

Capabilities of In-Situ Generated Stannous/Tin Oxide as a Germicidal Means for Produced Water Treatment

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ABSTRACT

The oil and gas industry faces significant environmental and regulatory challenges with produced water management. Traditional treatment methods often come with high costs and secondary waste issues. A technology (AMS's SafeGuard™ H₂O) generating a stannous/tin oxide (SnO₂) reagent in-situ has been developed. This novel technology provides a powerful germicidal solution to mitigate environmental impact and enhance the viability of produced water for discharge while paving the way for more sustainable practices. The outcomes of using the in-situ generator unit and its liquid form, SnO₂, as a germicidal agent in oil/gas-produced water samples of various matrices will be presented.

INTRODUCTION

The oil and gas industry generates vast quantities of produced water—often exceeding several barrels per barrel of oil extracted—containing a complex mix of hydrocarbons, heavy metals, salts, and microbial contaminants. Managing this wastewater is not only a logistical challenge but also a critical environmental and regulatory concern, as untreated or improperly handled produced water can lead to soil contamination, aquifer depletion, and ecological disruption. Current treatment methods, including mechanical separation, chemical oxidation, and biological processes, have demonstrated effectiveness but often come with high operational costs, energy demands, and secondary waste generation.

A newly developed advanced solution that generates a stannous reagent in situ, mitigates environmental impacts, and enhances the viability of produced water for discharge or reuse, ultimately fostering a more sustainable approach to resource management in the industry. This patented technology generates a stannous reagent on-site and on-demand through an electrolytic process, offering an effective reagent delivery method. The system's electrolytic process requires only two widely available consumables: a certified non-toxic tin precursor and electricity.

Due to the unstable, corrosive, and toxic nature of industrially produced stannous-based bulk reagents, the implementation of stannous species as a treatment reagent has been limited. However, now, with the ability to produce a non-toxic reagent in-situ, the limitations of bulk stannous are eliminated and the germicidal power of tin, in its oxidative state of SnO₂ can be fully explored.

A study was undertaken at a water research facility in College Station, Texas to evaluate the germicidal efficacy of the SnO₂ reagent on produced water. The evaluation showed the effectiveness of the SnO₂ reagent in biofilm degradation and preventative application capacities for produced water treatment, storage and reuse.

GENERATING STANNOUS ONSITE

Producing a controlled amount of stannous ions in-situ is accomplished through the process of electrolysis, wherein a current is passed through electrolytic cell (electrolyzer) containing a tin anode (Figure 1). Stannous ions are generated on demand as a result of the anodic dissolution of tin metal. Because electrogenerated tin possesses multiple oxidation states, specific parameters of electrolysis were developed and maintained to achieve a high stannous ion generation efficiency.

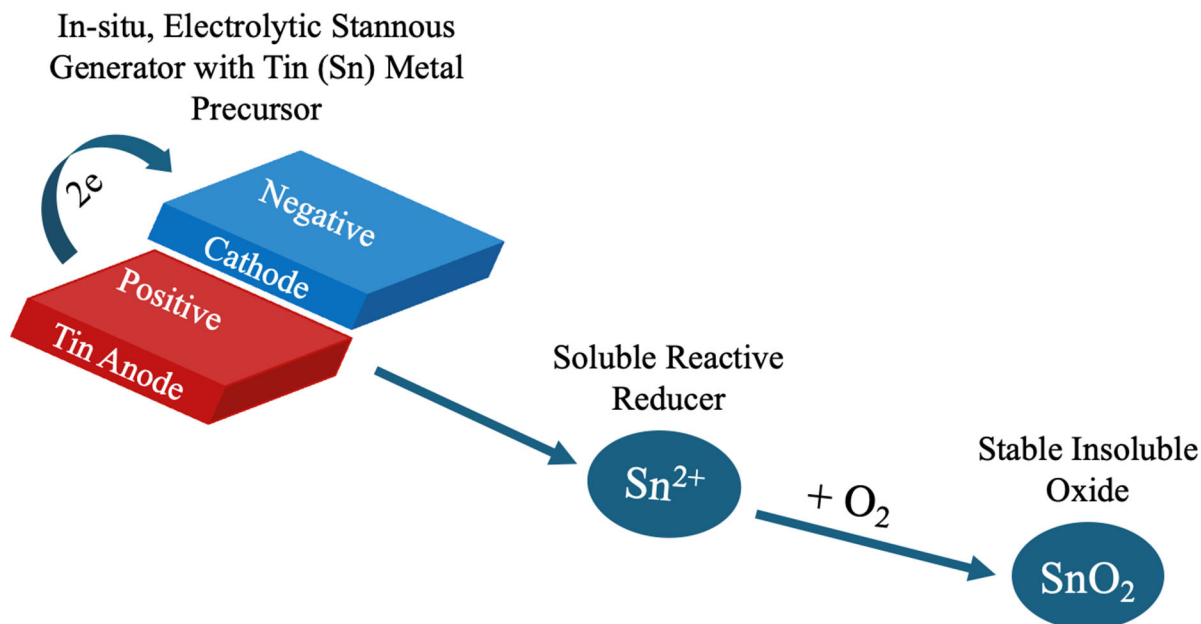
The quantification of electro-generated stannous ions that are produced can be understood through the well-studied laws of electrolysis, originally proposed by Michael Faraday in 1834 (Bhattacharyya, 2015). Faraday's laws of electrolysis (Equation 1) established the relationship between the charge passed through the electrolytic cell and the mass of anodic dissolution that occurs:

$$m = \left(\frac{Q}{F}\right) \left(\frac{M}{z}\right) \quad (1)$$

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

Figure 1:

Electrolytic Method to Generate SnO₂ Onsite Introduces Tin as Stannous Ions



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 a fresh and highly reactive stannous ion reagent can be easily adjusted in real time using the in-situ regeneration approach.

ADVANTAGES OF ELECTROLYTIC GENERATED REAGENT - Three of the most significant benefits of the in-situ electro-generated SnO₂ reagent treatment approach over traditional stannous reagents include:

1. Electro-generated stannous ions are highly 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 tin metal, which eliminates the possibility of wasted reagent and lost capital since additional costs are incurred when having to dispose of expired bulk stannous reagents. The rapidly degrading nature of bulk stannous reagents 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 a broad range of concentrations.
2. Electro-generated stannous ions are non-toxic in nature. While bulk stannous solutions are highly acidic, toxic and corrosive, a stannous ion reagent is produced in-situ using highly inert food grade tin metal. Unlike dangerous and corrosive bulk stannous 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 - tin and electricity.

ELECTROLYTIC IN-SITU STANNOUS GENERATION SYSTEM - The system generates and 'captures' the high oxidative state of SnO_2 , which can be used over an extended period or generated as needed.

Figure 2:

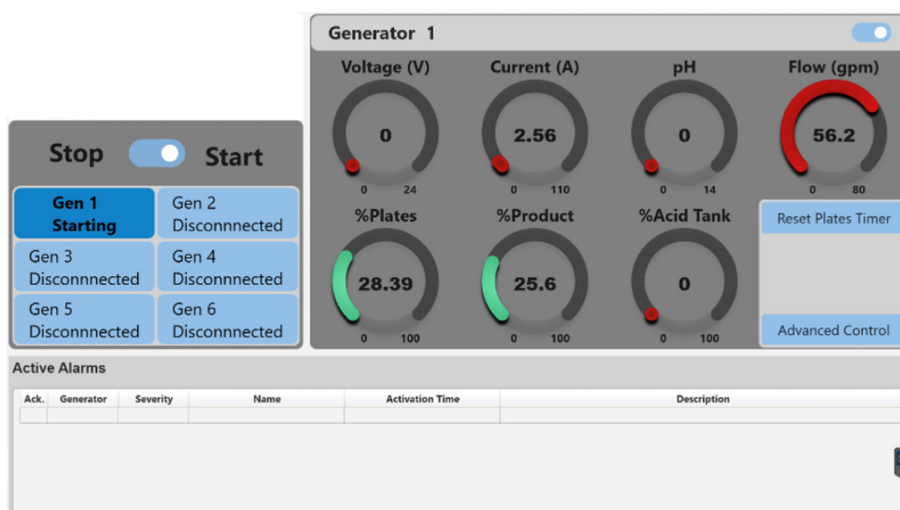
Dr. Vladimir Dozorstev with Proprietary SnO_2 Generation System and Tin Electrode



With the system's proprietary control (Figure 3), generation of the SnO_2 reagent can be easily adjusted in real-time. Additionally, the 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.

Figure 3:

Proprietary SnO₂ Generation System Control Panel (Running Mode Displayed)



EVALUATION STUDY

BACKGROUND - The germicidal power of tin in its oxidative state of SnO₂ is well documented (Cooney, 1989). Stannous dioxide as a germicidal agent arises primarily from its potential to reactivate oxygen species that damage bacterial cellular walls. Studies have demonstrated that SnO₂ in the form of nanoparticles can be incorporated into antimicrobial coatings, suggesting the reagent can have applications as a corrosion inhibitor in flowlines, tanks, and other such oil/gas-related lease assets.

A novel electrolytic reagent system generates and ‘captures’ the high oxidative state of SnO₂. This green chemistry solution was evaluated for its germicidal potential in oil/gas-produced water samples.

METHODS - Produced water samples, with varying water matrices, were obtained from the Permian Basin, Texas (Table 1). The evaluation followed QA/QC bacteriology protocols and used Bactiquant Mycometer and BTS Phenol Reg Bug Bottles during the kill study.

Table 1:*Water Quality of Produced Water Samples*

Water Quality Parameter	PW-A Sample Measurement	PW-B Sample Measurement
Alkalinity as CaCO ₃	3,012.0 ppm	2,541.0 ppm
COD	1,698.0 ppm	979.0 ppm
TOC	955.5 ppm	803.1 ppm
Ammonia	400.0 ppm	310.0 ppm
TDS	128,400 ppm	111,030 ppm
pH	6.6	6.8

RESULTS - The technology generated stannous on-site at a concentration of approximately 600 ppm. Using varying SnO₂ dose rates, the germicidal efficacy of the SnO₂ reagent was undertaken during a 30-day evaluation by dosing the two produced water samples (PW-A, PW-B) and performing 4-day, 14-day and 30-day kill study assays (Table 2). The onsite-generated SnO₂ reagent demonstrated a significant germicidal effect by reducing log-growth over the 30-day growth study. The %BQ reduction ranged from 98.26 to 99.93 and the kill rate remained consistently high for each %BQ reduction value during the study. Moreover, the SnO₂ reagent maintained its germicidal residual in the produced water samples utilized in this study. Through microbiological assessments, the effectiveness of the SnO₂ reagent in biofilm degradation and preventative application capacities for produced water treatment, storage and reuse was proven.

Table 2:*Kill Study Assays (4-day, 14-day and 30-day) of Onsite Generated SnO₂*

	Sample	SnO₂ Dosage (ppm)	Int. BQ	4-Day BQ	%BQ Reduction+Kill	14-Day BQ	%BQ Reduction+Kill	30-Day BQ	%BQ Reduction+Kill
6/8/24	PW-A	2	45356	56.38	99.87+High	61.34	99.86+High	60.3	99.86 + High
	PW-A	10	45356	50.55	99.89+High	53.65	99.91+High	50.11	99.88 + High
	PW-A	15	45356	45.36	99.9+High	50.1	99.87+High	50.09	99.87 + High
	PW-A	50	45356	210.3	99.54+High	107.4	99.76+High	90.01	99.80 + High
7/6/24	PW-B	2	29064	868.1	97.01+High	244.5	99.15+High	251	99.13 + High
	PW-B	5	29604	733.8	97.47+High	179.4	99.38+High	203.7	99.3 + High
	PW-B	10	29604	510.7	98.27+High	337	98.84+High	310.4	98.93 + High
	PW-B	2.5	29604	743.2	97.49+High	391	98.68+High	441.6	98.51 + High
	PW-B	3	29604	549.4	98.14+High	416.8	98.59+High	520.7	98.24 + High
	PW-B	3.5	29604	600.9	97.97+High	588.5	98.01+High	514	98.26 + High

CONCLUSION

By integrating the onsite-generated SnO₂ method and liquid form of the reagent into produced water management practices, the oil and gas industry can achieve a more sustainable, cost-effective, and scalable approach to water treatment. This innovative solution aligns with industry trends toward water reuse, reducing reliance on freshwater sources, and minimizing environmental liabilities associated with wastewater disposal. Additionally, the ability to generate a non-toxic reagent on-site enhances operational flexibility while reducing chemical handling risks, making this novel technology a transformative tool for the future of produced water treatment.

REFERENCES

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