Stannous & Tin Dioxide for Waterborne and Airborne Contaminant Removal

Transforming the Way We See Water
Agenda

• Introduction to Stannous and Tin Dioxide
• SafeGuard™ H2O In-situ Stannous Generator Applications
• SafeGuard™ H2O Applications of Tin Dioxide
Stannous & Tin Dioxide

A safe, non-toxic metal for drinking water treatment, industrial wastewater treatment and airborne contaminant removal.
Novel Method Introduces Tin as Stannous Ions

The Fate of Electro-Generated Stannous Reagent

In-situ, electrolytic Stannous generator with Tin metal precursor

Soluble reactive reducer

$\text{Sn}^{2+}$ + $\text{O}_2$ -> Stable insoluble absorbent

$\text{SnO}_2$
In-situ Stannous Generator SafeGuard™ H2O

- Automated (remote control options)
- Controlled reagent dose
- Compact, modular and scalable
- NSF 61 Pending
- Economical (tin and electricity)
- On-demand reagent generation
- Stop and run mode
The Power of Stannous & Tin Dioxide

Waterborne Contaminants:
- As
- Cr(VI)
- Pb/Cu
- Se
- Fe/Cu

Airborne Contaminants:
- H₂S/SO₂/NOX/CO

Industrial & Commercial Cooling Systems
- Anti Corrosion

Municipal/Residential
- Groundwater
- Anti Corrosion

Small Private Wells
- Process Effluent

Heavy Industry and Energy
- Process Effluent

Mineral Mining
- Leaching & Byproducts

Semi Conductor
- Process Effluent

Mineral
- Mining

Heavy Industry and Energy
- Flue & Process Gases

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Heavy Industry and Energy
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Applications for Stannous (Sn$^{2+}$)

SafeGuard™ H2O

- Biocide
- Cr(VI) reduction
- Corrosion inhibition: Pb, Cu, Fe
- Dissolved Hg removal and recovery
- Se(IV) reduction and recovery
Biocide: Drinking Water & Cooling Systems

• Stannous ion introduced into cooling water penetrates biofilm in affected areas causing degradation (removal) and supressing bio-corrosion
  – Inhibitor dose tightly controlled
• Stannous reagent residuals converted into Tin Dioxide precipitate on exposed metal zones and isolate them from exposure to oxidizers

SnO₂ → Sn²⁺ + O²⁻ + H₂O → SnO₂·H₂O + 2H⁺
## SafeGuard™ H2O Biocide: Drinking Water & Cooling Systems

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<tr>
<th>FEATURES</th>
<th>BENEFITS</th>
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<tbody>
<tr>
<td>Stannous generated in-situ, on demand</td>
<td>No bulk chemical deliveries, storage and handling</td>
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<tr>
<td>Small footprint, modular/scalable</td>
<td>Ideal for deployment at commercial and industrial sites</td>
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<td>Addresses both biological and electrochemical corrosion</td>
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<td>Tin and electricity are the only consumables</td>
<td>Non-toxic reagent (Tin), displaces problematic orthophosphates (supply chain security, downstream impacts on waste treatment plants and the environment)</td>
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<td>Avoids corrosion caused by treatment chemicals and oxidants (chlorine, chlorides, etc...)</td>
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<td>Low operating costs and maintenance</td>
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<tr>
<td>Dosing controlled automatically</td>
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<td>Remotely monitored</td>
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Cr(VI) Reduction Enhanced with SnO$_2$ Filter

Well → SafeGuard™ H2O Stannous Generator → Self-assembled Composite SnO$_2$/Media Filter → Effluent Cr (VI) <2ppb

$3\text{Sn}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 3\text{Sn}^{4+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
# SafeGuard™ H2O
## Cr(VI) Reduction Drinking Water

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<tr>
<td>Stannous generated in-situ, on demand</td>
<td>No bulk chemical deliveries, storage and handling</td>
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<tr>
<td>Skid-mounted, small footprint</td>
<td>Ideal for urban locations (point-of-supply/point-of-entry)</td>
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<td>Requires minimal civil works, reduces engineering overhead</td>
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<tr>
<td>Tin and electricity are the only consumables</td>
<td>Non-toxic precursor (Tin) and useful by-product (Tin Dioxide)</td>
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<tr>
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<td>Low operating costs and maintenance</td>
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<tr>
<td>Dosing controlled automatically</td>
<td>Operates unattended, reduces site supervision requirements</td>
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<tr>
<td>Low system inertia</td>
<td>Ideal for unattended non-continuous well operation</td>
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<tr>
<td>By-product (Tin Dioxide) can be reused</td>
<td>Reduces net operating costs, enables waste reuse</td>
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Corrosion Inhibition: Lead

- Stannous is injected into lead service lines serving residential zones and buildings, schools, day cares, etc...
- Stannous turns into suspended insoluble tin dioxide
  - Precipitates on internal surface of the corroding pipe to form a protective layer
  - Inhibits massive electrochemical corrosion of lead metal by corrosive agents (oxygen, chlorine, etc...)

City Water with SnO₂ supplied by SafeGuard™ H₂O
### SafeGuard™ H2O
Corrosion Inhibition: Lead in Drinking Water

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<tr>
<td>Small footprint</td>
<td>Ideal for localized deployment in urban risk zones (schools, day-care, residential areas and buildings)</td>
</tr>
<tr>
<td>Tin and electricity are the only consumables</td>
<td>Non-toxic reagent (Tin), displaces problematic orthophosphates (supply chain security, downstream impacts on waste treatment plants and the environment)</td>
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<td>Avoids corrosion caused by treatment chemicals and oxidants (chlorine, chlorides, etc...)</td>
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<td></td>
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<tr>
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<td>Remotely monitored</td>
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<td>Can respond immediately to increased risk of lead/copper corrosion caused by transient changes in water quality (see MetalGuard Lead Alert™)</td>
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Corrosion Inhibition: Cooling Systems

- Generator side stream comes from the pressurized water system
- SafeGuard H2O™ produces a predetermined amount of reagent which is discharged into intermediate holding tank
- Heavy duty, high pressure pump injects fresh reagent into the pressurized water system to maintain desirable reagent concentration
# SafeGuard™ H2O
## Corrosion Inhibition: Cooling Systems

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<td>No bulk chemical deliveries, storage and handling</td>
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<tr>
<td>Small footprint, modular/scalable/mobile</td>
<td>Ideal for localized deployment at commercial and industrial sites</td>
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<tr>
<td>Tin and electricity are the only consumables</td>
<td>Non-toxic reagent (Tin), displaces problematic orthophosphates (supply chain security, downstream impacts on waste treatment plants and the environment) Low operating costs and maintenance</td>
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<td>Dosing controlled automatically</td>
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Dissolved Mercury Recovery

Hg Contaminated Coal-ash Pond Water

Galvanostat/Controller

SafeGuard™ H2O Stannous Generator

Stannous

Contactor

Sn^{2+} + Hg^{2+} = Hg^{0} + Sn^{4+}

Hg^0 Trap

Hg Free Air

Hg^0 Stripper

Air Flow

Hg^0 Free Water

Galvanostat/Controller

H2O Stannous Generator

Stannous
Selenium Recovery

Selenite Contaminated Wastewater → Galvanostat/Controller → SafeGuard™ H2O Stannous Generator → Contactor

Contactor: $\text{Se}^{4-} + 2\text{Sn}^{2+} \rightarrow \text{Se}^0 + 2\text{Sn}^{4+}$

Treated Effluent → Elemental Selenium
# SafeGuard™ H2O

**Selenium & Mercury Recovery: Industrial Wastewater**

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</thead>
<tbody>
<tr>
<td>Stannous generated in-situ, on demand</td>
<td>No bulk chemical deliveries, storage and handling compared to physicochemical alternatives</td>
</tr>
<tr>
<td>Ease of operation and reliability</td>
<td>Operates under wide range of ambient conditions compared to biotreatment systems</td>
</tr>
<tr>
<td>Small footprint</td>
<td>Rapid to deploy and mobile</td>
</tr>
<tr>
<td>Tin and electricity are the only consumables</td>
<td>Low operating costs and maintenance compared to organosulfides and biotreatment</td>
</tr>
<tr>
<td>Recovery of elemental mercury and selenium</td>
<td>Eliminates toxic waste disposal costs associated with biotreatment and physicochemical processes</td>
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<tr>
<td></td>
<td>Valuable non-renewable resources (Selenium)</td>
</tr>
</tbody>
</table>
Applications for Tin Dioxide (SnO₂)

- Airborne metal removal: Hg, Cr, etc...
- Corrosion inhibition: Pb, Cu, Fe, etc...
- Dissolved metal removal: As, Cr, Pb, Hg, etc...
- Dissolved non-metal removal: hydrocarbons, phenol, organic dyes
- Gas desulfurization: SO₂, H₂S
Drinking Water Treatment

As, Hg, Cr(VI), Pb, removal for homes and wells (point-of-entry, point-of-supply)

Pb removal for homes (point-of-entry, point-of-use)
Arsenic ($\text{As}^{3+} / \text{As}^{5+}$) Removal

The “active mass” of the dynamic composite filter accumulates continuously as tin dioxide is deposited and this increases its capacity.
Arsenic Removal: Point-of-Supply (Wells)

- Non-toxic Tin Dioxide active material applied uniformly onto substrate without additional process steps
- Sorbent can be removed from substrate in controlled, automated manner which allows media regeneration and reuse
- SafeGuard™ H2O suitable for 1-600 gpm

Generator Power Consumption
- 20-100 gpm system: 0.2 – 1.0 kW
- 100-600 gpm system: 1.0 – 5.0 kW
Step 1: Composite Filter Formation

- **Fresh** in-situ, electro-generated stannous reagent concentrate added into clean sand filter media
- **Insoluble** Tin Dioxide absorbent formed by oxidizing Stannous by oxygen during air purge step
- **Stabilized** onto the sand granules Tin Dioxide serves as an active mass for contaminant removal
Step 2: Arsenic Remediation

- **Contaminated** water passed through series of freshly prepared composite filters to reduce Arsenite (As$^{3+}$) and Arsenate (As$^{5+}$) to <5 ppb
- **Polisher** media filter traps any Tin Dioxide particles and Arsenic traces that break through from the composite filter
Step 3: Composite Filter Regeneration

- **Contaminated** polisher and composite filters periodically back washed by treated water to remove loose Tin Dioxide layer with adsorbed Arsenic
  - If required, chelator solution can be used to remove adhesive fraction of the Tin Dioxide
- **Refreshed** filters reused by applying fresh Tin Dioxide to the composite filter (Step 1)
Backwash Water Reuse Through Residual Arsenic Monitoring

- **Backwash water** collected into sludge settling tank held to decant Tin Dioxide/Arsenic particulates to the bottom of the tank
- **Online** MetalGuard™ Analyzer continuously monitors clear water in upper part of the tank to ensure its high purity for reuse in media filter backwash
- **Backwash** frequency automatically adjusted to optimize sludge quality for landfill disposal
## Bench Scale Arsenic Removal Data
### Preliminary Results

<table>
<thead>
<tr>
<th>Arsenic Specie</th>
<th>Before Treatment (ppb)</th>
<th>After Treatment (ppb)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenite</td>
<td>50</td>
<td>6.1</td>
<td>88</td>
</tr>
<tr>
<td>Arsenate</td>
<td>20</td>
<td>1.1</td>
<td>95</td>
</tr>
<tr>
<td>Arsenate</td>
<td>2000</td>
<td>217</td>
<td>89</td>
</tr>
</tbody>
</table>
# SafeGuard™ H2O
## Arsenic Removal

<table>
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<tr>
<th>Feature</th>
<th>Benefit</th>
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<tbody>
<tr>
<td>In-situ, on-demand, active reagent generation</td>
<td>No toxic chemical, storage, handling</td>
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<td>No pH adjustment required</td>
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<tr>
<td></td>
<td>Non-toxic Tin Dioxide sorbent produced on demand</td>
</tr>
<tr>
<td></td>
<td>Non-toxic Tin Dioxide material applied uniformly onto substrate without additional process steps</td>
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<td>Sorbent can be removed from substrate in controlled, automated manner</td>
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<td>Low system inertia</td>
<td>Ideal for ‘stop-go’ and unattended wells</td>
</tr>
<tr>
<td>Small footprint, modular, skid mounted</td>
<td>Minimal civil works, fast to deploy, scalable to wells of any size, ideal for small sites in urban areas</td>
</tr>
<tr>
<td>Tin and electricity are the only consumables</td>
<td>Low capital, operating and maintenance cost</td>
</tr>
<tr>
<td>Dosing controlled automatically, remote monitoring optional</td>
<td>Operates unattended – ideal for remote, infrequently attended sites</td>
</tr>
<tr>
<td>Removes $\text{As}^{3+}$ and $\text{As}^{5+}$</td>
<td>Eliminates pre-oxidation step</td>
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Lead Corrosion Inhibition & Lead Removal

5 Mechanisms

A. Lead Service Line/Plumbing

B. \( \text{Pb}^{2+} + \text{SnO}_2 \rightarrow \text{SnO}_2 \text{Pb} \)

C. City Water with \( \text{Sn}^{2+} \)

Contaminated Water

Active Mass

Lead/Tin Free

\[ \text{Pb}^0 \rightarrow 2e \]
Mechanism 1: Lead Corrosion Inhibition

Stannous turns into suspended insoluble Tin Dioxide which precipitates on internal surface of the corroding pipe to form a protective layer that inhibits massive electrochemical corrosion of lead metal by corrosive agents (oxygen, chlorine etc).
Mechanism 2: Lead Corrosion Retention

Lead corrosion occurs in areas where the lead surface is exposed.

Corrosive agents have access to the surface causing oxidation of the lead metal.

Due to the high affinity of dissolved lead species to suspended Stannic Dioxide particles, a significant amount of dissolved Lead is retained by suspended Tin colloids converting highly toxic dissolved Lead species into easy to particulates that can be easily filtered.
Mechanism 3: Dynamic Lead Filtration

Household water supplies containing dissolved and insoluble Lead as well as Tin Dioxide particles pass through a series of filters.

The filtration system is set to retain the particles of different size (several micron to sub micron).

The filters efficiently retain Tin Dioxide colloidal particles of different sizes and, thus, acquire a ‘self assembled’ layer of ‘colloidal sludge’ on their surface. This sludge serves as an ‘active mass” which efficiently removes remaining dissolved Lead species.
Lead Removal: Point-of-Entry/Point-of-Use Filter

Normal Filter Operation

- Pb/Sn & SnO₂ free
- H₂O

Time (Days)

Saturated Filter

Key
- Pb
- Pb/SnO₂
- SnO₂
### SafeGuard™ H2O Lead Treatment System

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Protects</td>
<td>The system removes/inhibits biofilm formation and significantly inhibits dissolved and particulate lead corrosion</td>
</tr>
<tr>
<td>Retains</td>
<td>The system effectively addresses both dissolved and total Lead species retention through stannous reagent water treatment</td>
</tr>
<tr>
<td>Point-of-Use Filters</td>
<td>The “active mass” of the dynamic composite filter increases continuously as Tin Dioxide is deposited and this increases its capacity to retain dissolved Lead</td>
</tr>
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Industrial Wastewater Treatment, Airborne Contaminant Removal & Resource Recovery

Coal Plants, Refining, and Process Industries
Coal-Fired Power Plants – Multiple Applications

- Tin Dioxide adsorption media for stack gas desulfurization and mercury removal
- Tin Dioxide composite filter remediates multiple metal contaminants from plant wastewater

![Diagram showing processes in a coal-fired power plant including Fly Ash, ESP or Fabric Filter, Fabric Filter, FGD, Sluiced Fly Ash, Sluiced Hg Control Wastes, FGD Wastewater, Ash Pond, and River (or POTW).]
Flue Gas Desulfurization, Media Regeneration & Sulfur Recovery

SnO₂ + H₂ + H₂S → SnS + 2H₂O – Hydrogen Sulfide removal
SnS + SO₂ → SnO₂ + S₂ – media regeneration with Sulfur Dioxide
SO₂ + H₂ + H₂S → S₂ + 2H₂O – combined Claus process

H₂S/SO₂ → Sulfur for reuse
SafeGuard™ H2O: Cooling System Corrosion Inhibition

• Tin dioxide self-assembled composite filter remediates metal ion corrosion process by-products (Cu, Fe, Ni, etc...) prior to discharge.
Stannous & Tin Dioxide

A safe, non-toxic metal for drinking water treatment, industrial wastewater treatment and airborne contaminant removal.
# The Power of Stannous & Tin Dioxide

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<td>Airborne Contaminants</td>
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**Anti Corrosion**

**Flue & Process Gases**
Contact Us

info@aquametrologysystems.com
www.aquametrologysystems.com