	Manually initiated through complete system shutoff and valve and filter adjustments	12 L/min flow

Section 3 – Materials and Methods

3.1 Influent Water

The influent water for the pilot test was taken from well C2 located at 4781 W. Ramsey, Banning, CA. The well is chlorinated, however, the chlorination is performed downstream past the point where water was diverted for this pilot test. Table 3-1 presents the general water quality information of Well C2, *as obtained from the City of Banning*.

Table 3-1 General Water Quality of Well C2

Parameter	Unit	Value
Cr6	ug/L	14-17
Arsenic	ug/L	<2
Nitrate	mg/L	7.7-11
Sulfate	mg/L	9.3-10
Alkalinity	mg/L as CaCO3	150-160
TDS	mg/L	210-240
pH	su	7.9
Calcium	mg/L	41-44
Hardness	mg/L as CaCO3	140-150
Uranium	pCi/L	0.2

3.2 Study Site

The study was conducted at the City of Banning Well C2 located in Riverside County, California. The City of Banning has nine potable water supply wells which exceed the pending new California Cr(VI) MCL of 10 μg/L. Well C2 is favorable for this study due to the availability of a well building and surrounding land; as well as the treated water discharge possibility. Figure 3-1 to 3-3 present the areal map of the site area, the site location, and the well sampling point.

Figure 3-1 Well C2 Aerial View

Figure 3-2 Well C2 Building

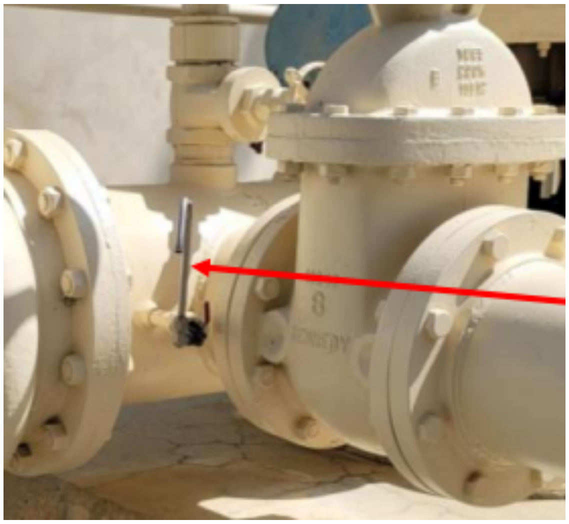


Figure 3-3 Well C2 Sampling Point – Pre-Chlorination Point

3.3 Test Conditions and Timeline

3.3.1 Pre-Testing

The initial configuration of the SG-H2O utilized two 275-gallon totes and two conical 50-gallon tanks to hold supply water when Well C2 was not in operation (1 hour per day, timing based on fluctuating demand). After algae developed in both 275-gallon totes, the configuration was modified with direct plumbing of the raw water from the well to the treatment system. The two conical totes remained on-site but were isolated from the setup. Both 275 gal totes were cleaned and rinsed to remove any remaining algae and repurposed as backwash holding tanks. Figures 3-4 and 3-5 present the initial set-up with totes and direct plumbing solutions.

Figure 3-4 Initial Feed Water Tank System Configuration

Figure 3-5 Totes Disconnected and Direct Plumbing Installed

One week of pre-testing was provided at the beginning of the pilot study. The purpose of the pre-testing period was to resolve any pilot equipment setup issues and to adjust the treatment equipment similar to what would occur during the startup of a full-scale treatment unit. Startup issues and their resolution, and initial adjustment procedures were documented below.

Table 3-2 Start-up Issues and Resolutions

Issue	Initial Adjustment Procedures
Insufficient Power	To retain constant operation, a new breaker and outlet were installed to meet the power requirements
Temperature Threshold	Elevated temperatures on-site in Banning, CA required the implementation of an AC unit to obtain a temperature range of approximately 80 to 88 F for optional equipment operation
Insufficient Inflow Requirements	The addition of a small booster pump allowed for a consistent water inflow of 3 gpm
Algae in Supply Water	Initially, two 275-gallon totes were utilized to hold supply water when Well C2 was not in operation. After algae developed in these totes, they were repurposed for holding backwash water

3.3.2 Pilot System Operation

After pre-testing and resolving the onsite issues, the system began operation. The system operated continuously except for scheduled maintenance such as backwashing and chemical changeouts. A total of XX gallons of water were treated by the pilot system during the testing period. Twelve sets of manual grab samples were taken during the testing period from the untreated feed, the treated effluent from the pilot, and the intermediate stream after the SG-H2O contractor and measured of Cr(VI), Cr(T), Tin, and aluminum.

After pre-testing and resolving the onsite issues, the system began operation from 07/12/2022 to 08/31/2022. The system operated continuously except for scheduled maintenance such as backwashing and chemical bottle replacement. Basic on-site duties include:

- Maintain the well site.
- Perform record management sample shipments and inventory records.
- Perform pre and post-well site equipment inspection and document as required

Five samples were collected twice a week (Mondays and Wednesdays) and taken and stored to be shipped overnight on Wednesdays to the certified laboratory for third-party testing. Samples were taken from the untreated feed, the treated effluent from the pilot, and the intermediate stream after the SG-H2O contractor for measurements of Cr(VI), Cr(T), Tin, and aluminum. Backwashing was scheduled once per week on Fridays for optimal weekend performance or if elevated filter pressure was observed (whichever came first). Aside from the manual adjustment of certain flow valves (generator flow and backwash procedure), the pilot system was majorly remotely monitored and controlled, with system maintenance being performed as soon as possible, with replacement parts and chemicals being shipped directly to the operator overnight. If the sampling schedule coincided with maintenance, then samples were taken after 1 hour of stable operation post-maintenance. Challenge testing was conducted during the last month of operation over the course of two weeks (08/04/2022 - 08/16/2022) to allow for system stabilization in between tests. A total of approximately 216,000 (at 3 gpm) gallons of water were treated by the pilot system during the testing period. Twelve sets of manual grab samples were taken during the testing period from the untreated feed, the treated effluent from the pilot, and the intermediate stream after the SG-H2O contractor and measurements of Cr(VI), Cr(T), Tin, and aluminum.

3.3.3 Water Supply Failure

The purpose of this test was to simulate an unexpected interruption of the feed water supply. The test was accomplished by shutting off the influent pump which did not allow for water to reach the main system. The expected system response was for the system flow meters to detect a no-flow condition; shut off power to the generator, and produce a system shut-down alarm.

CHALLENGE TEST DATA COLLECTION PLAN		
Condition	**Data**	**Notes**
1 minute after the water supply failure	System shutdown (yes/no) Alarm generation (yes/no)	Immediate system shut off, email alarm generated; flow 1 range interlock

3.3.4 RG Electrical Failure

The purpose of this challenge test was to simulate a loss of power to the RG electrodes. The test was accomplished by disconnecting an RG electrode cable from the galvanostat /control module. The expected system response was for the current to the electrode to drop to zero, after which the signal was detected by the controller, which then shut the system down and generated a system failure alarm.

CHALLENGE TEST DATA COLLECTION PLAN		
Condition	**Data**	**Notes**
1 minute after the electrode disconnect	System shutdown (yes/no) Alarm generation (yes/no)	Immediate system shut off email alarm generated: voltage limit interlock

3.3.5 Delayed Electrode Replacement

The purpose of this challenge test was to simulate a condition where the water system operator does not replace the electrode when notified to do so by the controller. The mass of tin released by the electrode is directly proportional to the charge applied to the electrode. The system controller uses this relationship to monitor the remaining electrode mass and to generate a notification alarm when 30% of the electrode mass remains. The expected system response when the electrode is not replaced by the time there is only 20% mass remaining is to shut the system down.

CHALLENGE TEST DATA COLLECTION PLAN		
Condition	**Data**	**Notes**
When the controller reaches 30% estimated remaining electrode life	Notification alarm generation (yes/no)	Email alert generated: media life interlock
When the controller reaches 20% estimated remaining electrode life	System shutdown (yes/no)	Email alert generated: media life interlock

3.3.6 Startup Response After Shutdown

The purpose of this challenge was to determine how long it would take the RG to resume acceptable stannous reagent dosing after the system had been taken offline for an extended period of time. This test consisted of shutting down the RG for 24 hours and then restarting the system. Treated water samples were collected from upstream of the contactor at intervals 10, 20, 30, and 60 minutes after the system operation had resumed. To simulate the 10-minute treated water contactor, the water samples were separately held for 10 minutes in a beaker prior to transferring the samples to the laboratory collection bottles.

CHALLENGE TEST DATA COLLECTION PLAN		
Condition	**Data**	**Notes**
10, 20, 30, and 60 minutes after the 24-hour shutdown	Laboratory Tin, Cr(VI), Cr(T) after 10 minutes of simulated contact time	Data recorded in Section 4

3.3.7 Total Power Failure

The purpose of this challenge test was to simulate a total loss of power to the SG-H2O system followed by the return of power. The MG analyzer is able to resume operation without operator interaction; however, the RG requires an operator on-site before it returns to service. The purpose of this test was to demonstrate that the SG-H2O system detects the loss of power and provides an operator alarm notification, and to demonstrate that the system will continue to produce properly treated water during the time it takes the operator to re-initialize the MG analyzer. To accomplish this test, the master power to the galvanostat/controller was turned off for a 24-hour period and then turned back on. The controller was monitored to confirm that the appropriate alarm was generated immediately.

CHALLENGE TEST DATA COLLECTION PLAN		
Condition	**Data**	**Notes**
Immediately before shutting the power off	Record MetalGuard-Cr reading; Laboratory Tin, Cr(VI), Cr(T) in treated effluent	Data recorded in Section 4
After the power is shut off	Power failure notification alarm generated (yes/no)	Immediate system shut off, email alarm generated: 24 V DC power interlock
10, 20, 30, 60, and 120 minutes after power is restored	Laboratory Tin, Cr(VI), Cr(T) in treated effluent	Data recorded in Section 4
2 hours after power is restored	Shutdown alarm generated (yes/no)	Email generated; 24 V DC power interlock OK and cleared

3.3.8 Acid Feed Failure

The purpose of this challenge test was to demonstrate the effects of discontinuing the generator conditioning solution (i.e. hydrochloric acid) feed during otherwise normal operation. This was intended to simulate a potential failure of the chemical feed system at a full-scale treatment plant.

This test was accomplished by turning off the power to the hydrochloric acid feed pump. Elevated pH levels in the stannous reagent concentrate produced caused the system to generate a shutdown alarm. The response to a resumption in conditioning solution feed was also demonstrated. The expected response to the resumption of feed was a rapid return to normal treatment performance.

CHALLENGE TEST DATA COLLECTION PLAN		
Condition	**Data**	**Notes**
Immediately before shutting the acid feed pump off	Record MetalGuard-Cr reading; Laboratory Tin, Cr(VI), Cr(T) in treated effluent	Data recorded in Section 4
After the acid feed pump is off	Shutdown alarm generated (yes/no)	Email generated; pH range interlock
10, 20, 30, 60, and 120 minutes after the acid feed pump is off	Laboratory Tin, Cr(VI), Cr(T) in treated effluent	Data recorded in Section 4
10, 20, 30, 60, and 120 minutes after the system returns to service with the acid feed	Laboratory Tin, Cr(VI), Cr(T)	Data recorded in Section 4

Section 4 – Results and Discussions

4.1 Pilot System Operation

The following figures present the operational data of the pilot system during the testing period, this includes influent feed rate, media filter pressure levels, and RG pH levels. RG was manually adjusted to remain at a stable 150 mL/min. Figures 4-4 and 4-5 present the RG amperage and voltage data.

The influent flow rate data in Figure 4-1 presents continuous operation throughout the testing period aside from times when the well was not in operation or challenge testing. The two anomalous values where the flow rate spiked to approximately 30 L/min in two instances may be neglected, as the raw data shows that the peak value occurred for only a short duration for each instance.

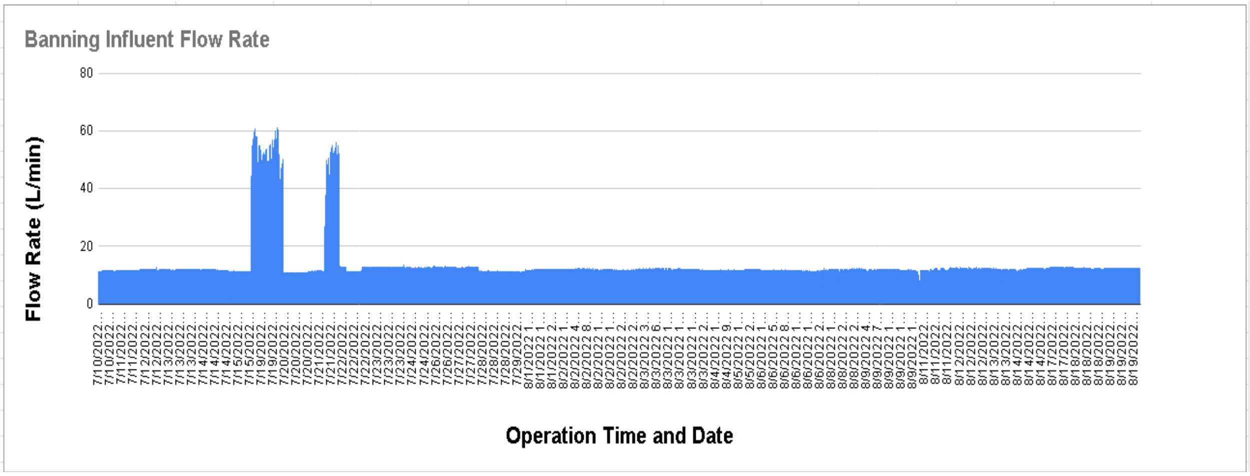


Figure 4-1 Cr Treatment Pilot System Influent Feed Rate

Figure 4-2 presents media filter pressure, the frequency at which backwash was conducted once weekly on Fridays to produce reliable operation during weekends when an operator was not present. Pressures observed at 7-8 psi would be remedied with a 15-20 minute backwash (depending on pressure build-up) and would return to stable operation at 3-4 psi. Pressures reaching 0 psi in the data illustrate system shutoffs, with MG still operational.

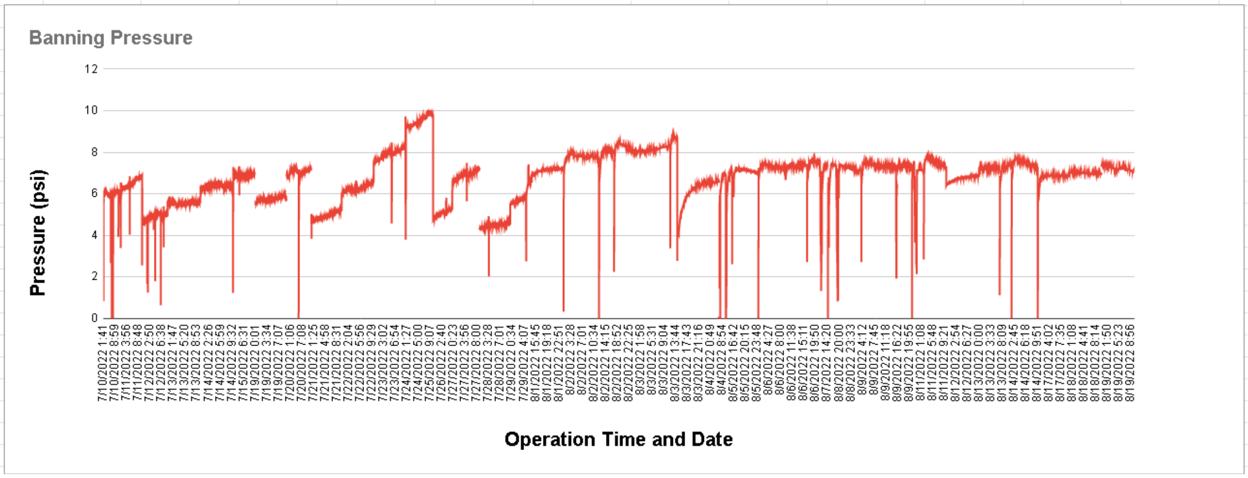


Figure 4-2 Cr Treatment Pilot System Media Filter Pressure

The following figure presents RG pH data that illustrates the optimal condition, which is in the range of operation between 1 and 2 (Figure 4-3). Aside from elevated levels from the acid feed failure test, spikes in the data are concurrent at times when the original generator flow valve would fluctuate due to a defective servo valve. After 08/11/2022, the drop in pH to zero is due to a leak in the plumbing that shorted the pH probe HUB. The operation continued without the probe for the final period of testing.

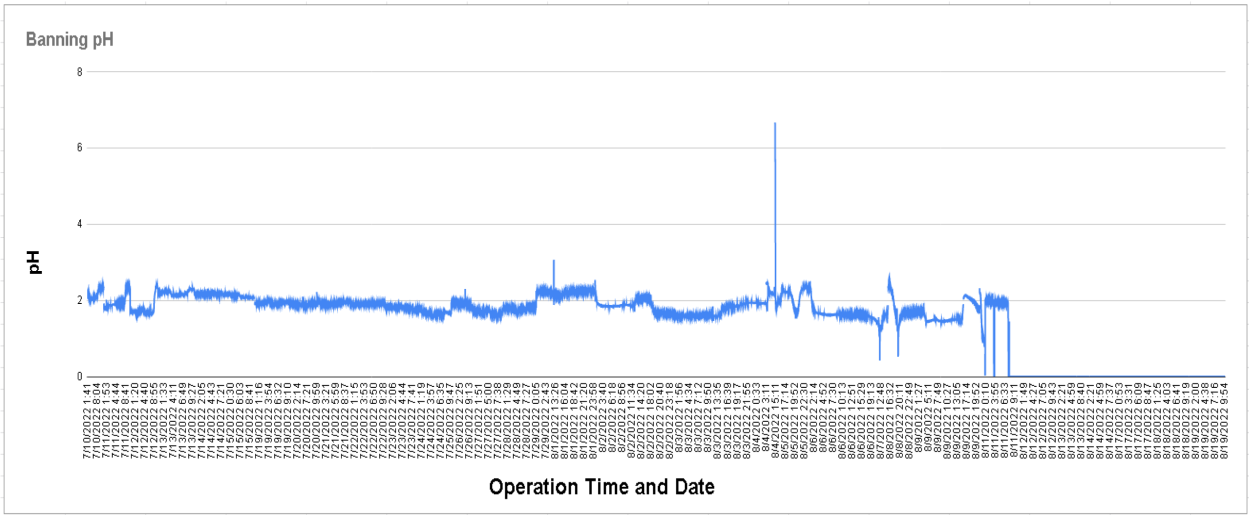


Figure 4-3 Cr Treatment Pilot System RG pH

Two figures below (Figures 4-4 and 4-5) present the voltage and amperage of the SG-H2O system. Comparing the influent Cr(IV) with the amperage and voltage of RG enables to demonstrate the responsiveness of the optimized dosing of the system. Equation 3 from Section 2 illustrates the relationship between amperage and generator stannous ion production (µg/L). Amperage was stabilized between 0.1 to 2.5A allowing for optimal concentration of the RG ion. Comparing the date 08/09/2022 to pilot effluent on the same date, Cr(VI) values were recorded at 0.12 µg/L as opposed to the 18 µg/L raw influent.

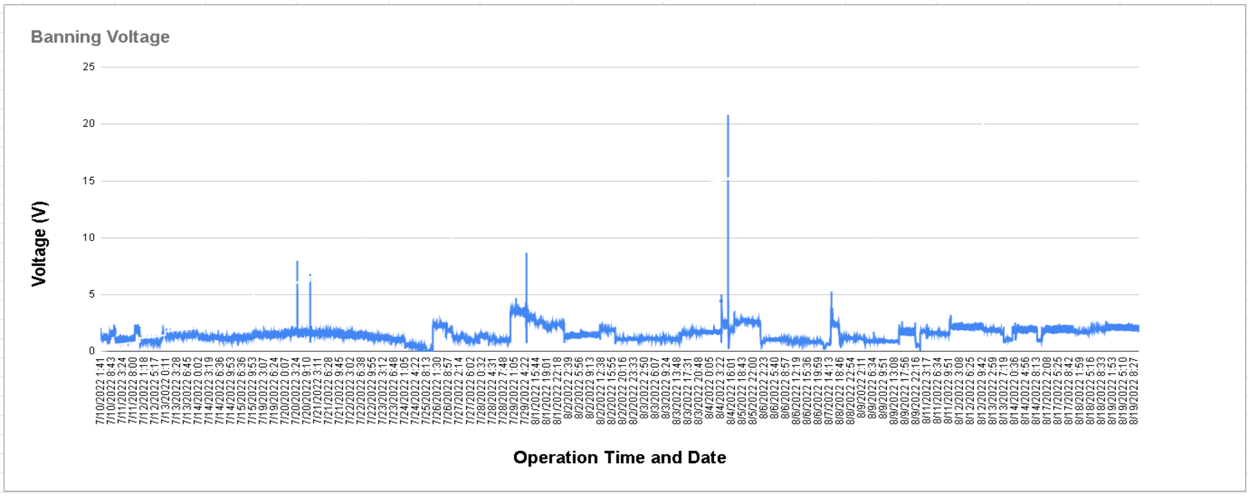


Figure 4-4 Cr Treatment Pilot System Voltage

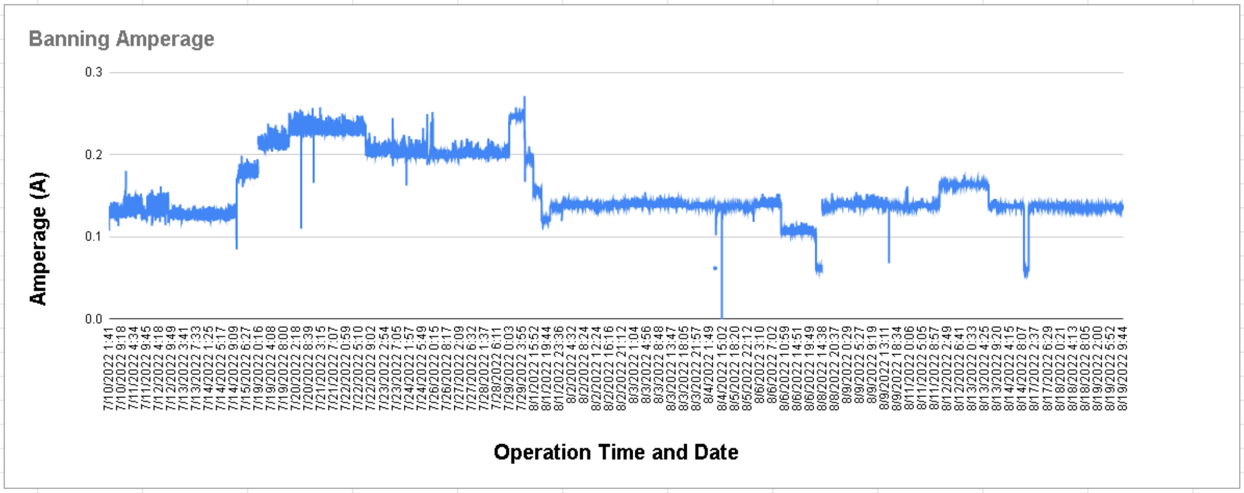


Figure 4-5 Cr Treatment Pilot System Amperage

4.2. Cr(VI) Removal Performance

During the initial and optimization periods prior to challenge test conditions, the pilot system performed well with a high 90% removal rate for treating the background Cr(VI) in the groundwater. Table 4-1 presents the overall treatment results from laboratory analytical data of the grab samples from the SG-H2O pilot system. As noted, the % removal ranged from 97.8 to 99.8, except for one instance where the removal rate was 94.1% for the feed rate of up to 18 µg/L. This is the range of typical concentrations for many Cr(VI) impacted wells, so a such high degree of removal rate ensures low Cr(VI) in the effluent with significant treatment safety margins.

Table 4-1 Cr(VI), Cr(T), Tin, Al Treatment Results

Sampling	**Feed Water**	**Pilot Effluent**					**SG-H2O Contactor Effluent**			
Date	**Cr(VI)**	**Cr(VI)**	***Cr(VI) % Removal***	**Cr(T)**	**Tin**	**Aluminum**	**Cr(VI)**	**Cr(T)**	**Tin**	**Aluminum**
7/12/2022	18	0.19	*98.9 %*	1.50	12	NA	0.081	16	210	NA
7/15/2022	17	1.00	*94.1 %*	1.60	9.6	NA	0.13	22	300	NA
7/18/2022	17	0.14	*99.2 %*	0.58	7.2	ND	1.30	15	160	73
7/20/2022	17	0.17	*99.0 %*	1.50	13	ND	0.73	19	280	92
7/22/2022	17	0.17	*99.0 %*	1.50	7.4	ND	1.20	36	310	110
7/26/2022	17	0.08	*99.5 %*	1.50	18	ND	0.04	20	300	88
8/1/2022	17	0.38	97.8 %	ND	10	ND	ND	49	430	49
8/2/2022	16	0.058	99.6 %	1.20	16	ND	ND	24	440	ND
8/9/2022	18	0.12	99.3 %	32	820	180	0.35	1.9	20	ND
8/10/2022	8.9	0.18	98.0 %	3.3	43	ND	1.3	ND	330	73
8/30/2022	7.3	0.12	98.4 %	4.50	49	NA	0.2	55	380	NA
8/31/2022	17	0.031	99.8 %	5.10	45	NA	0.31	19	200	NA

Results are Reported in µg/L NA = Not Tested ND = Not Detected (below PQL)

Cr(VI) - PQL of BC lab for EPA-218.6 method =0.20 ppb MDL= 0.020

Cr(T)- PQL of BC lab for EPA 200.8 method =3.0ppb

Tin- PQL of BC lab for EPA-200.8 method =1.0 ppb

Al- PQL of BC lab for EPA-200.7 method =50 ppb

The following plot (Figure 4-6) presents the raw feed, pilot effluent, and contractor effluent Cr(VI) concentrations in a continuous plot format. During the operation period, the feed Cr(VI) varied between 7.3 and 18 µg/L, with an average raw water concentration of 15.5 µg/L. The effluent Cr(VI) was consistently at or below 1 µg/L, with an average of 0.22 µg/L. The result demonstrates that the SG-H2O pilot system was able to effectively treat Cr(VI) in the drinking water source to below the newly proposed MCL level of 10 µg/L.

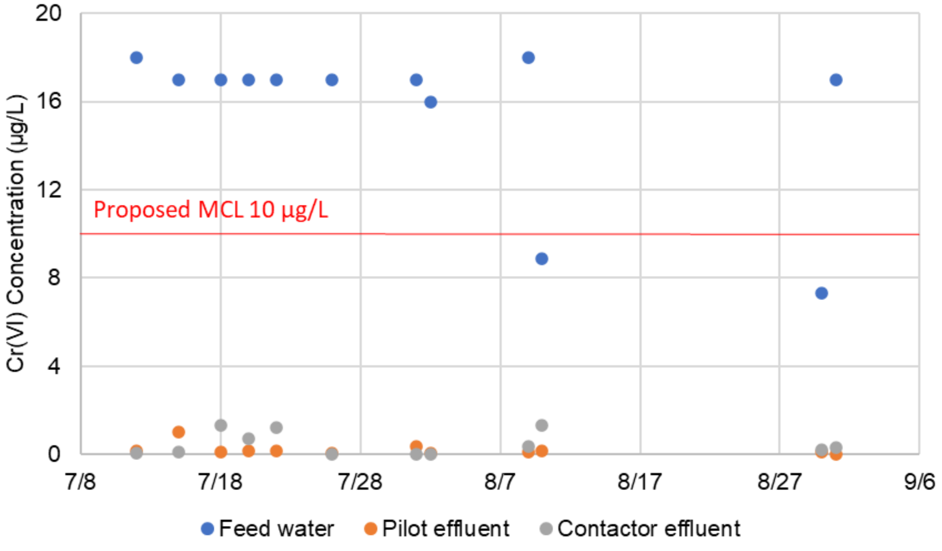


Figure 4-6 Cr(VI) concentrations from the feed, pilot effluent, and contactor effluent

The results also show that the pilot system successfully reached the testing objective of effluent Cr(VI) level below 5 µg/L. By comparing the pilot effluent data with the contactor effluent data, it can be seen that the differences between the two streams are very small, suggesting that the majority of the Cr(VI) was converted post-contactor, and the media filter did not affect Cr(VI) concentration, which is an expected result.

Figure 4-7 presents the Cr(T) data in the pilot effluent and contactor effluent. In the contactor effluent, Cr(T) ranged from 1.9 to 55 µg/L, with an average of 25.2 µg/L. The pilot effluent had Cr(T) from 0.59 to 32 µg/L, with an average of 4.93 µg/L. By comparison, it shows that the RG and the contactor, while effective in converting Cr(VI), cannot effectively remove Cr(T) which is mostly comprised of insoluble Cr(III). Combined with the media filter, the concentration in the pilot effluent was effectively reduced to at or below 5.1 µg/L, with the exception of one outlier data at 32 µg/L on 08/09/2022. The pilot system showed effective removal of Cr(T) to well below MCL of 50 µg/L. And the system was able to achieve the testing objective of Cr(T) less than 10 µg/L, except for the one outlier data on 08/09/2022 as noted.

In addition to Cr(T) and Cr(VI) data, tin concentrations were measured in the samples. Figure 4-8 presents the tin concentration in the pilot effluent and contactor effluent. Data from 08/09/2022 was not included due to abnormality during operation which corresponds to a high Cr level. The data shows that, on average, 93.1% of the generated stannous was removed. The pilot effluent had tin levels below 21 µg/L, which is well below the test objective of 50 µg/L. By comparing the Cr(VI) in the feed, and the Tin concentration in the contactor effluent, the molar dose ratio (MDR) of Sn-to-Cr(VI) can be estimated. The ratio varied between approximately 8.5 to 10.7 during the sampled period. According to Reaction (2) from Section 2.1.1, the stoichiometric Sn-to-Cr(VI) MDR for the reduction reaction is 1.5. Overdosing is commonly utilized to compensate for the hydrolysis reactions and other competing oxidative/reductive reactions. The MDR of the pilot system falls within the range of the MDRs reported in RCF systems using stannous chloride solution.[6]

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[6] Corona Environmental Consulting, LLC, 2018, Coachella Valley Water District: Improvement District 8: Full-scale Stannous Chloride Demonstration Results, Technical Memorandum, http://www.cvwd.org/DocumentCenter/View/4203/CVWD-Improvement-District-8-Full-Scale-Stannous-Chloride-Demonstration-Results

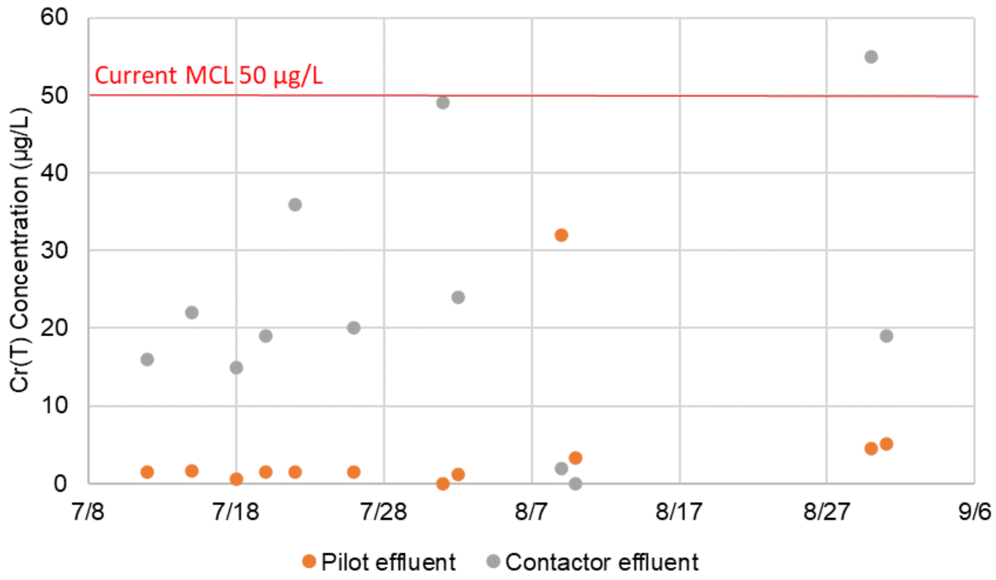

Figure 4-7 Cr(T) concentrations in the pilot effluent and contactor effluent

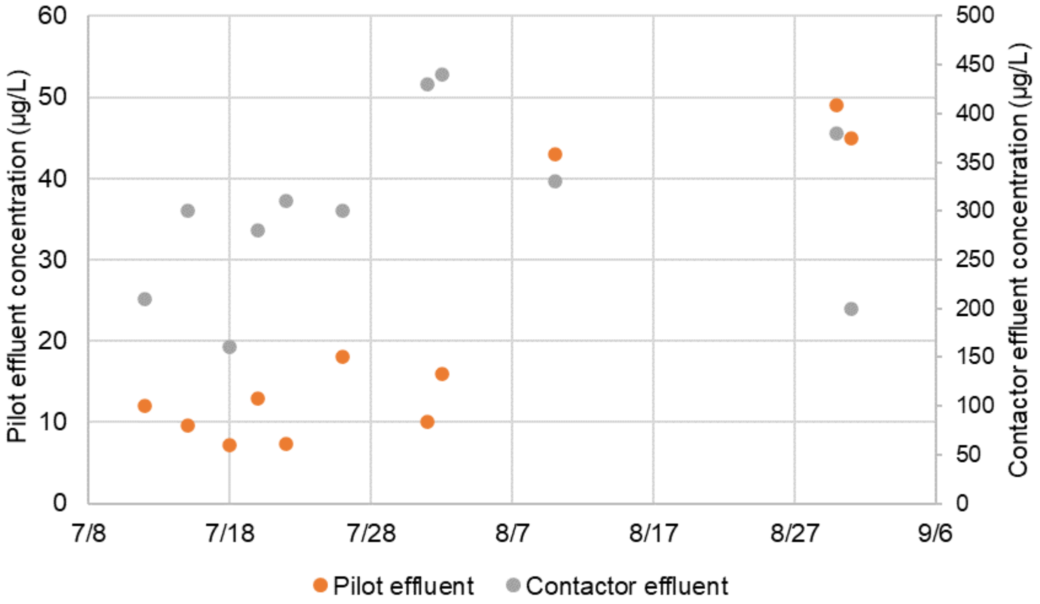

Figure 4-8 Tin concentrations in the pilot effluent and contactor effluent

4.3. Challenge Testing Results

Tables 4-2 and Figures 4-9 summarize the test results for the Startup Response challenge test. In this test condition, the RG was shut down for a period of 24 hours and then restarted. Water samples were collected from upstream of the contactor at intervals 0, 2, 5, 10, 30, and 60 minutes after the system operation had resumed. Water samples were separately held for 10 minutes in a beaker prior to transferring the samples to the laboratory collection bottles to simulate a 10-minute reaction time contactor.

Upon restarting the reagent generator, a steady decrease of Cr(VI) was observed. Cr(VI) decreased to below 10 µg/L after 30 min and to 1.3 µg/L after 60 min. As expected, the Cr(T) level ranged around 15 to 22 µg/L as RG only converts Cr(VI) to Cr(III) and does not remove the Cr(T). Tin, or stannous level, steadily increased and reached a plateau of 190 µg/L at around 30 min. Based on the result, it is expected that normal operation can resume in approximately 30 to 60 minutes after startup.

Table 4-2 Summary of Startup Response Test Results from Pre-Contactor Samples

Start time (min)	**Cr(VI)** µg/L	**Cr(T)** µg/L	**Tin** µg/L
0	15	22	94
2	16	16	25
5	13	15	56
10	11	17	110
30	9.3	20	190
60	1.3	16	190

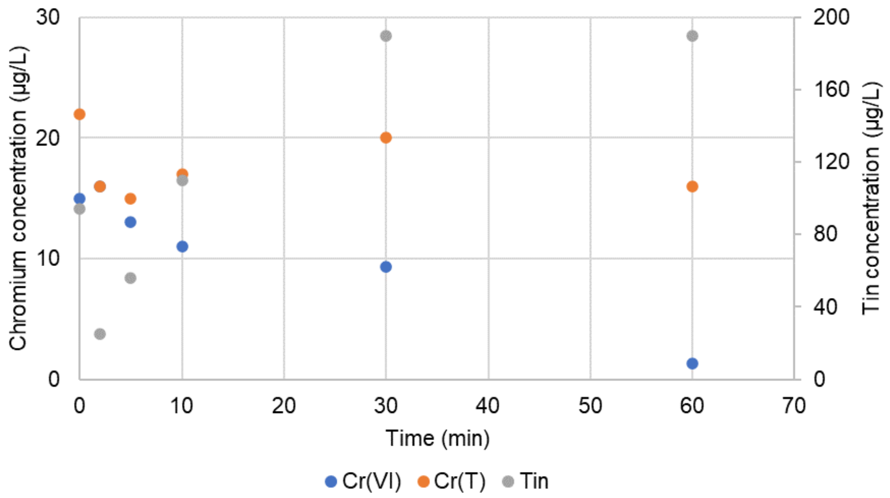

Figure 4-9 Startup response plot of Cr(VI), Cr(T), and Tin concentrations from Pre-Contactor Samples

Table 4-3 presents the test results for the Total Power Failure challenge test. In this test condition, the master power to System was turned off for a 24-hour period and then turned back on. Effluent samples were collected prior to the return of power, and from 10 min to 120 min after the return of power. The data illustrates that the system is capable of handling unexpected upset conditions such as power outages in maintaining the compliance level. Upon return of power, the pilot system was able to generate effluent with Cr(VI) and Cr(T) below their respective current and proposed MCLs.

Table 4-3 Summary Total Power Failure Test Results from Pilot Effluent

Return of Power (min)	**Cr(VI)** µg/L	**Cr(T)** µg/L	**Tin** µg/L
Pre	0.28	3.1	23
Post 10 min	0.12	2.0	18
Post 20 min	0.12	2.4	25
Post 30 min	0.10	2.7	20
Post 60 min	0.53	3.8	38
Post 120 min	0.84	4.2	32

Table 4-4 shows the test results for the Acid Feed Failure challenge test. In this test condition power to the hydrochloric acid feed pump was shut off. The elevated pH level in the stannous reagent concentrate produced caused an automatic system shut off 30 minutes post chemical shut off. Pilot effluent samples collected prior to and after the acid pump shut off illustrate only slight variations in Cr(VI) concentration in the effluent (from 0.10 to 0.20 µg/L with a standard deviation of 0.039 µg/L). Similarly, Cr(T) showed a 2.1 µg/L variation with an average of 4.5 µg/L. Effluent Tin had an average of 51.5 µg/L, with a maximum of 61 µg/L and a minimum of 34 µg/L. The results show that during a 30-min interruption of acid injection, the system was able to remain effective and maintain effluent Cr(VI) and Cr(T) at below 10% of the respective current and proposed MCLs.

Table 4-4 Summary of Acid Feed Failure Results from Pilot Effluent

Chemical Failure Time min	**Cr(VI)** µg/L	**Cr(T)** µg/L	**Tin** µg/L
Post Off 10 min	0.19	5.3	61
Post Off 20 min	0.13	4.9	60
Post Off 30 min	0.12	4.6	56
Post On 10 min	0.17	3.2	34
Post On 20 min	0.18	3.8	44
Post On 30 min	0.10	5.0	56
Post On 60 min	0.20	4.6	50

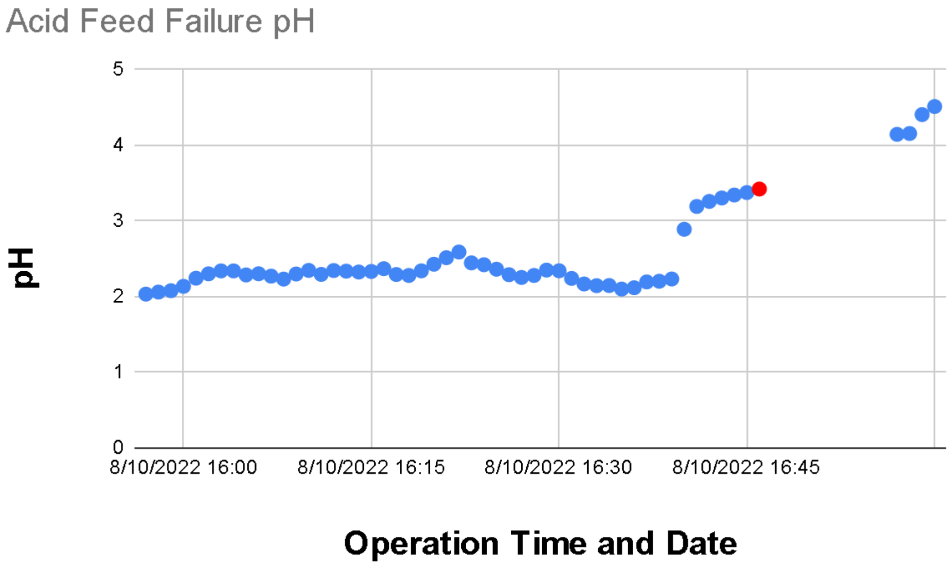

Figure 4-9 Red data point indicates the pH level reaching 3.4225 and then shutting off after reaching the 3.5 pH threshold

Section 5 – Summary and Conclusions

A pilot test was performed with an innovative RCF process, the SG-H2O technology, with the primary goals of demonstrating the technology's efficacy in treating Cr(VI) and Cr(T) to below MCLs and obtaining regulatory approval from the SWRCB DDW for drinking water treatment. The pilot test was performed on-site at Facility Well C2, located in the City of Banning, California, from June 2022 to September 2022. The main conclusions from the study are summarized below:

- The overall treatment results of the SG-H2O pilot system indicated that over the 3-month operation run-time, a total average of 15.5 µg/L of Cr(VI) detected in the Raw influent before treatment was reduced by an average of 98.55% to 0.22 µg/L. Cr(T) has also shown an effective reduction to an average of 4.79 µg/L. Both sampled results fell well under the current MCL of 50 µg/L for Cr(T) and the newly proposed MCL of 10 µg/L for Cr(VI).

- During start-up, the pilot system was able to generate stannous immediately after start-up and reach a plateau of stannous concentration after 30 min. The pilot was also able to treat Cr(VI) to below the 10 µg/L proposed MCL level after 30 min.

- In the event of a total water supply failure, the system response detected no-flow conditions by flowmeters. This shut off power to the system and generated the system shut-down alarm: Flow 1 Range Interlock. On reintroduction, the system returned to normal operation and generated the Flow 1 Range OK email notification.

- In the event of loss of power to the RG electrodes, the system controller detected a current drop to the electrode to be zero. This shut off the system and generated the system failure alarm: Voltage Limit Interlock email notification. Reintroducing the power allowed for the system to return to steady-state operation with a Voltage Limit OK email notification.

- In the event that the water system operator does not replace the electrode when notified to do so by the controller, the system generated the Media Life Interlock notification alarm when 30% of the electrode mass remained. The expected system response of shutting down was also achieved at 20% media mass remaining.

- In the event of the RG being taken offline, the system was able to automatically shut down and send out an alarm. Upon restarting RG, the system was able to resume normal operation.

- In the event of a total power failure, after power to the system was shut off, the system generated a 24V DC Power Interlock email alarm. Upon power reintroduction, the 24V DC Power Interlock OK email alarm was generated. The pilot system showed resiliency and was not impacted significantly by the challenge condition. Pilot effluent was able to maintain Cr(VI) under 1 µg/L and Cr(T) under 5 µg/L within 120 min after the restart.

- In the event of an acid feed failure, an elevation in pH levels in the stannous reagent concentrate initiated the system to generate the shutdown alarm: pH Range Interlock. Upon priming the system and achieving an optimal pH range of 1-2, the system generated the pH range OK alarm and resumed normal operation. During 30 min after the acid injection failure, and 60 min after resuming acid injection, the pilot effluent had Cr(VI) at or below 2.0 µg/L and Cr(T) at or below 5.3 µg/L, showing resiliency to acid injection failure.