Report

AQUA METROLOGY SYSTEMS

SafeGuard™ H2O Pilot Report

Intelligent Cr(VI) Treatment System

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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.

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Section 1

Executive Summary

Site Overview

New data on the efficacy of stannous chloride ($SnCl_2$) to treat Cr(VI) released in Fall 2016 highlighted the methodology as an economical treatment approach with the potential to significantly reduce the capital, operations, and maintenance costs of chromium remediation compared to Best Available Technologies (BATs) which have been surrounded by controversy over their high capital and operating costs.

Research has shown the reduction of Cr(VI) to Cr(III) by both stannous chloride and ferrous ions to be highly effective. However, conventional stannous reagent dosing methodology is not without disadvantages. Stannous salt solutions are a highly corrosive, toxic, and hazardous reagent requiring special shipping, storage, and handling. The reagent has a limited shelf life due to its chemical instability and once expired, it must be disposed of safely. Due to the high density, viscosity, and acidity of stannous salt solutions, the reagent may also require a complex delivery system design and control. All combined, conventional dosing approaches for stannous reagents are associated with high capital and operational costs.

An innovative approach to generate a stannous ion reagent[1] in-situ via an electrolytic process, SafeGuard™ H2O, has been developed by Aqua Metrology Systems (AMS). The SafeGuard H2O system also features an online Cr(VI) monitoring analyzer for real-time monitoring for the control, optimization, and treatment of Cr(VI). The fully integrated SafeGuard H2O online Cr(VI) remediation system eliminates the pitfalls of conventional dosing and aids in the delivery of an affordable and reliable Cr(VI) remediation process.

A SafeGuard H2O demonstration unit was installed at Los Banos Well #14 for a two-week demonstration period (11-22 December 2017). In addition to elevated Cr(VI) levels of 40 ppb, the characteristics of source water for Los Banos Well #14 includes high levels of uranium, conductivity and hardness. The demonstration will evaluate the SafeGuard H2O system's performance for consistently treating Cr(VI) below 10 ppb under extremely challenging water conditions.

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

Background

Aqua Metrology Systems, based in Sunnyvale, California, is a water technology company that has built a market leading position in the global market for the real-time online detection of contaminants such as Disinfection By-products (Trihalomethanes) and Trace Metals (e.g. Arsenic, Chromium, Copper, Lead, Mercury, Nickel, Selenium, Tin, Uranium, Zinc, and more).

Aqua Metrology Systems has been providing utilities with a accurate and reliable method to monitor Cr(VI) in real time since 2015. The AMS online Cr(VI) analyzer was the first fully automated, online multi-stream Cr(VI) analyzer commercially available to monitor drinking and wastewater.

The intelligent Cr(VI) monitor uses a self-calibrated voltammetric detector specifically developed to allow selective determination for hexavalent and total chromium down to 1 ppb. The analyzer features a robust and stable design that is capable of maintaining its sensitivity and calibrated status for an unlimited timeframe while operating reliably regardless of sample matrix conditions. The monitor evaluates multiple process streams and produces results in as little as 3 minutes. The monitor operates fully unattended and continuously, 24/7, delivering between 45 and 50 analytical readings per day.

The online Cr(VI) monitor technology has been used at several Cr(VI) treatment sites in California (e.g. Coachella Valley, Watsonville, and Citrus Heights) to support cities and engineers in their performance evaluation of Cr(VI) remediation and treatment plants (e.g. RCOF, $SnCl_2$). The monitor provides a high frequency of reliable data on influent and effluent Cr(VI) levels which helps to monitor critical process steps and aid in remediation process control and optimization.

As part of their work with Cr(VI) treatment sites, AMS supported the evaluation of $SnCl_2$ as a potential lower cost chemical reagent for treating the contaminant. Based on the results of these studies, industry peer observations, and the extensive experience of senior scientists at AMS, the company believes that certain characteristics of the traditional $SnCl_2$ reagent make it unsuitable for treating Cr(VI) in a consistent and predictable manner. As a result AMS designed the SafeGuard H2O, a patent-pending online Cr(VI) remediation system that generates a stannous ion reagent in-situ via an electrolytic process and also features an online Cr(VI) monitoring analyzer.

SafeGuard H2O is a novel chromium 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 since shipping and handling of a hazardous solution are eliminated.

The system also features built in online sensors to monitor influent water quality parameters and an online Cr(VI)/Total Cr/Tin monitoring system to continuously analyze components of interest in all critical process steps.

Data generated from the onboard Cr monitoring system helps drive a highly accurate remediation process by ensuring reliable reagent dosing control through manipulation of site-specific process parameters since real time adjustments to process parameters can be made and then reported to the main control system. Remote access capability allows system performance monitoring 24/7 by AMS.

The SafeGuard H2O system features low capital and operating costs, making it an economical and reliable Cr(VI) remediation system suitable for large and small water systems, point-of-supply systems, or as point-of-entry systems for individual residences.

Results

The SafeGuard H2O demonstration unit installed at Los Banos Well #14 underwent a two-week demonstration (11-22 December 2017). The demonstration was a success; the SafeGuard H2O system consistently generated targeted stannous reagent levels (0.25-100 ppm) into the raw water stream.

The novel SafeGuard H2O system successfully demonstrated the ability to efficiently generate stannous reagent into contaminated well water source and to convert hexavalent chromium into trivalent form with high efficiency and stability.

The performance of the SafeGuard H2O system was monitored in real-time using the automated onboard SafeGuard Chromium monitor, a feature that contributed to fast system set up and optimization.

Analytical data from the online method and laboratory showed good agreement, further validating the ability of the SafeGuard H2O system to monitor the Cr(VI) remediation process in real-time.

The experimental results suggest a high probability for the scalability of the SafeGuard H2O system for point-of-supply systems and point-of-entry systems. Full-scale evaluation is required to further demonstrate the long-term system performance of SafeGuard H2O in field conditions.

Next Steps

Following this successful proof-of-concept demonstration confirming the robustness and stability of the SafeGuard H2O system to consistently generate a stannous ion reagent to treat Cr(VI) below 10 ppb, AMS is looking to secure funding and determine a facility where a full-scale independent validation of the SafeGuard H2O point-of-supply system can be undertaken.

AMS is also seeking to secure funding for a full-scale independent validation for SafeGuard H2O point-of-entry system.

Section 2

Demonstration Technology

SafeGuard™ H2O Online Cr(VI) Treatment System

Aqua Metrology Systems provided a demonstration unit (Figure 1) of the SafeGuard H2O intelligent Cr(VI) treatment system to the City of Los Banos for a two week demonstration period (11-22 December 2017). The demonstration unit, sized to accommodate a throughput capacity of 0.7-0.8 gpm, is suitable for point-of-entry use at individual residences. The SafeGuard H2O technology is suitable for water systems, point-of-use systems, and point-of-entry systems.

Figure 1: SafeGuard™ H2O Online Cr(VI) Treatment System Demonstration Unit

SafeGuard™ H2O Technology: Principles of Operation

SafeGuard H2O is a patent-pending intelligent Cr(VI) treatment system that generates a stannous ion reagent in-situ via an electrolytic process and also features an online Cr(VI) monitoring analyzer.

SafeGuard H2O 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 since shipping and handling of a hazardous solution are eliminated. The system has built in online sensors to monitor influent water quality parameters and an online Cr(VI)/Total Cr/Tin monitoring system — a unique feature not offered by other Cr(VI) remediation technologies.

Whereas other Cr(VI) remediation systems such as $SnCl_2$ are operated based on data from manual sampling and analysis, the SafeGuard H2O system has a highly accurate and reliable stannous ion dosing process because of the real-time Cr(VI)/Total Cr/Tin data provided every thirty minutes by the online trace metals analyzer. The fully integrated and intelligent Cr(VI) remediation system generates a stannous ion reagent onsite, and Cr(VI) levels are measured in real-time to ensure its efficacy.

Process Flow Diagram

In the process design of the SafeGuard H2O system,a stannous ion reagent generator is installed inline with the reagent generation stream and controlled by an automated galvanostat (amperostat). Galvanostat maintains a certain electric current sufficient to generate a stannous ion reagent into the stream at targeted levels, according to incoming Cr(VI) contaminant levels and flowrate. A stannous ion reagent is continuously produced and delivered by waterflow to the main water stream where it is mixed and further reacts with Chromate reducing it into Cr(III) in the contactor vessel. An online Cr/Tin monitoring system continuously analyzes Tin and Chromate levels at critical process steps and reports the results to the main control system. Tin dosing is adjusted according to real time process data, ensuring a high level of system automation and integrity. Treated water can either be incorporated into a water blending scheme or discharged for public consumption. The process flow is detailed in Figure 2.

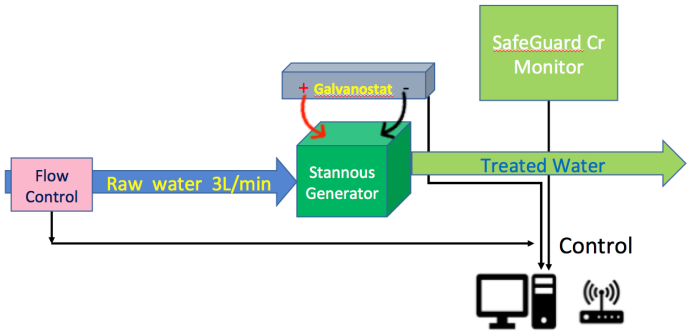

Figure 2- SafeGuard™ H2O Online Cr(VI) Treatment System Standard Process Diagram

Section 3

Test Results

Site Water Conditions

Water quality is of paramount importance to the efficiency and effective operation of water treatment technologies. The water quality parameters of Las Banos Well #14 are noted in Table 1. In addition to elevated Cr(VI) levels of 40 ppb, the facility has extremely challenging water quality due to high levels of uranium, conductivity and hardness in their source water. This type of water composition is particularly problematic for ion exchange, and zerovalent Cr(VI) remediation technologies and excellent for detailing the efficacy of the SafeGuard H2O system.

Table 1: Water Quality Parameters at California Drinking Water Facility

Hardness	566 mg/l
pH	8.0
Sulfate	318 mg/l
TDS	1,180mg/l
Uranium	13.2 ug/l
Cr(VI)	40 ppb

Testing Schedule

The SafeGuard H2O system automatically treats incoming raw water flow by injecting targeted stannous reagent levels into the stream. Influent and effluent Cr(VI) levels were analyzed by online and manual samples.

Aqua Metrology Systems' SafeGuard Cr(VI) monitor (0.5 ppb Quantitation Limit), that is integrated into the SafeGuard H2O system, analyzes treated water samples online in near real-time of 5-6 minutes (0 h).

Following a 24 hour delay (24 h), the samples are then reanalyzed at Aqua Metrology Systems' lab using another SafeGuard Cr(VI) monitor. In addition to analyzing online samples taken in real time, the SafeGuard Cr(VI) accepts manually collected samples via a grab sample port for analysis.

Manual water samples are split, preserved, and sent to certified analytical laboratory three times per week for third party analysis of the samples. Manual sampling is used to further validate performance of the SafeGuard H2O system against standard laboratory analysis (EPA Method 218.6 Practical Quantitation Limit 0.2 ppb).

BC Laboratories (BC Labs), a certified third party laboratory, undertook analysis of the manual samples for the duration of the demonstration period. The SafeGuard H2O system was commissioned 11 December 2017 and the demonstration project concluded on 22 December 2017.

Treatment Objective

The treatment objective of this demonstration project was to evaluate the SafeGuard H2O system's ability to consistently generate targeted stannous reagent levels (0.25-100 ppm) into the raw water stream.

Other objectives included:

- Study efficiency of hexavalent chromium conversion into trivalent form
- Investigate Tin-chromium reaction kinetics at different stannous/chromate ratios
- Optimization of the reagent generation parameters and reagent dose

Results

1.1 Determination of hexavalent-trivalent chromium conversion reaction efficiency.

Raw well water was continuously treated by *in-situ* generated stannous reagent (1.0 ppm dose).

Six samples of treated water were collected on 11 December 2017 and 13 December 2017 and immediately analyzed for Cr(VI) using the online SafeGuard monitor at site within 5-6 minutes after sampling (SG 0 h) and then again at 24 hours later at Aqua Metrology Systems' lab (SG 24 h) on another SafeGuard Cr(VI) monitor .

One representative sample from each daily series was split, preserved and delivered to third party certified lab (BC Labs) for further Cr(VI) analysis.

The residual Cr(VI) results from the 12 field samples that were analyzed by the online SafeGuard Monitor (SG) monitor and BC Labs are shown in Figure 3.

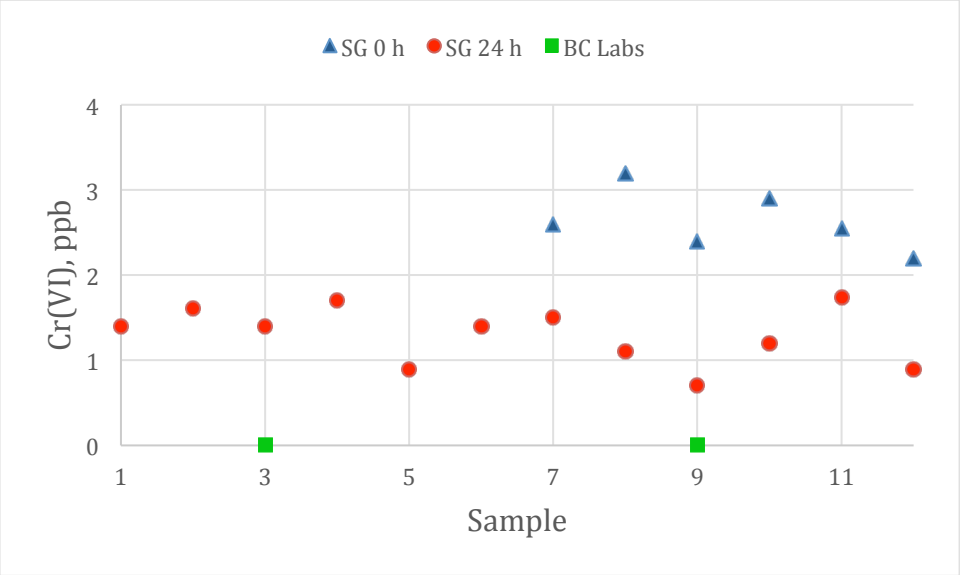

Figure 3- Residual Cr(VI) levels in treated raw water determined by online SafeGuard™ monitor and by EPA Method 218.6

Immediately after sample collection (SG 0 h Data) hexavalent chromium residuals levels were 2-3 ppb. However, within 24 hours Cr(VI) levels decreased to 1-2 ppb (SG 24 h Data). Hexavalent chromium results obtained in two split samples by the third party certified laboratory (BC Labs) were under the detection range (below 0.2 ppb).

Some additional decrease in residual hexavalent chromium levels in treated raw samples indicates ongoing reduction process after sampling.

Low residual hexavalent chromium levels detected by the SafeGuard monitor as well as BC Labs indicates a high hexavalent chromium conversion efficiency (see Table 2).

Conversion efficiency (η) calculated using (1).

$$\eta\ (\%) = (C_{Inf}-C_{Eff}\ /C_{Inf})x100 \quad (1)$$

C_{Inf} – concentration of hexavalent chromium in influent;

C_{Eff} - concentration of hexavalent chromium in effluent (6 test average)

Table 2. Hexavalent to trivalent chromium conversion efficiency

Cr(VI) Analysis	SG 0 hrs	SG 24 hrs	BC Labs
η (%)	93	96	100

1.2 Hexavalent-trivalent chromium conversion reaction kinetics study

Hexavalent chromium conversion kinetics (rate) is represented as fraction of converted Cr(VI) related to the initial level in untreated raw water as a function of reaction (contact) time.

The SafeGuard H2O system was set to generate stannous reagent into raw water flow at 1.0 ppm and 0.5 ppm. Treated water samples were collected and analyzed on the online SafeGuard Cr(VI) analyzer at 3-, 10- and 15-minute intervals. The minimal time required for testing on the SafeGuard analyzer is 3 minutes. Results are detailed in Table 3 and depicted in Figure 4.

Table 3. Hexavalent chromium levels in treated raw water found after different time periods

Tin-Chromium	Hexavalent Chromium	
Reaction Time	Reagent 1.0 ppm	Reagent 0.5 ppm
3 min	3.3 ppb	4.7 ppb
10 min	2.4 ppb	4.2 ppb
15 min	2.1 ppb	3.8 ppb

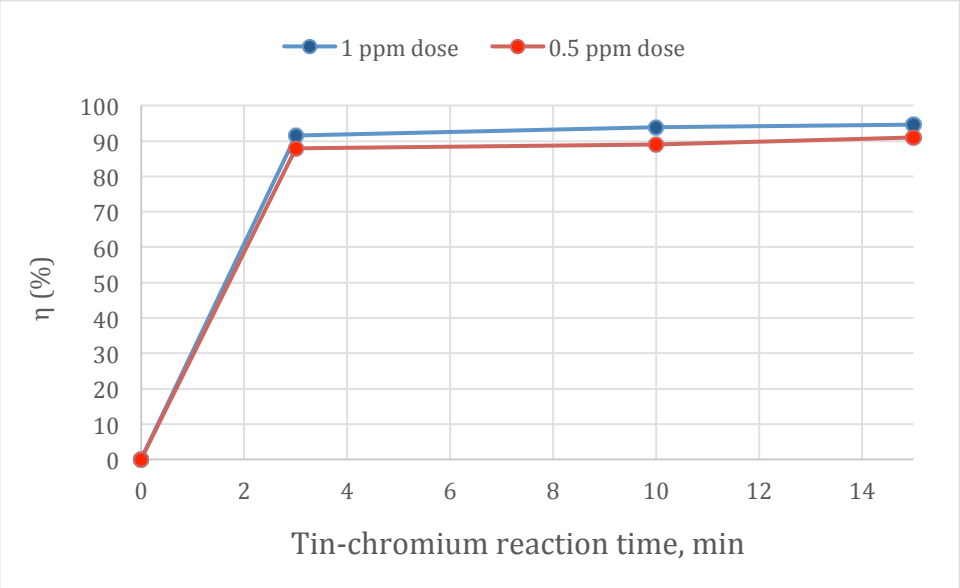

Figure 4- Hexavalent chromium conversion rate obtained with 1.0 and 0.5 ppm stannous reagent dose plotted vs reaction time

The hexavalent chromium conversion reaction rate is fast. At the 1.0 ppm reagent dose rate over 90% of initial Cr(VI) levels can be converted into trivalent form within a 3 minute contact time. At the 0.5 ppm reagent dose rate approximately 88% of initial Cr(VI) converted into trivalent form during a 3 minute contact time. There was an insignificant effect on conversion reaction at both dosing levels (1.0 ppm, 0.5 ppm) when the contact time was increased to 15 minutes.

2. 1 SafeGuard™ H2O system performance under optimized operational conditions

For the duration of the trial period important process parameters, such as reagent generation efficiency, water flow, and reagent dosing were studied and optimized.

The highest reagent generation efficiency and reagent-contaminant reaction rate occurred with a stannous generation rate of 50-100 mg/min at given (3 l/min) treated water flow. The SafeGuard H2O system performance under optimal conditions is detailed in Figure 5.

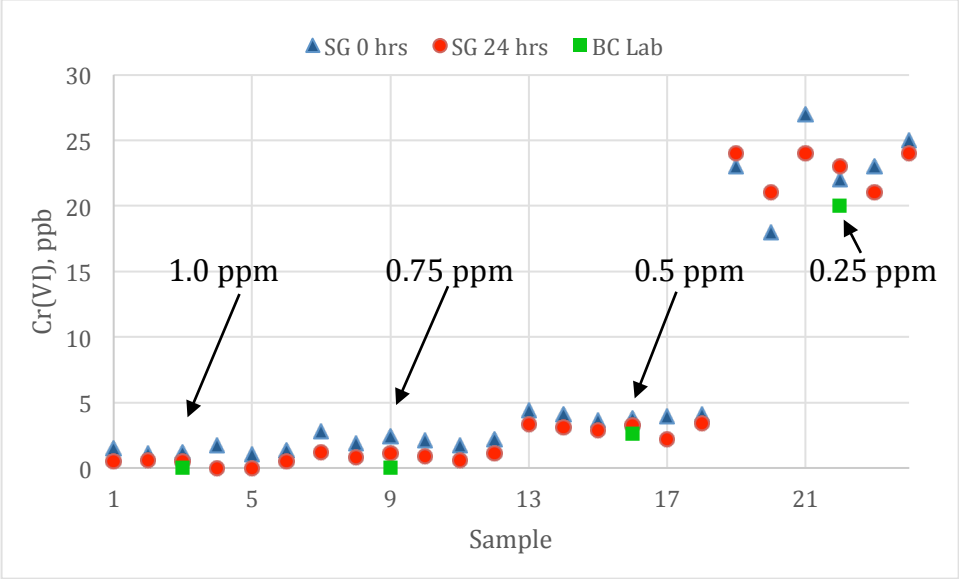

Figure 5- Residual Cr(VI) levels in treated raw water determined by SafeGuard™ Monitor and by EPA Method 218.6

At the 1.0 and 0.75 ppm reagent dose rates, the online SafeGuard Cr(VI) monitor detected trace levels of residual hexavalent chromium while outside lab results (BC Labs) were under the detection range. These low residual Cr(VI) contaminant levels indicate a high efficiency (over 90%) of the conversion process from Cr(VI) to the trivalent form.

High kinetics of Cr(VI) conversion reaction were confirmed in under five minutes from the treated water sample collection to the SafeGuard analyzer displaying results.

Decreasing the reagent dose rate down to 0.5 ppm resulted in a lower conversion efficiency, approximately 90%. At a stannous reagent dose of 0.25 ppm, data from the online SafeGuard analyzer and BC Labs support a conversion efficiency of less than 50 %.

Conclusion

Aqua Metrology Systems has supported the evaluation of $SnCl_2$ as a potential lower cost chemical reagent for treating Cr(VI) contamination through studies at remediation sites. AMS believes that certain characteristics of the traditional $SnCl_2$ reagent make it unsuitable for treating Cr(VI) in a consistent and predictable manner.

As a result, AMS designed the patent-pending SafeGuard H2O, an intelligent Cr(VI) treatment system that generates a stannous ion reagent in-situ via an electrolytic process and also features an online Cr(VI) monitoring analyzer.

The SafeGuard H2O demonstration unit installed at Los Banos Well #14 underwent a two-week demonstration (11-22 December 2017). The demonstration was a success; the SafeGuard H2O system consistently generated targeted stannous reagent levels (0.25-100 ppm) into the raw water stream.

The novel SafeGuard H2O system successfully demonstrated the ability to efficiently generate stannous reagent into contaminated well water source and to convert hexavalent chromium into trivalent form with high efficiency and stability.

The performance of the SafeGuard H2O system was monitored in real-time using the automated SafeGuard Chromium monitor, a feature that contributed to fast system set up and optimization. Analytical data from the online method and laboratory showed good agreement, further validating the ability of the SafeGuard H2O system to monitor the Cr(VI) remediation process in real-time.

The experimental results suggest a high probability for the scalability of the SafeGuard H2O system for point-of-supply systems and point-of-entry systems. Full-scale evaluation is required to further demonstrate the long-term system performance of SafeGuard H2O in field conditions.

Acknowledgements

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