Steam Generator Maintenance Measures as Part of an Integrated Management in PWRs

S. Weiss, A. Drexler, J. Fandrich (AREVA / IBOC-G)
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Introduction
Introduction

Steam generator condition is a key factor for
- plant performance and high plant availability,
- possible life time extension and
- plant safety.

Major safety function of SGs is acting as a barrier between the radioactive primary side and the non-radioactive secondary side of PWRs.

Main reason for SG tube failure is the accumulation of deposits contributing to formation of local aggressive conditions.

Keep Steam Generators as clean as possible!
Steam Generator Cleanliness Assessment

Water Chemistry Data (e.g. iron ingress, hide-out)

No measures required

Steam Generator Assessment

Inspection Results (e.g. visual, sludge mapping)

Measures required

Thermal Performance (e.g. heat transfer)

Steam Generator Cleaning

Preventive Chemical Cleaning

Curative Chemical Cleaning

Mechanical Cleaning (e.g. Tube sheet and/or inner bundle lancing, upper bundle flushing)

Improvement of Water Chemistry

Continuous Steam Generator Surveillance
Steam Generator Cleanliness Assessment

Water Chemistry Data (e.g. iron ingress, hide-out)

Inspection Results (e.g. visual, sludge mapping)

Thermal Performance (e.g. heat transfer)

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Steam Generator Cleaning

Preventive Chemical Cleaning

Curative Chemical Cleaning

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Improvement of Water Chemistry

Continuous Steam Generator Surveillance
AREVA Chemical Cleaning Processes: Customized Chemical Cleaning (C³)

![Graph showing the relationship between accumulated deposits and cycles for different cleaning processes. The graph includes a legend with the following information:
- **DMT**: 250 to 1000 kg per SG
- **DART LT inhibited**: 500 to 2000 kg per SG
- **DART HT**: 500 to 2000 kg per SG
- **HTCC**: > 2000 kg per SG
- **AFCC**: > 2000 kg per SG
- **EPRI SGOG**: > 2000 kg per SG

The graph indicates preventive and curative cleaning strategies and shows the progression of accumulated deposits over cycles for each process.
DMT Process

Preventive Chemical Cleaning Process
DMT Chemical Cleaning Process

- The DMT process is the only SG chemical cleaning process which does use oxalic acid instead of EDTA.

- Basic chemistry process:

\[ \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{Fe}[\text{Fe(C}_2\text{O}_4)_3]\ + \text{FeC}_2\text{O}_4 \downarrow + 4\text{H}_2\text{O} \]

  Soluble = removed by SG draining

- Oxalic acid has the following advantages:
  - High iron dissolution capacity
  - Low corrosion rates on carbon steel due to self-inhibition effect
  - No use of hydrazine (N$_2$H$_4$) or other chemicals, which are carcinogenic, mutagenic or toxic for reproduction (CMR)
  - No release of ammonia (NH$_3$) to environment
Corrosion of the base material is present as competitive reaction to magnetite dissolution in any chemical cleaning process.

Oxalic acid (DMT process)

- **Fe + H₂C₂O₄ → FeC₂O₄↓ + H₂↑**
- A highly insoluble product is generated, forming an adherent closely protective Fe(II)-oxalate layer on the base metal surface.

EDTA

- **Fe + H₂[(NH₄)₂EDTA] → Fe(NH₄)₂EDTA + H₂↑**
- A soluble product is built, hence corrosion is continuous until EDTA is used up.

The self-inhibition effect of oxalic acid on carbon steel is an important advantage of the DMT process and ensures extremely low corrosion rates of carbon steel.
Test coupons with dark olive protective layer of Iron(II)-oxalate.

Homogeneous layer, tightly adherent.

**self-inhibiting DMT process:**
Corrosion stops after few microns; due to formation of tightly adherent protective layer

- Protective layer is formed in initial phase.
- After initial phase corrosion is ~ 10-15 nm/h
DMT Chemical Cleaning Process
Cleaning Efficiency Calculations

Total removed iron:

\[ m_{Fe} = 0.5 \times \rho_{OA} \times (M_{OA})^{-1} \times V_{SG} \times M_{Fe} \]

Iron originate from corrosion:

\[ m_{corr} = l_{corr} \times A_{cs} \times d_{cs} \]

Iron originate from Magnetite:

\[ m_{magn} = m_{Fe} - (l_{corr} \times A_{cs} \times d_{cs}) \]

- \( l_{corr} \) (oxalic acid) \( \equiv 2 \ \mu m \)
- \( l_{corr} \) (EDTA) \( \equiv 20 \ \mu m \)
- \( \rho_{OA} = \rho_{EDTA} = 10 \ g \times l^{-1} \)
- \( A_{cs} = 420 \ m^2 \)
- \( V_{SG} = 90 \ m^3 \)
DMT Chemical Cleaning Process
Steam generator scale porosity

- High scale porosity is considered to be beneficial due to improvement of boiling efficiency and enhanced heat transfer

- Laboratory test with original SG hard sludge scale flakes:
  - Increase of scale porosity
    - overall + 224% increase
      (porosity before DMT 14% to porosity after DMT 47%)
    - outer layer area: + 129% increase
      (porosity before DMT 28% to porosity after DMT 65%)
  - Decrease of Vicker’s hardness
    - overall - 26% decrease
      (Vickers hardness before DMT 450 to after DMT 320 (HV 0.1))
DMT Chemical Cleaning Process
Steam generator scale porosity

Before DMT
- Total porosity: 14%
- Porosity of outer layer: 28%

After DMT
- Total porosity: 47%
- Porosity of outer layer: 65%
DMT Process

Field Experiences & Waste Treatment
DMT Chemical Cleaning Process
Field Experiences

- DMT process were applied with great success in
  - two 3-loop PWRs in USA and one 4-loop PWR in France
  - additional applications in France are scheduled for 2012

- Excellent sludge removal capacity and extreme low base material corrosion were confirmed.

- Neither selective corrosion nor corrosion phenomena in heat affected zone (i.e. welding) were observed.

<table>
<thead>
<tr>
<th></th>
<th>DMT Fe Step (kg Fe₃O₄)</th>
<th>DMT Conversion step (kg Fe₃O₄)</th>
<th>Rinsing (kg Fe₃O₄)</th>
<th>Lancing (kg Fe₃O₄)</th>
<th>Total (kg Fe₃O₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant A&lt;sup&gt;a&lt;/sup&gt;</td>
<td>752.8</td>
<td>165.3</td>
<td>3.6</td>
<td>76.6</td>
<td>998.3</td>
</tr>
<tr>
<td>Plant B&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3167</td>
<td></td>
<td>---</td>
<td>415</td>
<td>3582</td>
</tr>
</tbody>
</table>

<sup>a</sup> single DMT process, 3-loop PWR
<sup>b</sup> double DMT process, 4-loop PWR
Calculations were confirmed by plant results (Plant B).

- **Average corrosion:** $7 \cdot 10^{-6}$ m (determined by weighing of coupons)
- **Iron amount originated by corrosion** was ~23 kg versus ~550 kg of removed iron originated from magnetite.

![Bar chart showing iron amounts](chart.png)
DMT Chemical Cleaning Process
Field Experiences: Oxide mapping

- Significant reduction of deposit load could be achieved over the entire high of the steam generators.

- A TSP clogging assessment prior and after the DMT application showed that the opening ratio returned to 3 year back condition.

DMT Chemical Cleaning Process
Waste Treatment

- The amount of generated waste by chemical cleaning processes is principally of concern of plant operators.

- Especially in case of maintenance chemical cleaning process, which can be applied periodically.

- DMT associated waste treatment process, based on Fenton reaction, answers easily to this issue.

- This process produces three waste forms for secondary disposal
  - Filters which are dry active waste
  - Re-formed solids which are also handled as dry active waste
  - Ion exchange resin for water cleanup (if applied)

- All water from DMT chemistry can be returned to the plant for either re-use or for discharge at the outfall.
DMT Chemical Cleaning Process
Field Experience: Waste Treatment

► Application with single DMT (2009) removed:
  ◆ ~980 kg of magnetite
  ◆ ~15 kg of copper
  ◆ ~165 kg of deposits during sludge lancing
  ◆ ~1160 kg total of magnetite and Cu inventory removed from 3 SGs

► Water used for DMT process has been treated on-site with AREVA patented process treatment:
  ◆ Only solid particles and ion exchange resin left for disposal by plant.
  ◆ Waste treatment was performed within 7 days after the DMT application.
  ◆ All water could be re-used or discharged.

► Overall waste: 3.7 m³ of dry solid waste
Conclusion
Conclusion

- Due to its key functions a SG cleanliness management program is mandatory to ensure
  - high plant performance regarding efficiency as well as
  - component integrity.

- AREVA is providing a tool box of measures to improve SG cleanliness status.

- AREVA’s SG chemical cleaning DMT process
  - is based on the proven CORD® decontamination process.
  - has a field proven high Fe removal capacity.
  - has extremely low carbon steel corrosion (self-inhibiting effect) and no impact on stainless steels and Ni base materials.
  - provides an easy on-site liquid waste treatment (Only clean water and solid iron oxides remain).
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