

THE USE OF ADVANCED SCALE CONDITIONING AGENTS FOR MAINTENANCE OF THE SECONDARY SIDE OF NUCLEAR PLANT STEAM GENERATORS

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Summary

Maintaining the secondary side of steam generators within a pressurized water reactor (PWR) free of deposited corrosion products and corrosion-inducing contaminants is key to ensuring their long-term operation. New cleaning processes have become available to aid nuclear plant personnel in optimizing secondary side maintenance strategies. These strategies include both maintaining nuclear steam generators corrosion free while maintaining full power operation.

Introduction

There are concerns among nuclear industry personnel that even small quantities of magnetite-based (Fe_3O_4) deposits, especially those containing small amounts of copper or lead, increase the potential for accelerated tube degradation of steam generators within the secondary side of a pressurized water reactor nuclear power plant. These deposits may adversely affect the operational and thermal hydraulic performance of the plant.

There are various mechanical and chemical cleaning methods available to remove steam generator deposits. One of these methods, steam generator chemical cleaning (SGCC), involves the introduction of chemicals to dissolve deposits while the plant is offline or in the process of a scheduled shutdown. In the early 1980s, the Electric Power Research Institute (EPRI) and the Steam Generator Owner's Group (SGOG) developed one commonly used series of SGCC solvents and associated application processes. These solvents successfully dissolve magnetite and copper-based deposits. Despite the established effectiveness of SGCC, many utilities are reluctant to employ such processes due to a high cost, complicated equipment mobilization, large chemical quantity requirements and significant waste generation. Steam generator chemical cleaning is best suited for use at plants with significant deposit accumulation (an estimated 1,400 kgs per steam generator). For plants with less deposit accumulation per generator, the use of SGCC is often not considered cost-effective. Because industry personnel recognize the benefits of maintaining the cleanliness of replacement steam generators (RSG), or those that have been recently restored to baseline conditions by SGCC, the need for intermediate type cleaning processes now exists.

To address this need, Westinghouse Electric Company, Dominion Engineering, Inc., and Hokkaido Electric initiated research and development work in 2000 which resulted in the development of Advanced Scale Conditioning Agent (ASCA) technology. This technology has now been successfully used at various nuclear power plants to aid the Utilities in maintaining and improving their steam generator programs for the long term.

What is Advanced Scale Conditioning Agent (ASCA) Technology?

ASCAs were developed as a new chemical technology to be used to promote some dissolution of the overall deposit inventory and mineral species from the secondary side deposit matrix. Prior to the development testing, acceptance criteria and requirements for several classes of ASCAs were established. Four types of ASCAs are available to address specific deposit management objectives. They include full bundle maintenance cleaning for removal of scale deposits, top-of-tubesheet treatment used to soften deposits for better mechanical removal, a copper/lead removal ASCA to remove these known corrosion inducing contaminants from deposits, and a high pH form of the maintenance ASCA to be used for improving steam pressure in plants where steam pressure loss due to dense deposits has occurred.

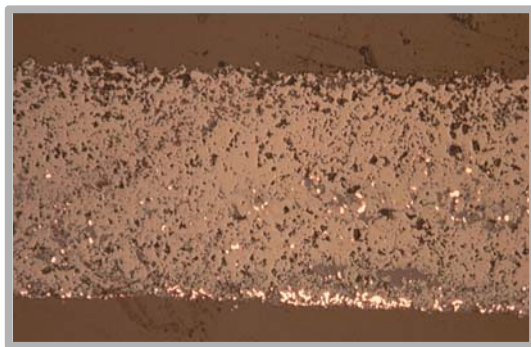
Maintenance Full Bundle ASCA

The deposit removing maintenance cleaning ASCA treatment is a chelant-based solution containing amines, a reducing agent and a surfactant. The dissolution capacity of this class of ASCAs was set at a minimum of one-to-three cycles of corrosion-product-transport for a plant with average to better-than-average feedwater chemistry control. To allow for repeated application of the process over the life of the plant, carbon steel corrosion limits were established.

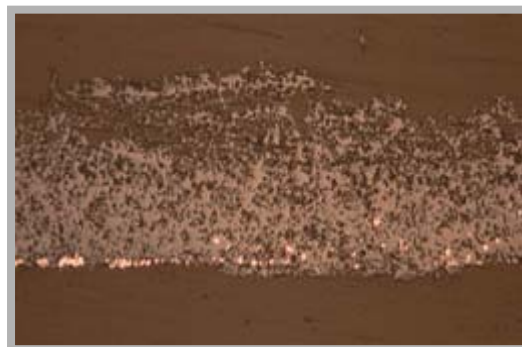
Second generation, or replacement steam generators, contain Alloy 600 or Alloy 690 thermally treated (TT) tubing, and stainless steel, quatrefoil-designed tube support-plates to increase corrosion resistance. The best strategy for the long-term operation of these units is maintaining their cleanliness on a regular basis. A recent phenomenon observed in operating steam generators is dense tube scale formation. This environment yields very low heat-transfer margin, which raises concerns over short-term thermal performance.

The specific goals of the ASCA process are to: (1) reduce the small deposit inventory that had accumulated since start of operation, (2) increase the porosity of existing tube scale as an enhancement to heat transfer, and (3) prevent further deposit accumulation to minimize corrosion and maximize thermal performance. To preclude the need for chemical cleaning, Westinghouse recommends the use of a preventative maintenance approach.

Figure 1 illustrates the structure of the tube scale before and after maintenance cleaning ASCA qualification test. The change in cross section of a deposit structure (increased porosity) is evident after a 24-hour treatment at 76 °C.



Before ASCA Soak



After ASCA Soak: Reduced magnetite deposits and increased porosity

Figure 1: Full Bundle Maintenance Cleaning ASCA Effect on Deposit Structure

Top of the Tubesheet Cleaning ASCA

The top-of-tubesheet ASCA treatment is a slightly stronger, lower pH chelant-based solution as compared to the maintenance cleaning process. The acceptance criteria established for the TTS process, when used in combination with CECIL, was 90% removal of the top-of-tubesheet, hard sludge collars.

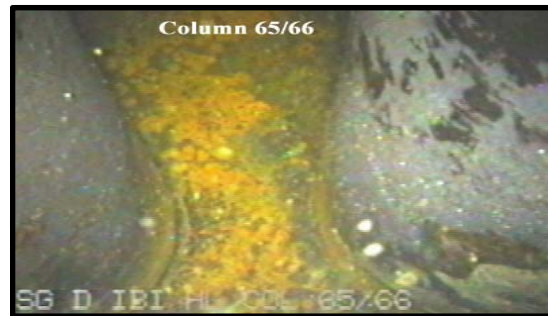
Top-of-tubesheet deposits in original steam generators and plants with replacement steam generators typically contain zinc and/or magnesium aluminosilicates and other binding agent materials. These elements contribute to the dense nature of the deposits and render them resistant to removal by tubesheet sludge lancing. Top of tubesheet Advanced Scale Conditioning Agent applications weaken the structural integrity of TTS deposits rendering them more susceptible to removal by CECIL. Advanced Scale Conditioning Agents contain a sufficient amount of chelant to partially dissolve the deposits and enhance the penetration of amines into the deposit matrix.

The goal of the TTS cleaning is to soften or weaken the TTS hard-scale collars by dissolution. Figures 2 and 3 show the before and after pictures of a plant's TTS deposits when

exposed to a 24 hour ASCA soak at 170 °F followed by CECIL (Figure 2) and followed Ultrasonic Energy Cleaning (Figure 3).



Before ASCA/CECIL



After ASCA/CECIL

Figure 2: Top of the Tubesheet Cleaning ASCA/CECIL Effect on Deposit Structure



Before ASCA/UEC



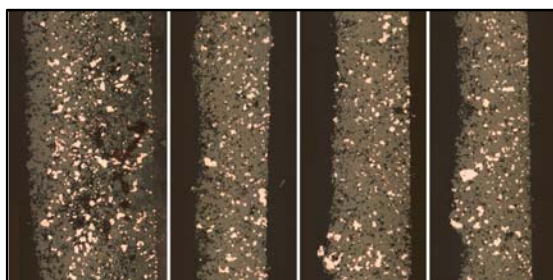
After ASCA/UEC

Figure 3: Top of the Tubesheet Cleaning ASCA/UEC effect on Deposit Structure

Copper and Lead Removal ASCA

The copper and lead removal ASCA treatment consists of a lower concentrated chelant solution applied at higher pH with a mild oxidant. To render this ASCA essentially non-corrosive, pH limits were established. The acceptance criteria established for the copper/lead ASCA was the dissolution of a minimum of 90% of the copper and lead from tube-scale deposits, including removal from the tube to tube-scale interface.

Many older plants contain steam generators with significant residual copper (>0.5 weight percent) and lead inventories (> 300 to 500 ppm). The ASCA formulation can reduce or eliminate copper and lead inventory that might lead to tube degradation in the future. The specific acceptance criteria established for the ASCA demonstrates that a one-time application could reduce copper concentrations in the tube scale from an excess of 3% to less than 0.5%. Figure 4 shows the before and after results of the ASCA treatment. Initial copper content (shown as white particles in the before photos) was reduced to below 0.2% with no measurable carbon steel corrosion. Two applications reduced lead concentrations from 300 ppm to less than detectable levels. In the field experience successive (at least two) applications will remove detectable copper from the SG deposits.



Before ASCA Soak

After ASCA Soak

Figure 4: Removal of Copper and Lead from Steam Generator Deposits

Thermal Hydraulic Recovery and Maintenance ASCA

The steam pressure returning ASCA is similar to the maintenance ASCA chemistry and can be used for maintenance, however, it is performed at a significantly higher pH promoting a slower chemical reaction. This slower reaction rate creates more porosity in existing deposits than does the lower pH ASCA thus aiding the improvement in steam generator heat transfer. At the Tomari plants this type of full bundle ASCA soak has resulted in the return up to 18 psi (1.2 Bar) of steam pressure.

High pH ASCA has also been found to be effective in the recovery from blocked quatrefoils in newer design steam generators. Blocked quatrefoils in the upper support plate areas of newer design steam generators, (Figure 5), has led to power reductions due to steam generator water level oscillations in some plants. In others the condition is developing and requires correction. At Tomari, quatrefoil blockage was improved by as much as 2-4 fuel cycles of operation. Also, during the Tomari applications, waste volume was significantly reduced by injecting the copper removal chemicals into the spent iron solvent waste.

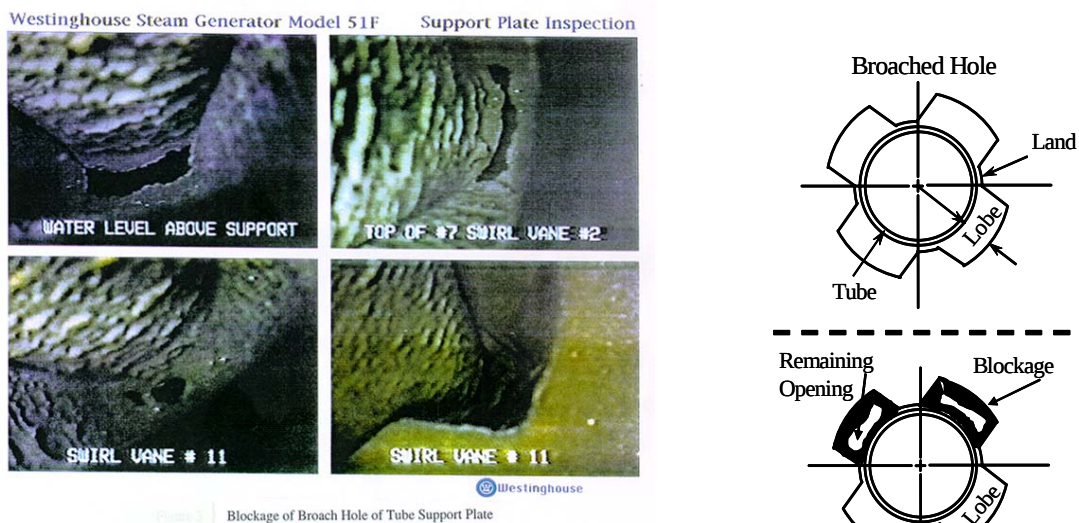


Figure 5: Blocked quatrefoils from a US Plant Steam Generator

In general, ASCA applications provide several benefits: short duration (typically 24 hours), effective deposit removal (90 to 227 kgs per steam generator per application), and low carbon steel corrosion. Application temperature typically ranges from ambient to 76 °C. Applying the process multiple times over the life of the plant is achievable with less than 15 micron (~0.5 mil) carbon and low alloy steel corrosion expected per application. Chelant replenishment can also be employed to increase deposit removal, if desired.

Summary

ASCA solutions have been developed for use in nuclear plant steam generators to address three deposit management objectives: (1) full-bundle applications for general preventative maintenance (corrosion and thermal performance); (2) top-of-tubesheet applications, where porosity of the deposits prevents effective use of conventional SCA solutions, and (3) targeted copper and lead removal. Advanced Scale Conditioning Agents provide effective cleaning in a short period at relatively low temperatures, reduce the amount of waste produced and yield low carbon steel corrosion during the cleaning process.

Experience

The conference presentation will discuss ASCA use and the major field experience acquired in the last several years in the United States and in Japan. Hokkaido Electric, Dominion Engineering, Inc. and Westinghouse cosponsored the development of ASCAs for use in the Nuclear Utility industry, and all three are active in field use programs. Westinghouse owns the worldwide rights for ASCA implementation except in Japan where MHI and NEL have been granted licenses to apply ASCAs. Dominion Engineering Inc., owns the ASCA patents and performs the laboratory qualification testing associated with the ASCA programs, and Hokkaido Electric are joint patent holders for ASCAs and have been implementing their use at the Tomari plants for cleaning and thermal hydraulic performance enhancements. The specific experience discussed in the presentation will include:

1. Full Bundle Maintenance ASCAs at Vogtle Units 2 and 2 and Wolf Creek (USA)
2. Top of the Tubesheet ASCAs with CECIL at Wolf Creek and UEC at Vogtle Units 1 and 2 (USA)
3. Thermal Hydraulic Recovery and Maintenance ASCAs at the Hokkaido Electric Tomari Units 1 and 2 (Japan)

The technical results of these field applications will be discussed during the presentation.

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