Report

AQUA METROLOGY SYSTEMS

SafeGuard™ H2O Pilot Report

City of Los Banos, California

AQUA METROLOGY SYSTEMS

SafeGuard™ H2O Pilot Report

April 2021

This report summarizes results of the Aqua Metrology Systems' SafeGuard™ H2O intelligent Cr(VI) treatment system pilot study and details the system's ability to mitigate chromium contamination in drinking water at Los Banos, California.

- Report written by Vladimir Dozortsev, Development Manager
- Report reviewed by Rick Bacon, CEO
- Report approved by Rick Bacon, CEO

1225 E. Arques Avenue
Sunnyvale, CA 94085
Tel: +1 408 523 1900 • E-mail: info@aquametrologysystems.com
www.aquametrologysystems.com

Table of Contents

Executive Summary 2
- Overview 2
- Results 3
- Next Steps 3

Demonstration Technology 4
- SafeGuard™ H2O Intelligent Cr(VI) Treatment System 4
- Overview 4
- Background 5
  - Electrolytic Stannous Reagent Generation 5
  - Advantages of Electrolytic Stannous Reagent Generation 6
- Pilot System Setup and Operation Mode 7
- Online Chromium Monitoring 9

Test Results 10
- Treatment Objective 10
- Grab Sampling and Laboratory Analysis 11
- Results 11
- SafeGuard H2O™ System Maintenance 22
- Conclusions 29
- Acknowledgements 29

Section 1

Executive Summary

Overview

Traditional trace metal remediation systems are expensive and associated with high capital and operating costs. To reduce the cost of treatment, support tighter regulatory standards and widen access to safe drinking water for all, an innovative remediation treatment approach (SafeGuard™ H2O) has been developed by Aqua Metrology Systems (AMS).

SafeGuard H2O generates a stannous ion reagent[1] in-situ via an electrolytic process to effectively and economically address trace metal contaminants such as hexavalent chromium [Cr(VI)]. The SafeGuard H2O system also features an online trace metal water quality analyzer for real-time monitoring of contaminant levels to help control and optimize the treatment process — a feature that is unique to this intelligent technology.

The fully integrated, online SafeGuard H2O treatment approach eliminates the pitfalls of conventional systems and aids in the delivery of an affordable and reliable remediation process. There are no similar technologies to SafeGuard H2O that integrate a low life-time cost contaminant treatment system with real-time performance controls. The scalability of the SafeGuard H2O technology, from large and small water systems, to point-of-use systems, will bring to homes and small communities a cost-effective method to achieve safe drinking water free of toxic contaminants.

A full-scale SafeGuard H2O demonstration unit with a treatment capacity of 10 gallons per minute (gpm) was installed for the City of Los Banos, California, at Well #14 for a 10-day evaluation period (24 February-5 March 2021). The characteristics of the source water for Los Banos Well #14 are extremely challenging; in addition to elevated Cr(VI) levels of 40 parts per billion (ppb), it includes levels of uranium (U), conductivity, sulfate, and hardness that can be particularly problematic for traditional Cr(VI) remediation systems because of the potential to interfere with the Cr(VI) removal process.

The demonstration at Los Banos Well#14 evaluated the performance of the SafeGuard H2O system to treat Cr(VI) to non-detect levels (under 1 ppb) in unchlorinated well water; providing confirmation of the technology's efficacy and third-party validation of the system as a cost-effective alternative to traditional Cr(VI) treatment systems.

[1] Stannous ion reagent is a species formed when stannous ions react with the raw water matrix.

Results

The SafeGuard H2O technology evaluation at Los Banos Well #14 (24 February-5 March 2021) demonstrated the high capability of the technology to effectively convert Cr(VI) into trivalent chromium [Cr(III)], in unchlorinated water and remove treatment process by-products providing effluent at 0.03 ppb which is well below the non-detect level of 1 ppb, using a stannous dose of 1.0 ppm.

SafeGuard H2O showed a fast and reliable response to treatment process parameters which allowed automated online treatment system tuning and adjustments. In addition, the system's versatile automated treatment design, in combination with frequent and online Cr monitoring via the online SafeGuard™ trace metal analyzer also manufactured by AMS, enabled the operation of an unattended and low maintenance Cr(VI) treatment system under field conditions.

The sand filters, used as part of the complete SafeGuard H2O treatment process, also demonstrated a high capacity to remove both total chromium [Cr(T)] and tin (T) to safe levels. A high media filter recovery after backwash ensured stable filter performance.

The SafeGuard H2O system reduces Cr(VI) to non-detect levels and its corresponding sand filter system is effective at removing Cr(III) and T.

The SafeGuard H2O system operation has no effect on dissolved uranium (U), if present.

Next Steps

Following the results of the SafeGuard H2O 10 gpm pilot at the City of Los Banos, the technology has been proven to be an effective and economical alternative to traditional Cr(VI) treatment systems. Next, a full-scale demonstration pilot of the SafeGuard H2O technology (greater than 1 mgd) will be undertaken in California.

Section 2

Demonstration Technology

SafeGuard™ H2O Intelligent Cr(VI) Treatment System

AMS' SafeGuard H2O technology is a novel remediation system that generates a stannous ion reagent on demand using non-toxic, food grade reagent precursor material. As a result, there is no shelf life of the reagent and operational costs are drastically reduced because shipping and handling of a hazardous solution are eliminated.

SafeGuard H2O also features automatic dosing and incorporates AMS' proprietary, continuous, real-time monitoring of contaminant levels at the influent and effluent to ensure optimal treatment and compliance with regulatory and operational targets 24/7/365. Data generated from the onboard Cr monitoring system, the online SafeGuard trace metal analyzer, helps drive a highly accurate remediation process by ensuring reliable reagent dosing control through manipulation of site-specific process parameters.

Unlike traditional treatment systems, which cannot operate unattended, the SafeGuard H2O system can be fully controlled, monitored and optimized remotely, and the presence of personnel on site for supervision is not required, further reducing operating costs. Depending on treatment size needs and site requirements, a system can be designed to operate unattended for up to several weeks.

The stannous reagent generator within the SafeGuard H2O system has a modular and flexible design that can be scaled to any size. The system features low capital and operating costs making it an economical and reliable Cr(VI) remediation system.

Overview

Stannous ions are powerful reducing agents that have been used to remove numerous toxic contaminants such as hydrogen sulfide, selenite, dissolved mercury and hexavalent chromium from water. The stannous ions reduce carcinogenic heavy metals to less harmful and/or easy to remove forms. For instance, stannous ion converts insoluble and highly toxic Cr(VI)to low solubility Cr(III), which is about one-hundred times less toxic to humans.

$$3Sn^{2+} + 2CrO_4^{2-} + 4H_2O \rightarrow 3SnO_2\downarrow + 2Cr(OH)_3\downarrow + 2H^+ \qquad (1)$$

What makes stannous ions such an attractive reagent for this application is not only the reductive power of stannous ions but also the insoluble nature of the oxidized T species, tin dioxide (SnO_2), in water. This insoluble precipitate can be filtered out after treatment.

The literature presents well-reviewed studies which all possess the following commonalities: stannous ions were used to reduce a toxic chemical species to provide a safer or more manageable product, stannous forms an insoluble precipitate when reacted which aids in the adsorption and capture of the noxious chemicals of interest, there was no observed health effects from stannous ions on biological systems.

A stannous chloride reagent, an alternative to stannous in its ionic form, has been proposed as a reducing agent for Cr(VI) treatment. However, a stannous chloride reagent is completely unsuitable for drinking water treatment. The high corrosivity and toxicity of this reagent mandates careful handling and supervision. The poor stability of this stannous species makes this reagent impractical for water treatment use because required dosage rates are unpredictable.

Background

Aqua Metrology Systems (AMS), based in Sunnyvale, California, is the leader in real-time water quality analysis and online detection of contaminants such as disinfection by-products (trihalomethanes [THMs]) and trace metals (e.g., arsenic, chromium, copper, lead, mercury, nickel, selenium, tin, uranium, zinc, and more). AMS has been providing utilities with an accurate, reliable and real-time method to monitor Cr(VI) since 2015.

In 2017, AMS applied its water quality and process knowledge to the development of an intelligent treatment system to help drive down the costs of improving water quality supplies by providing an accurate, reliable and affordable remediation solution for Cr(VI) and other toxic trace metal contaminants. SafeGuard H2O is a highly automated and patented in-situ electro-generated stannous reagent treatment approach.

Historically, metal removal drinking water treatment systems have been unintelligent – not incorporating real-time process performance feedback. They have not had capacity to determine whether they were under-treating or over-treating nor the ability to identify performance issues in a timely fashion. Additionally, the systems didn't have the ability to optimize performance amidst sudden and unpredictable changes in influent quality, unanticipated hardware component failures, operator errors, seasonal variations and more.

Electrolytic Stannous Reagent Generation

With SafeGuard H2O, AMS has developed a unique approach to produce a controlled amount of stannous ions in-situ. This is accomplished through the process of electrolysis, wherein a current is passed through electrolytic cell (electrolyzer) containing a T anode. Stannous ions are generated on demand as a result of the anodic dissolution of T metal. Because electrogenerated T possesses multiple oxidation states, specific parameters of electrolysis were developed and maintained to achieve a high stannous ion generation efficiency.

The quantification of electro-generated stannous ions that are produced can be understood through the well-studied laws of electrolysis, originally proposed by Michael Faraday in 1834. Faraday's laws of electrolysis established the relationship between the charge passed through the electrolytic cell and the mass of anodic dissolution that occurs:

$$m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right) \qquad (2)$$

Where m is the mass of anodic dissolution, Q is the total electric charge passed through the metal, F= 96.485 C° mol^{-1}, known as Faraday's constant, M is the molar mass of the substance, and z is the electrons transferred per ion.

An important characteristic of electrolytic stannous ion generation on demand is the precision of its control. A high efficiency of stannous ion generation ensures accurate reagent dose in a broad concentration range. Generation of fresh and highly reactive stannous ion reagent can be easily adjusted in real time, based on changing treatment process conditions. Moreover, the stannous ion generator can be terminated immediately simply by switching the power off, and restored as soon as power is switched on, making it highly suitable for stop-and-run operation modes associated with many city wells that do not run continuously.

The unique stannous ion generator is integrated with an online trace metal monitoring capability. As with any water treatment system, high frequency continuous monitoring of contaminants at critical treatment process steps supports process automation, optimization and reliability and can give remote visibility of system performance for the utility and their customers.

Advantages of Electrolytic Stannous Reagent Generation

Three of the most significant benefits of the in-situ electro-generated stannous reagent treatment approach, SafeGuard H2O, over traditional stannous reagents include:

1. Electro-generated stannous ions are highly stable and reactive. In contrast to conventional stannous solutions which chemically degrade in the presence of oxygen in air and thus have a limited shelf-life once opened, electro-generated stannous ions are produced on an as-needed basis at the height of their reactivity. The precursor to electro-generated stannous ions is highly stable T metal, which eliminates the possibility of wasted reagent and lost capital since additional costs are incurred when having to dispose of expired stannous chloride reagent. The rapidly degrading nature of a stannous chloride reagent makes accurate dosing nearly impossible, resulting in less effective treatment if an aged or expired reagent is used. In contrast, an electro-generated stannous ion reagent can be dosed with high accuracy in broad range of concentrations.

2. Electro-generated stannous ions are non-toxic in nature. While stannous solutions are highly acidic, toxic and corrosive, a stannous ion reagent is produced in-situ using highly inert food grade T metal. As opposed to dangerous and corrosive stannous chloride concentrates, the electrolytic stannous ion generation process does not require special complex infrastructure or safety protocols.

3. The electrolytic approach to stannous ion generation offers a more economical and simpler alternative to conventional stannous solutions. In fact, this method utilizes inexpensive and readily available resources - T metal and electricity. For the first time, smaller and often underserved municipalities now have an affordable treatment option available to remove heavy metals and other contaminants traditionally treated by prohibitively expensive stannous solutions. Additionally, the high automation of electrogenerated stannous reagent approach, coupled with enhanced monitoring capability allows entire treatment process optimization, timely response to process

changes, reduced system maintenance with increased overall uptime. Another highly important advantage of electrolytic approach to generation of stannous ions on demand is scalability of the electro-generation system. In fact, quantitative laws of electrolysis mentioned (Equation 1) can be applied to electrolytic systems of different sizes. Stannous ion generators of different sizes can be suitably built to treat water flows ranging from less than 1 gpm to thousands of gpm. This hardware design flexibility allows the system to provide a broad range of treatment options, including a design for small scale water treatment pilots. In fact, the SafeGuard H2O small footprint, inexpensive and low waste pilot systems can be easily deployed at sites and evaluated at a low cost. These mini-pilot SafeGuard H2O modules are flexible and can be adjusted to specific site conditions; they also operate in unattended mode. Continuous online Cr contaminant level monitoring allows for a drastic reduction in pilot costs by eliminating the need for grab sample collection and analysis.

Pilot System Setup and Operation Mode

AMS provided a full-scale 10 gpm pilot system (Figure 1A) of the SafeGuard H2O intelligent Cr(VI) treatment system to the City of Los Banos for a 10-day demonstration period (24 February-5 March 2021) at Los Banos Well #14. The objective of the pilot was to evaluate the ability of the SafeGuard H2O system to reduce Cr(VI) from the unchlorinated well water down to a non-detect level under 1 ppb. The SafeGuard H2O's corresponding sand filter system was evaluated for its ability to remove Cr(III) and T. The SafeGuard H2O system was also evaluated to see if operation had an effect on dissolved U present.

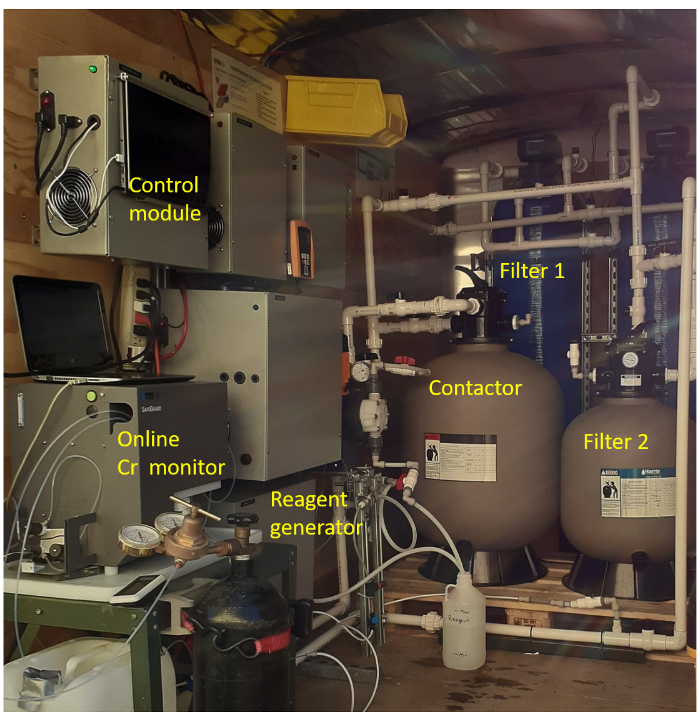

Figure 1A. SafeGuard™ H2O Cr(VI) Removal Pilot

Figure 1A shows the SafeGuard H2O treatment system which consists of five main components: stannous reagent generation control module, electrolytic reagent generator, contactor, two sand media filters in series and online Cr(VI) monitor. The schematic of the treatment system pilot is detailed in Figure 1B.

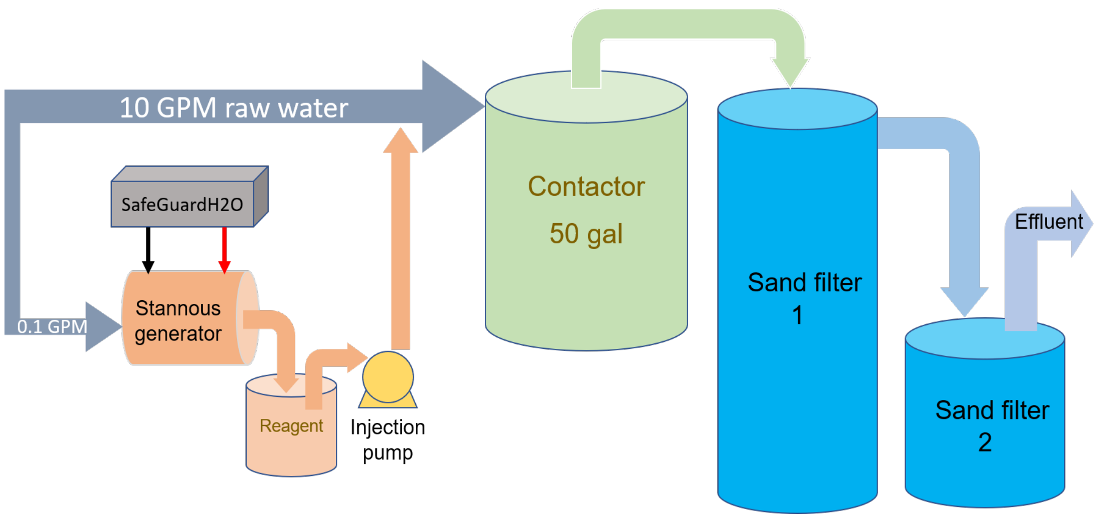

Figure 1B. SafeGuard™ H2O Cr(VI) Removal System Pilot Schematic

Within the SafeGuard H2O pilot system, the unchlorinated well water flow (10 gpm) was treated with a stannous reagent concentrate produced within a side stream of the process water by the electrolytic generator. The electrogenerated reagent concentration was pre-set and controlled to provide a desirable reagent dose after blending of the reagent stream and treated water stream.

The blended water stream passed through a contactor vessel (5 minutes nominal contact time), in which reduction of Cr(VI) into the Cr(III) form takes place, the treated water then passed through two sand filters (HLR 7.2-7.6 gpm/ft^2). The contactor vessel volume can potentially be reduced to provide a shorter retention time of approximately 3 minutes.

Filter sand with an effective size of 0.45–0.55 mm, a uniformity coefficient of 1.5 and a depth of 4.5 ft (Filter 1) and 1.5 ft (Filter 2), was used to remove both Cr(III) and T particulates from the treated water.

An online SafeGuard Cr analyzer (not shown in Figure 1B), continuously monitored Cr(VI) effluent levels and reported measurement data to the Cloud for remote monitoring in real time.

In addition, the key parameters of the electrolytic reagent generation process (reagent dose, etc.) were controlled by the proprietary SafeGuard H2O software (Figure 2).

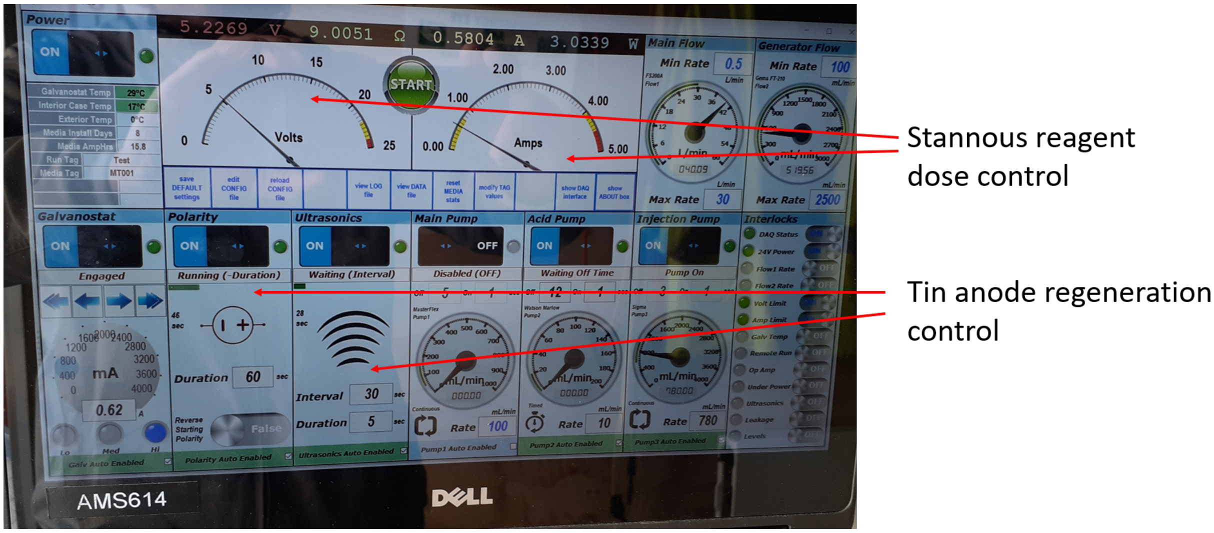

Figure 2. Proprietary SafeGuard™ H2O Control Panel

Online Chromium Monitoring

Cr(VI) residuals in the treated water were monitored by an online SafeGuard Cr analyzer in a continuous manner during the entire demonstration period. The treated water aliquot was drawn from the sample fast loop sampling chamber and analyzed by the monitor with a frequency of three tests per hour. Over 80 data points were recorded and analyzed during the entire trial period. The highly sensitive probe allowed Cr(VI) readings down to non-detect levels (below 1 ppb).

A robust sensor self-regeneration mechanism delivered both high probe stability and system uptime. Cr(VI) quantitation was performed automatically by the Method of Standard Additions and enabled the SafeGuard H2O system's self-calibrated status to be maintained during the entire trial period with minimal manual interventions and costs.

Section 3

Test Results

Treatment Objective

The main objective of this pilot was to demonstrate the ability of a full-scale 10 gpm SafeGuard H2O Cr(VI) treatment system to remove Cr(VI) from untreated well water down to non-detect levels (below 1 ppb).

Other objectives included:

- To determine optimal treatment process conditions (stannous dose) allowing non-detect Cr(VI) levels in the treatment system effluent;
- To demonstrate the SafeGuard H2O Cr(VI) treatment system performance under steady state treatment conditions;
- To demonstrate the SafeGuard H2O Cr(VI) treatment system performance under a stop-and-run operation mode;
- To demonstrate online treatment process optimization (stannous reagent dose control) through continuous Cr(VI) monitoring in the effluent;
- To demonstrate the accuracy and reliability of the online SafeGuard Cr monitoring system by validating continuous online data vs certified lab analysis of split grab samples;
- To evaluate the ability of sand media filter to effectively remove the treatment process byproducts; Cr(T) and T and evaluate the treatment process effect on dissolved U that is present in the raw water;
- To evaluate media filter performance and maintenance requirements (e.g., backwash) and investigate treatment process byproduct toxicity;
- To estimate the operational costs for a 10 gpm SafeGuard H2O Cr(VI) removal system.

Grab Sampling and Laboratory Analysis

Manual sand filter effluent grab samples were collected daily by AMS personnel and analyzed for Cr(VI), Cr(T) and T and U by a certified laboratory (BC Labs). Determination of dissolved Cr(VI) was performed using EPA method 218.6 (MDL 0.032 ppb) while both Cr(T) and total T were determined using EPA method 208.8 with NDL's 0.5 ppb and 0.12 ppb respectively. Grab samples were also collected by the City of Los Banos for independent confirmation after treatment and prior to the first backwash event. Results for Cr(T) and Cr(VI) were ND (RL 1.0 ppb) and ND (RL 0.05 ppb) respectively.

Results

Determination of the Optimal Stannous Reagent Dose

Previous laboratory test results performed with Los Banos Well #14 water at AMS facilities in January 2021 as well as SafeGuard H2O field pilot results (November-December 2019) have shown that complete Cr(VI) removal (below 1 ppb) can be achieved with a stannous reagent dose between 1.4-1.8 ppm.

> Note, the throughput of the SafeGuard H2O system used for all previous trials was relatively low at 0.025-0.075 gpm. Therefore, it was important to find the optimal range of the stannous reagent dose that needed to be added in order to achieve the treatment goals for a full-scale 10 gpm pilot system.

The diagram in Figure 3 demonstrates online Cr(VI) levels obtained from the 10 gpm SafeGuard H2O treatment system effluent as a function of the stannous reagent dose. A stannous dose of 1.4 ppm resulted in non-detect Cr(VI) residual levels in the effluent (Figure 3 - Area A).

After deliberately terminating reagent generation into the treated water, Cr(VI) levels in the treatment system effluent demonstrated a sharp increase and stabilized around an influent level of 38-39 ppb (Figure 3 - Area B). Then, the stannous dose was increased to 0.7 ppm which resulted in some effluent Cr(VI) level reduction to 18 ppb (Figure 3 - Area C).

A further increase of the reagent dose to 1.0 ppm caused Cr(VI) levels to decrease to below 1 ppb and remained steady for next six hours of system operation (Figure 3 - Area D). These results demonstrate that a stannous reagent dose of 1.4 ppm appears to be significantly higher than that required for complete Cr(VI) removal. Whereas a stannous reagent dose of 0.7 ppm is insufficient for achieving treatment goals.

Because a stannous reagent dose of 1.0 ppm ensures nearly zero residual contaminant levels in the effluent it was taken as an optimal reagent level for achieving the treatment goal of less than 1 ppb.

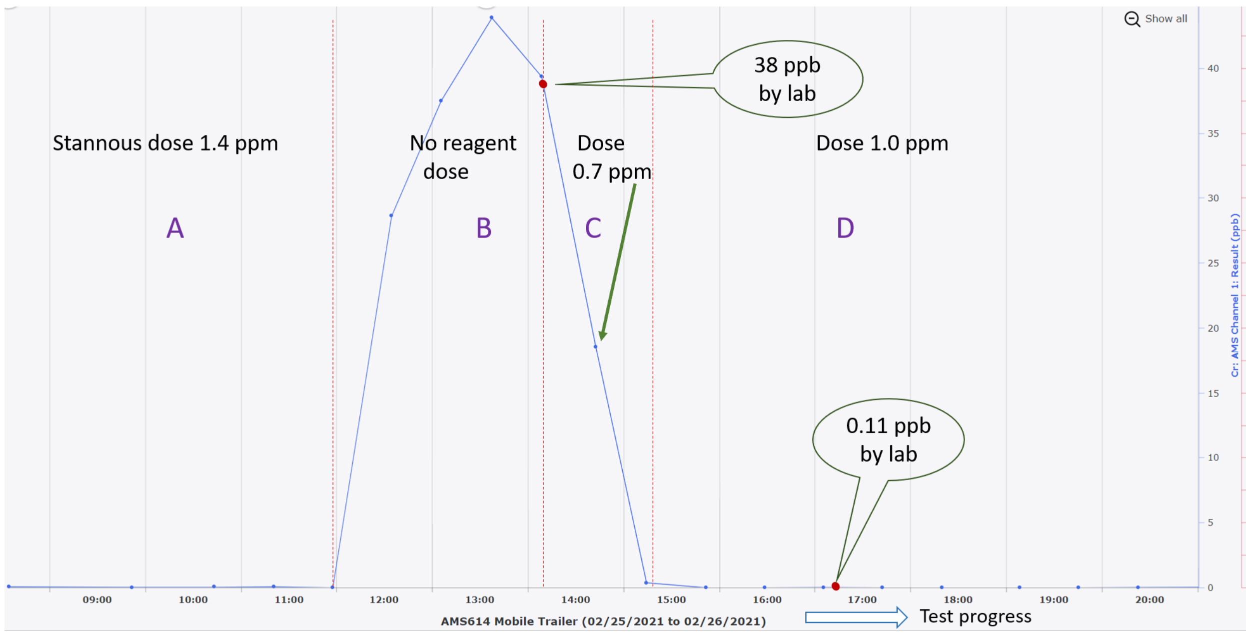

Figure 3. Effect of Stannous Reagent Dose on Cr(VI) Removal

Treatment System Performance Under Steady Optimal Treatment Conditions

SafeGuard H2O treatment system performance under steady conditions is shown in Figure 4. The Cr(VI) level in the treatment system effluent, without the addition of a stannous reagent was 36 ppb (Figure 4 - Area A). After initiating an optimal stannous reagent dose of 1.0 ppm into the water flow, the effluent Cr(VI) level sharply decreased to below 1 ppb and then stabilized around non-detectable readings for over eight hours. This demonstrated stable and reliable treatment conditions (Figure 4 - Area B).

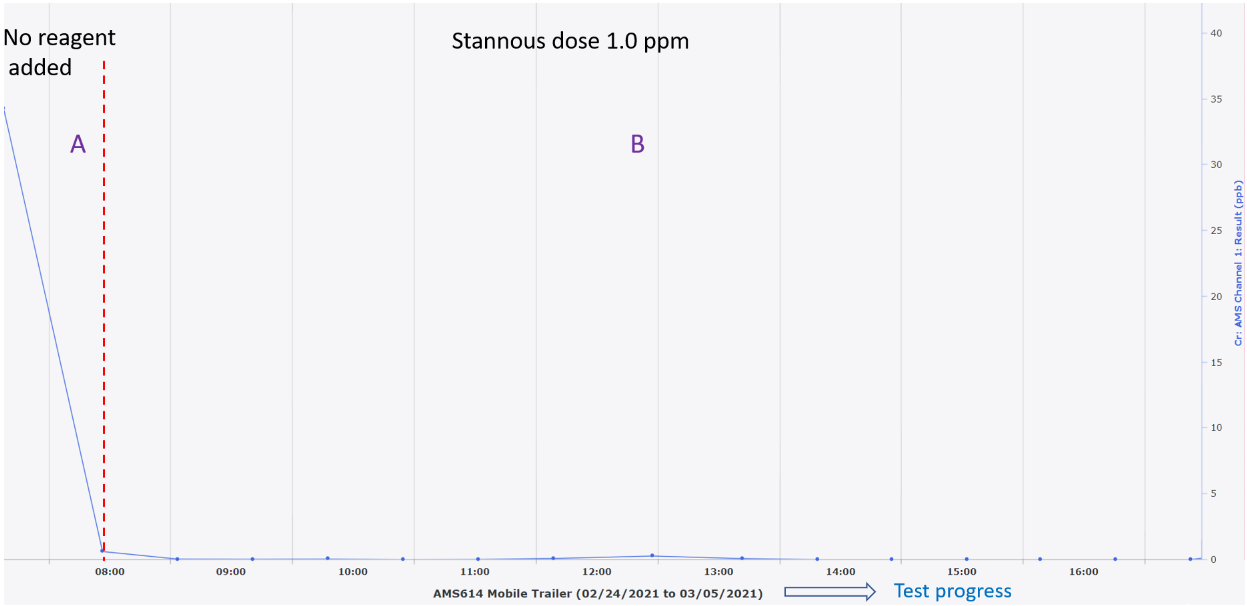

Figure 4. SafeGuard H2O™ Treatment System Performance Under Steady Process Conditions

Treatment System Performance Under Stop-and-Run Operation Mode

The vast majority of groundwater wells operate under a stop-and-run mode during which the treatment process is shut down in a prescheduled manner or in an unpredictable or incidental manner. Oftentimes, the restart of a treatment system after a shutdown period can be a challenging task. For instance, some chemical reagents utilized in the treatment process may degrade and then lose their effectiveness during the system shutdown period. In other treatment approaches, the treated water parameters must be modified and tightly controlled (pH, ORP, etc.) which requires lengthy, chemical and labor-intensive process stabilization periods. This slow treatment response (high system inertia) significantly reduces treatment system uptime, effectiveness, and results in a higher treatment process cost.

One of the most important features of the SafeGuard H2O treatment approach is that the stannous reagent is produced *in-situ* on demand which ensures the 100% freshness and reactivity of the reagent. In addition, the tin metal precursor (anode) used for reagent generation is highly stable and is unaffected during virtually unlimited shut off time periods.

As soon as the treatment process is restarted and the water flow through the stannous generator is initiated, freshly produced reagent is available for treatment. Also, the reduction reaction between stannous ion and Cr(VI) specie is fast and proceeds to completion under a broad range of treated water parameters (water composition, pH, etc.). The reaction byproducts (Cr(III), SnO_2) coagulate rapidly which allows their effective removal by a media filter. SafeGuard H2O demonstrates a relatively simple, low dead volume, straightforward treatment process which responds rapidly to changing key process parameters.

The SafeGuard H2O treatment system behavior and performance under a stop-and-run operation mode is detailed in Figure 5.

The diagram illustrates a fraction of the effluent data collected during 24 hours, from 3 p.m. 25 February 2021 to 3 p.m. 26 February 2021. Between 3 p.m. and 10 p.m. on 25 February 2021, the SafeGuard H2O treatment system was running under steady treatment conditions with a stannous reagent dose of 1.0 ppm demonstrating an effluent with residual Cr(VI) levels under 1 ppb (Figure 5 - Area A).

At 10 p.m., the treatment process was shutdown (Figure 5 - Area B) and then restarted on 26 February 2021 at approximately 10 a.m. under the same conditions prior to the shutdown. The first Cr(VI) effluent reading after the treatment process was restarted was below 1 ppb (Figure 5 - Area C, 11:30 a.m.); indicating a fast recovery of the SafeGuard H2O system after shutdown.

Immediately after completion of this measurement the generator was turned off again and the next Cr(VI) effluent value obtained was 27 ppb.

Then, the reagent generation process was restored, and the SafeGuard H2O treatment system instantly reduced effluent Cr(VI) levels to under 1 ppb. Effluent Cr(VI) levels remained low (below 1 ppb) for several consecutive runs.

This testing scheme demonstrated how the SafeGuard H2O treatment system recovered rapidly after a lengthy shutdown and stabilized under optimal conditions.

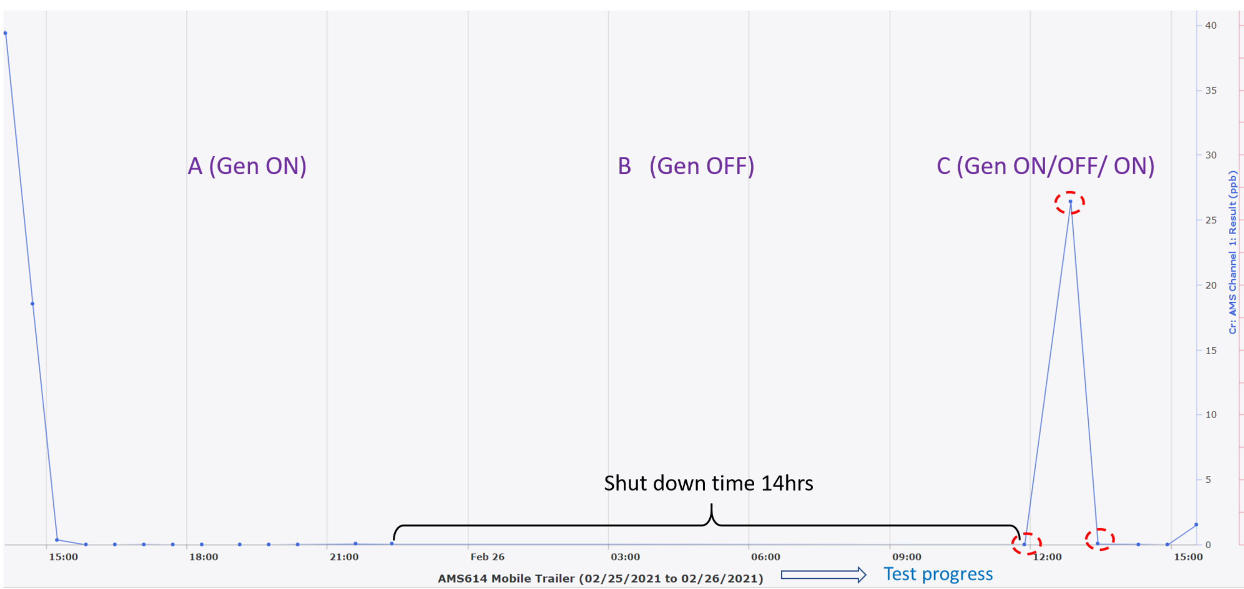

Figure 5. SafeGuard H2O™ Treatment System Performance Under Stop-and-Run Mode

Treatment System Response on Reagent Alternation Mode

The SafeGuard H2O treatment behavior when reagent dose changes in a step mode (alternates) between its lowest (zero) and maximum value is an important characteristic of the system inertia. Generally, the shorter the time required to stabilize system performance within a reagent dose alternation cycle, the lower the treatment system inertia.

The diagram in Figure 6 demonstrates the SafeGuard H2O treatment system response under alternating reagent modes:

- Figure 6 - Cycle 1: The treatment process started at 8 a.m. with a stannous reagent dose of 1.0 ppm which resulted in a nearly zero Cr(VI) level in the effluent. Then, the reagent dose was terminated and that resulted in a high Cr(VI) reading above 33 ppb. Next, the reagent generator was turned on and a 0.7 ppm stannous reagent dose was introduced into the treated water. This stannous reagent dose level resulted in an effluent Cr(VI) reading of 17 ppb which indicated insufficient treatment. As soon as the effluent measurement was completed, the stannous reagent dose was increased to 0.9 ppm and that dose level resulted in two consecutive Cr(VI) measurements of 2 ppb Cr(VI).

- Figure 6 - Cycle 2: The same sequence from Cycle 1 was repeated, with the only difference being the reagent dose restored was little higher than during Cycle 1, which resulted in lower first effluent Cr(VI) reading around 10 ppb. Similarly, further increasing the reagent dose to 0.9 ppm caused the residual Cr(VI) value to be slightly below 2 ppb (last reading in Cycle 2).

- Figure 6 - Cycle 3: The stannous dose used after zero reagent was added was increased to the 1.0 ppm optimal value which caused instant treatment system stabilization with effluent Cr(VI) readings at non detect levels. This test has illustrated once again low treatment system inertia, high accuracy and reliability of the in-situ stannous reagent generation approach along with fast and predictable treatment system response enhanced by an accurate and timely effluent monitoring approach.

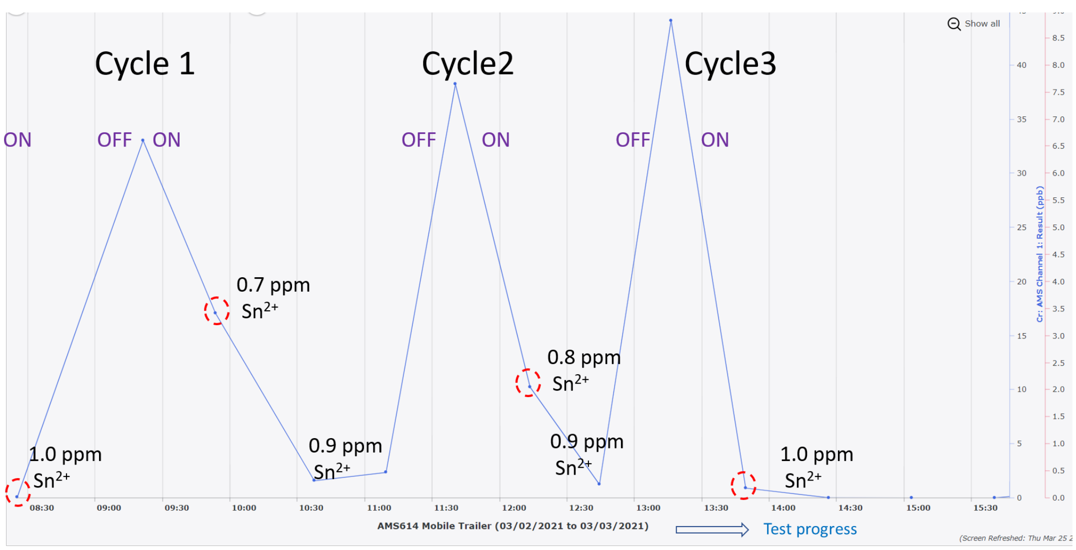

Figure 6. SafeGuard H2O™ Treatment System Response Under Alternating Reagent Generation

Treatment Process Optimization Through Continuous Cr(VI) Monitoring of the Effluent

The SafeGuard H2O treatment system has demonstrated reliable operation under optimal (steady) conditions providing high quality effluent with Cr(VI) levels below 1 ppb. However, changing the treated water matrix or varying the incoming Cr(VI) levels may affect the treatment process stability. Also, the MCL for Cr(VI) will determine the treatment target for Cr(VI) residual levels in the effluent.

SafeGuard H2O treatment system optimization and fine tuning through continuous high frequency effluent monitoring is detailed in Figure 7. The diagram demonstrates the SafeGuard H2O treatment system effluent online Cr(VI) results (blue) as a function of stannous reagent dose (red). Changing the electrogenerated reagent dose between 0.9-1.0 ppm, a resolution of 0.1 ppm, caused a fast and reproducible treatment system response that allowed the residual Cr(VI) level in the effluent to be kept tightly below 2 ppb (green dotted line). The high treatment system controllability (timely and adequate treatment system response on the reagent dose change) is due to:

- High accuracy and stability of the electrolytic reagent generator;
- High reactivity of produced in-situ fresh stannous reagent resulted in fast Cr(VI)/Cr(III) conversion;
- Optimal, straightforward and low dead volume SafeGuard H2O treatment system design using a relatively short contact time for the reaction between Cr and T;
- The feedback from the sensitive and accurate online SafeGuard Cr monitor.

The innovative reagent generation technique integrated with the advanced effluent monitoring approach leads to a fully automated intelligent SafeGuard H2O Cr treatment system design.

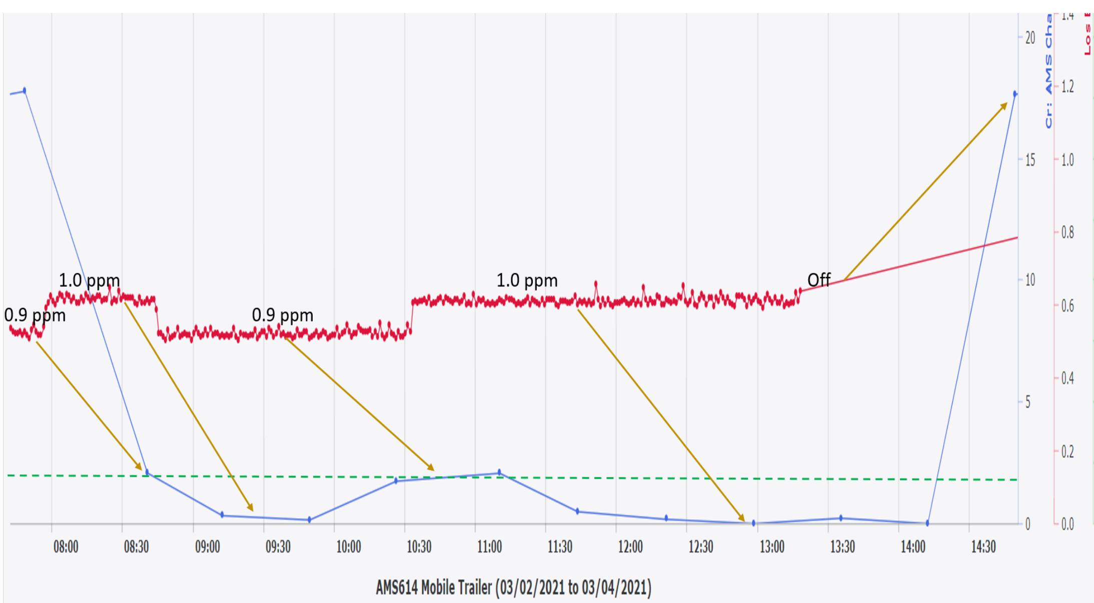

Figure 7. SafeGuard H2O™ Treatment Process Optimization and Fine Tuning

Correlation Between Online Cr(VI) Results and Corresponding Grab Sample Lab Results

Figure 8 demonstrates the correlation between Cr(VI) online data collected during the entire trial period and grab sample Cr(VI) results obtained from BC Labs, the certified laboratory (red dots). At least one grab sample has been collected daily and sent to the certified lab for Cr(VI) analysis.

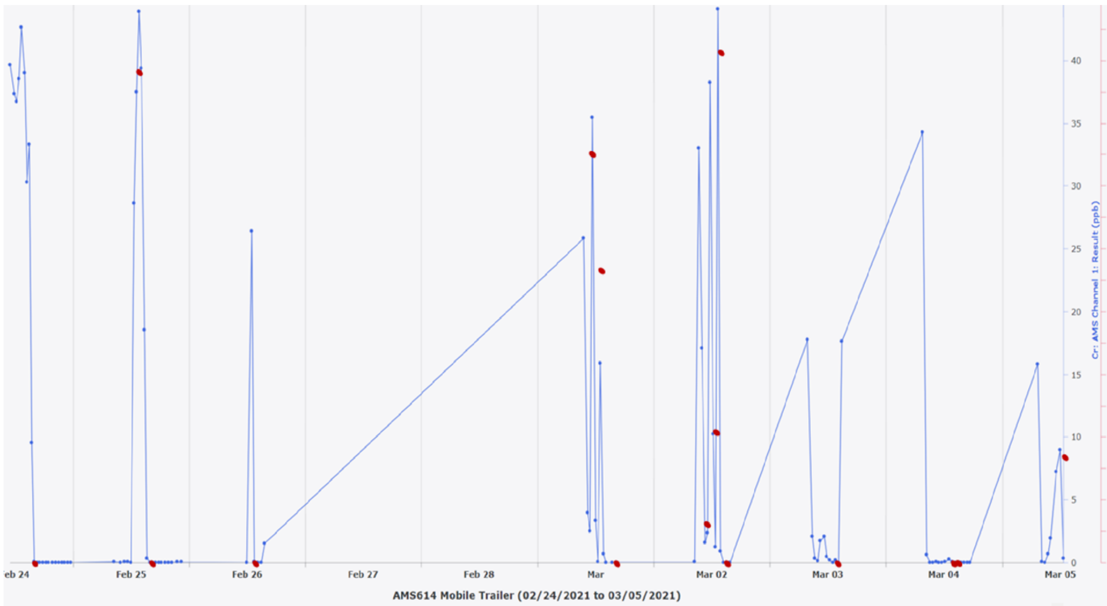

Figure 8. SafeGuard H2O™ Treatment Process Online Results vs Grab Sample Lab Results

Note, some effluent grab samples have been collected during steady state treatment system conditions when attempting to keep targeted Cr(VI) levels in the effluent below 1 ppb (eight data points).

In other cases, grab samples have been taken during non-optimized treatment conditions where the stannous reagent dose was intentionally deviated from its optimal value. Generally, online Cr(VI) results have demonstrated a very good correlation with grab sample lab results during the entire trial period.

Table 1 summarizes the SafeGuard H2O treatment system effluent Cr(VI) results versus lab measurements when the system was operated under optimal and steady conditions. Online Cr(VI) results demonstrate excellent correlation in all eight comparative tests.

Laboratory tests have shown that residual Cr(VI) levels in the effluent did not exceed 1 ppb which is close to the public health goal and an order of magnitude lower than California's originally promulgated MCL.

Table 1. Comparative Online SafeGuard™ Cr Analyzer Results vs Lab Measurements Under Optimal Conditions

Sample	Cr(VI) ppb	
	Online SafeGuard™ Cr Analyzer	BC Labs
2/24 16:30	<1	ND
2/26 16:30	<1	0.11
2/26 14:15	<1	0.11
3/1 16:20	<1	0.12
3/2 15:10	<1	0.1
3/3 13:40	<1	ND
3/4 12:45	<1	0.07
3/4 13:00	<1	0.1

Table 2 summarizes the SafeGuard H2O treatment system effluent Cr(VI) results versus lab measurements when the treatment system was deliberately operated during non-optimized performance.

The online Cr(VI) results are in very good agreement with those obtained by the certified laboratory.

Table 2. Comparative Online SafeGuard™ Cr Analyzer Results vs. Lab Measurements Under Deliberately Non-Optimized Performance

Sample	Cr(VI) ppb	
	Online SafeGuard™ Cr Analyzer	BC Labs
2/25 14:30	39.4	38
3/1 11:40	35.4	32
3/1 13:05	15.9	23
3/2 11:15	2.4	3.9
3/2 12:15	10.2	10
3/2 13:05	44.1	37
3/5 11:30	8.9	8.4

SafeGuard H2O™ Treatment System Effluent [Cr(VI), Cr(III) and T] Lab Analysis Results

Figure 9 demonstrates Cr(VI), Cr(III) and total T results found in eight treatment system effluent grab samples certified by analyses from BC Labs and plotted against trial progress (hours).

All Cr(VI) results (blue dots) are nearly zero ppb during the entire cumulative 55 hours of the trial (see Table 1). The Cr(III) effluent values (yellow) calculated as a difference between respective Cr(T) and Cr(VI) values demonstrated a sharp increase from 1 ppb to 3.8 ppb within the first 17 hours and then stabilized around 6.5 ppb through the end of the trial. Total T results in the treatment system effluent varied between 14 and 21 ppb without any noticeable trend (green dots).

Based on the fact that Cr(VI) levels in the effluent were reliably under the detection limit (1 ppb) it can be concluded that nearly 100% of the initial Cr(VI) present, 38-39 ppb, was converted into Cr(III) in the contactor prior to entering sand filters. Therefore, Cr(III) residuals in the effluent were the result of the sand media breakthrough only.

It is of interest to control residual Cr(III) in the effluent at low levels in order to avoid potential re-oxidation of Cr(III) into Cr(VI) after the chlorination step. Such a stringent Cr(III) effluent control can be achieved by:

- Enhanced effluent filtering capability;
- Frequent sand filter backlash;
- Cr(III) effluent monitoring;
- A combination of all three.

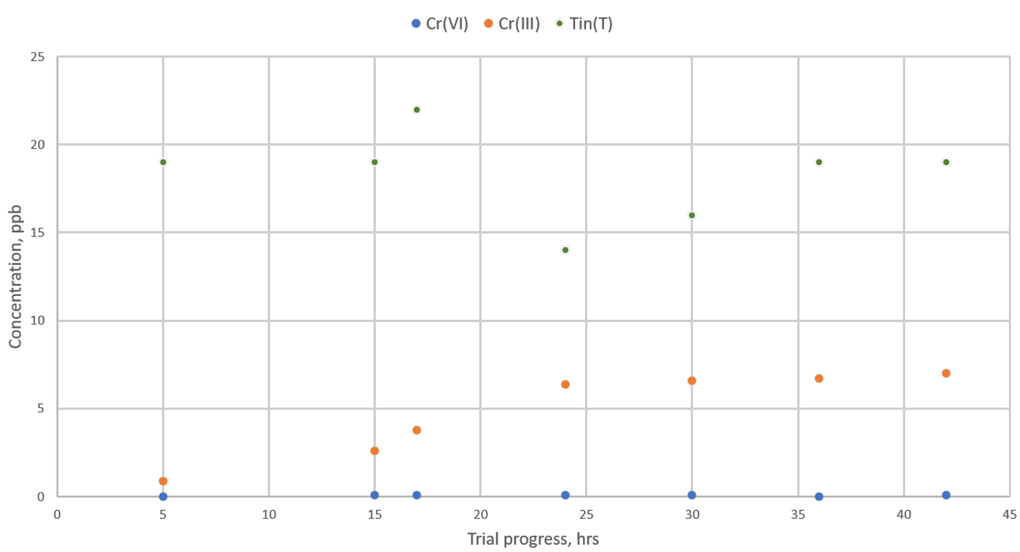

Figure 9. SafeGuard H2O™ Effluent Lab Results as a Function of The Trial Progress

The diagram in Figure 10 presents superimposed Cr(III) effluent levels and pressure readings across the filter as a function of the trial progress.

The media filter differential pressure changed from approximately 11 psi to approximately 14 psi during the entire trial period. In particular, during the first 24 hours of the trial while Cr(III) levels underwent a sharp increase from 1 ppb to 6 ppb the pressure change was insignificant. Therefore, pressure monitoring cannot be used as a sensitive enough and reliable indicator for media filter breakthrough and filter backwash triggering criterion.

Effluent samples have been collected after the first and second sand media filters in order to determine the effect of sequential sand media filtration on both Cr(III) and T removal efficiency. Cr(III) and T results after the first sand filter were 6.9 ppb and 19 ppb respectively, and 6.3 ppb and 19 ppb respectively after the second sand media filter. Note, Cr(VI) levels in both cases were under the detection limit. The insignificant difference in Cr(III)/T breakthrough levels after the first and second media filters indicates an efficient particulate removal by the first sand filter unit and reduces the necessity of a second, polishing, sand filter.

In order to prevent elevated Cr(III) levels in the effluent and potential risk of its re-oxidation by chlorine in the distribution system, it is clear that a comprehensive Cr(VI)/Cr(III) effluent monitoring approach should be implemented.

It should be noted that there is ongoing debate on the "safe level" of residual Cr(III) levels and its reoxidation risks. Multiple studies on Cr(III) re-oxidation performed suggest that kinetics of the re-oxidation process may vary according to water and distribution system conditions.

AMS' capability to monitor Cr(VI) and Cr(III) with the online SafeGuard Cr monitor allows for comprehensive effluent quality control, by triggering and optimizing the filter backwashing routine based on the contaminant limits set.

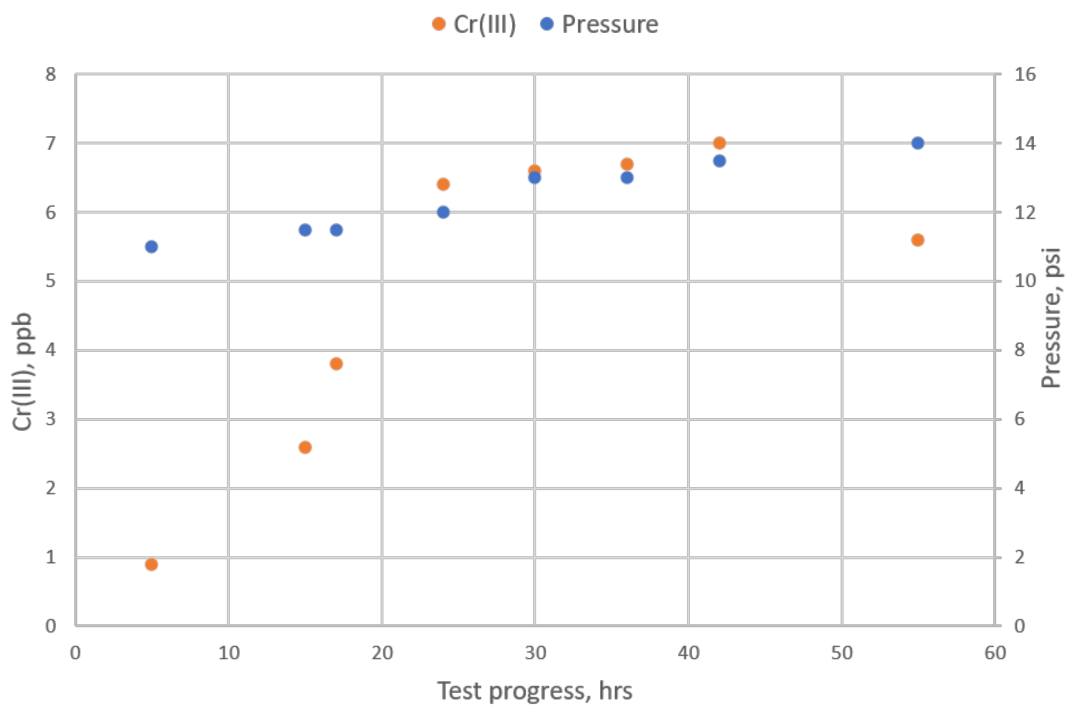

Figure 10. SafeGuard H2O™ Effluent Cr(III) Levels vs Sand Media Filter Pressure

SafeGuard H2O™ Treatment System Effect on Dissolved Uranium in Untreated Well Water

Los Banos Well # 14 historical data, as well as recent grab sample laboratory tests, indicate that total U levels in the well water varies between 14 ppb and 15 ppb. Figure 11 presents total U levels in the treatment system effluent grab samples collected under optimal treatment conditions. Effluent U levels match perfectly untreated water levels which indicates no U retention by the SafeGuard H2O treatment system.

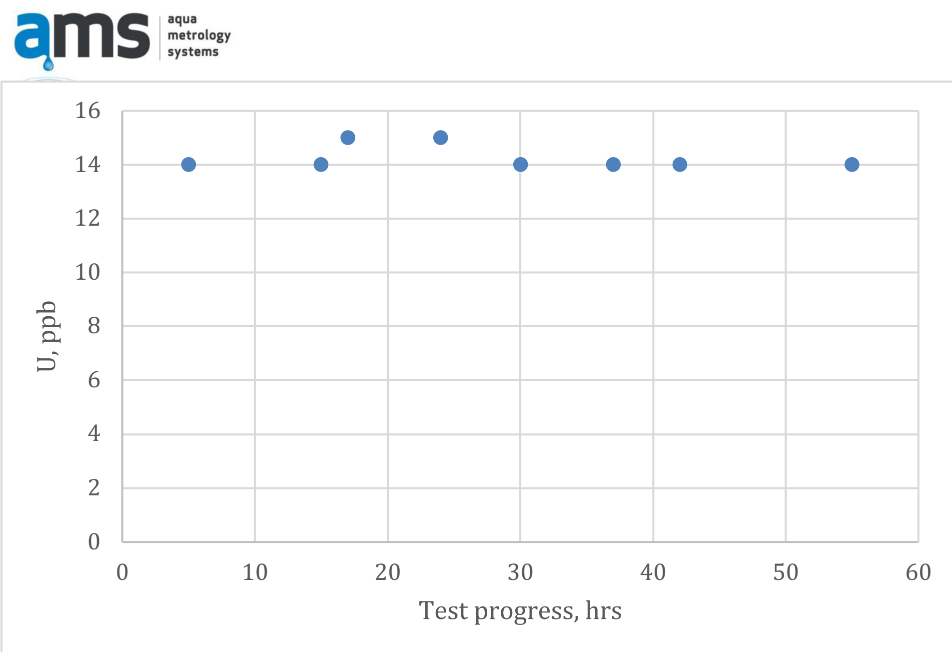

Figure 11. SafeGuard H2O™ Treatment System Effluent Uranium Laboratory Test Results

SafeGuard H2O™ System Maintenance

SafeGuard H2O™ Treatment System Maintenance Schedule

The SafeGuard H2O treatment system requires periodic maintenance to ensure its ability to perform reliably and effectively. The system maintenance includes:

- Replacing self-sacrificial tin anodes when required;
- Replenishing online SafeGuard Cr monitor consumables and reagents;
- Backwashing media sand filters.

The SafeGuard H2O stannous generation sub-system contains modular tin anode cartridges which should be replaced when a critical preset capacity level is reached. Proprietary software continuously monitors the tin anode (precursor) condition and will switch automatically to a spare cartridge module upon exhaustion of the operational one.

In parallel, a preventive maintenance request message is sent to the system operator to replace the spare cartridge. Because the SafeGuard H2O stannous generator tin precursor load was sufficient to operate continuously over 300 hours end exhausted less than 20% of its capacity, maintenance on the generator was not required during the trial period.

The online SafeGuard Cr analyzer reagents and consumables reserves ensure the monitor will operate unattended for three consecutive months; as a result, monitor maintenance was not required or performed during the trial period.

Sand filter backwash is periodically required for two main reasons: (1) increased hydrodynamic filter resistance (head loss); (2) risk of accumulated treatment process byproduct (T and Cr(III)) breakthrough. The pressure change during the entire trial period was insignificant. However, during the first 24 hours of system operation, Cr(III) residuals in the effluent increased sharply and then stabilized and remained unchanged for the rest of the trial period (see Figure 11).

Based on the grab sample test results, the optimal backwash cycle should be between 20-24 hours of system uninterrupted operation to ensure Cr(III) levels in the effluent remain below 5 ppb. Once again, Cr(III) effluent level online monitoring can be effectively used to trigger the sand filter backwash cycle.

SafeGuard H2O™ Treatment System Sand Filter Backwash

The backwash of the media sand filter was performed at the AMS facility in Sunnyvale, California, after the completion of the trial period (treatment of 33,000 gallons of water). Prior to the backwash procedure the sand filter vessel was opened, and a sand media sample was taken, pre-washed and sent to the laboratory for analysis. Similarly, another sand media sample was collected for analysis after completing of the backwash process.

The backwash parameters include:

- Backwash water – Sunnyvale tap water;
- Backwash water flow rate – 4 gpm;
- Backwash volume- 50 gallons.

Figure 12 shows photographs of 10 gallons of backwash water collected before and after settling. The unsettled backwash water is a high turbidity suspension. However, the particulates agglomerate and settle fast showing complete separation in a less than 4 hours of stagnation.

Figure 12. SafeGuard™ H2O Media Filter Backwash Water Settling Process

The clear fraction of the backwash water after settling has been tested for Cr(VI) using the online SafeGuard Cr analyzer, and only 1 ppb of Cr(VI) was detected. A sample of the backwash sludge has also been collected and sent to a certified laboratory for analysis.

SafeGuard™ H2O Treatment System Material Balance

Backwash sludge was collected from the entire 50 gallons of backwash water by filtering it through a 0.5-micron filter. The total wet sludge weight was 247.7 g with a solids fraction over 25% (61.9 g). A material balance across the SafeGuard H2O treatment system was performed based on the following assumptions:

- Tin oxide (SnO_2) and chromium oxide (Cr_2O_3) are the only insoluble species produced during the treatment process and removed by the media filter;
- Sunnyvale, California tap water (containing trace amounts of both Cr(T) and T at levels of 1.4 ppb and 7.0 ppb respectively based on certified laboratory analysis) was used as the source water for the filter backwash. Due to low levels of both contaminants in the backwash water their effect was not taken into consideration in the material balance quantifications since they had no effect on sludge amount and composition.

Under the assumptions above the material balance was performed according to following equation (3):

$$S_{Tot} = S_T + S_{Cr} \qquad (3)$$

S_{Tot} – total sludge amount;
S_T – sludge due to T reagent produced;
S_{Cr} – sludge due to insoluble Cr(III)

Tin Oxide (SnO_2) Sludge Calculation

The tin anode mass loss (Δm) during the trial period was determined as the difference in an anode weight before and after the trial. The mass loss was 41.7g. The resulting SnO_2 sludge amount (S_{Tin}) was estimated according to (4):

$$S_T = k\,\Delta m \qquad (4)$$

k- correction coefficient due to addition of oxygen to T atom;
Δm – T anode mass loss (g);

$$S_T = 1.27 \times 41.7 = 52.8 \text{ g}$$

Chromium Oxide (Cr_2O_3) Sludge Calculation
The sludge amount due to Cr_2O_3 (S_{Cr}) was estimated through equation (5):

$$S_{Cr} = k\; V_T\, 10^{-3}\, (C_{inf} - C_{eff}) \qquad (5)$$

k- correction coefficient due to addition of oxygen to Cr atom;
C_{inf} – influent Cr level (ppb);
C_{eff} – effluent Cr level (ppb);
V_T – total amount of water treated (L);

$$S_{Cr} = 1.49 \times 126300 \times 0.033 \times 10^{-3} = 6.2 \text{ g}$$

Total Sludge Amount Calculation

$$S_{Tot} = S_T + S_{Cr} = 52.8 + 6.2 = 59.0 \text{ g}$$

The total sludge amount calculated correlates well with the data found by the certified laboratory (61.9 g). This indicates a high overall treatment system performance as well as the effectiveness of the media filter regeneration process.

SafeGuard H2O™ Treatment System Waste Toxicity Study

A brief summary of waste toxicity analysis:

- TTLC (Total Threshold Limit Concentration) - This analysis determines the total concentration of each target analyte in a liquid, solid, sludge or particles. When any target analyte exceeds the TTLC limits the waste is classified as hazardous and its waste code is determined by the compounds present.
- TCLP (Toxicity Characteristic Leaching Procedure) - This test involves a simulation of leaching through a landfill and can provide a rating that can prove if the waste is dangerous to the environment or not. This is a federal guideline and differs from the State in several ways.
- STLC (Soluble Threshold Limit Concentration) - Waste Extraction Test (WET) - This analysis determines the amount of each analyte that is soluble in the WET leachate in Citric acid (pH 5). This WET leachate procedure is used for solid samples or for samples containing < 0.5% solids.
- STLC - Modified WET test determines the soluble portion of the analytes in DI water. From a regulatory standpoint it is only specifically used for Cr(VI) since the citric acid typically converts that to Cr(III) in the extraction. This is a federal guideline and differs from the State in several ways.

A brief summary of the regulatory limit:

Federal Resource Conservation & Recovery Act (RCRA) bases the toxicity of a waste on the results of a TCLP test, whereas California uses the criteria outlined in Table 3 to determine the toxicity of a waste following exceedances of TTLCs or STLCs for specific chemicals.

Table 3. Waste Characterization Limits

STLC/TTLC Regulatory Limits*	STLC-(TCLP) (mg/L)	TTLC (mg/Kg)
Cr(VI) Compounds	5	500
Cr (and/or Cr(III) compounds)	560** (5)	2,500

* Used for California regulated hazardous waste. Source is California Code of Regulations, Title 22, Chapter 11, Article 3.)
** If the soluble chromium, as determined by the TCLP set forth in Appendix I of chapter 18 of this division, is less than 5 mg/L, and the soluble chromium, as determined by the procedures set forth in Appendix II of chapter 11, equals or exceeds 560 mg/L and the waste is not otherwise identified as a RCRA hazardous waste pursuant to section 66261.100, then the waste is a non-RCRA hazardous waste.

Laboratory modified STLC and STLC results of the sludge and backwashed sand sample are summarized in Table 4.

The soluble Cr(VI) concentration found in both sludge and backwashed sand samples are under detection limit (below 0.002 mg/L) which is far below the regulatory limit (5 mg/L). The measured Cr(T) was 0.07 mg/L for the sludge sample and 0.28 mg/L for the sand sample which are far below the limit (see Table 3). The T regulatory limit is not mentioned in the official chart.

Table 4. Modified STLC* and STLC Results

Sample	Modified STLC*			STLC	
	Cr(VI)	Cr(T)	Total T	Cr(T)	Total T
Backwash Sludge	ND	0.07	0.59	140	NA
Backwashed Sand	ND	0.28	4.4	2.7	40
EPA Method	*7199*	*6010B*	*6010B*	*6010B*	*6010B*
MDL	*0.002*	*0.001*	*0.0072*	*0.009*	*0.034*

Note- All concentrations in mg/L.

Laboratory TTLC results obtained with the sludge sample and backwashed sand sample are summarized in the Table 5.

The Cr(VI) results for both backwash sludge and backwashed sand samples (15 mg/kg and 0.7 mg/kg) are significantly below regulatory limits (see Table 3). The Cr(T) results for both backwash sludge and backwashed sand samples (1700 mg/kg and 35 mg/kg) are significantly below regulatory limits as well. The T regulatory limit is not mentioned in the official chart.

Table 5. Laboratory TTLC Results

Sample	TTLC		
	Cr(VI)	Cr(T)	Total T
Backwash sludge	15	1700	17000
Backwashed Sand	0.7	35	500
EPA Method	*7199*	*6010B*	*6010B*
MDL	*0.002*	*0.001*	*0.0072*

Note- All concentrations in mg/kg.

SafeGuard™ H2O 10 gpm Treatment System Operational Cost Estimates

Based on the pilot treatment plant operational experience and the results obtained, the estimated capital and operational costs for a 10 gpm SafeGuard H2O system are estimated based on these assumptions:

- Incoming Cr(VI) level 40 ppb;
- Treatment goal below 1 ppb Cr(V); and below 8 ppb Cr(III);
- Continuous system operation;
- Service contract 10 years (warranty 10 years);
- Daily water consumption of 400 gallons per connection;
- Remote system condition monitoring (standard);
- Continuous online effluent quality monitoring not included in standard system version.

The estimated SafeGuard H2O capital, service and annual costs per connection per year are summarized in Table 5.

Based on a $200,000 capital investment and a $40,000 annual service fee, the annual water cost per connection is $1,700. The service fee will include tin anode materials supply, SafeGuard H2O treatment system maintenance and warranty support excluding the cost of electricity.

The estimated energy consumption for a 10-gpm electrolytic reagent generator is between 0.2-0.3 kW.

Table 6. Cost Estimate for a 10-gpm SafeGuard™ H2O Cr(VI) Removal Treatment System

System Size	Productivity	Connections	Cost (x1000)		
GPM	GPD	Served	Capital	Service (Annual)	Total (Annual)
10	14400	35	200	40	1.7

It is noted that these cost estimates are applicable to a system sized near the lowest-capacity end of the spectrum. Due to economies of scale, the capital cost and service fee per service connection are anticipated to drop dramatically as the system capacity is scaled up for larger municipal systems.

Conclusions

- The City of Los Banos full-scale 10 gpm SafeGuard H2O Cr(VI) removal pilot system demonstrated a high capability of removal incoming high Cr(VI) levels to virtually zero pbb (non-detect levels) under steady treatment process conditions;
- The SafeGuard H2O Cr(VI) treatment system demonstrated a high stability under steady treatment conditions as well as fast recovery under stop-and-run mode;
- The SafeGuard H2O Cr(VI) treatment system demonstrated an acceptable response to reagent dose control under continuous Cr(VI) monitoring of the effluent performed by the online SafeGuard Cr analyzer;
- The SafeGuard H2O Cr(VI) treatment system demonstrated the high accuracy and reliability of the online SafeGuard Cr monitoring system vs certified lab analysis of split grab samples;
- The SafeGuard H2O Cr(VI) treatment system demonstrated the ability to effectively remove the treatment process by-products, Cr(T) and T, which was confirmed by a material balance calculation. Dissolved U present in the water was not affected by the treatment;
- The SafeGuard H2O Cr(VI) treatment system generated low amounts of waste during operation, and the toxicity analysis of the treatment sludge and filter media demonstrated its non-toxic nature;
- SafeGuard H2O Cr(VI) treatment system cost estimates have been made.

Acknowledgements

AMS is extremely grateful to the City of Los Banos for the opportunity to conduct this demonstration project and the advice of Kevin Berryhill, P.E., PROVOST & PRITCHARD CONSULTING GROUP.