Integrated Management Program for CANDU® Steam Generator Cleanliness

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ABSTRACT

The status of steam generators (SG) is a key factor for plant performance, high plant availability, possible life time extension and important to NPP safety. The major safety function of SG is well-known as being a barrier between the radioactive primary side and the non-radioactive secondary side. Any degradation mechanism, which impairs this barrier function, is a significant safety concern.

The main reason for steam generator tube failure is known to be the accumulation of deposits contributing to formation of locally aggressive conditions. Furthermore, deposits on the primary as well as secondary side of SG tubes reduce the heat transfer performance. An SG cleanliness management program based on optimized water chemistry and mechanical and chemical cleaning processes is, therefore, mandatory to ensure high plant performance regarding efficiency as well as component integrity.

AREVA has developed an integrated management program for SG cleanliness. This program consists in principle of a closed cycle process with the following steps:

A Assessment of the current SG condition based on water chemistry data, inspection results and heat transfer data.

B Identification of measures based on assessment results and adjusted to plant operator's needs and requirements to improve the current status or even counteract on identified serious issues

C Implementation of identified improvements or countermeasures

The measures identified in step B include, on the one hand, possible changes in the water chemistry (including additives) and material concept. These changes aim to minimize unfavorable conditions to reduce the effort for later remedial measures. On the other hand, primary or secondary side mechanical or chemical cleaning measures may be recommended. Due to the interdisciplinary and unitary nature of the program, a harmonization between all involved sector and specialists is required. Therefore, it is especially important to minimize the interfaces among the participating parties.

The current paper presents the complete unitary and field-proved management program ranging from SG assessment, water chemistry improvements to primary side (e.g. mechanical cleaning by SIVABLAST) and secondary side SG cleaning (e.g. using AREVA's customized chemical cleaning (C^3) concept).

1. ASSESSMENT OF THE CURRENT STEAM GENERATOR CONDITION

1.1 Introduction

Operators of nuclear power plants pay attention on safe, reliable and efficient plant operation. As outlined above the status of the steam generators of PWRs and CANDU® reactors is the key issue and leads to an optimization in terms of life time and thermal performance by applying a systematic cleanliness program. It becomes even more interest with respect to lifetime extension program.

Especially on the secondary side of steam generator the accumulation of deposits contributing to formation of locally aggressive conditions is known as the main reason for SG tube failure. These risks have their origin not in the steam generators, but in the steam-water cycle. Therefore in case of determination and elimination of the cause for high SG deposit load not only the steam generator itself but also the water chemistry within the whole secondary circuit has to be assessed and evaluated.

The water chemistry applied within the steam-water cycle has to ensure that all fluids should have no influence, through corrosion processes on the construction materials [1]. Or in a more detailed form, the main objectives of the steam water cycle chemistry can be stated as follows:

- Minimize the metal release rates of the structural materials.
- Minimize the probability of selective or localized forms of corrosion.
- Minimize deposition of corrosion products on heat transfer surfaces.
- Avoid the formation of aggressive media, particularly local aggressive environments under deposits.

The formation of deposits on primary side of steam generator tubes (and also on the secondary side surface) reduces the heat transfer and deteriorates the plant efficiency.

1.2 Steam generator assessment

A SG cleanliness management program based on optimized water chemistry and mechanical and chemical cleaning processes is mandatory to ensure high plant performance regarding efficiency as well as component integrity. In order to establish such a cleanliness program it is important to define as exact as possible the current status of the steam generators. AREVA follows a holistic approach considering all aspects influencing steam generator status, which can be sorted as follows:

- Plant operating data
  - Chemistry parameters (normal operation, start-up, out of spec events)
  - Hide-out measurements whenever possible
  - Hide-out return chemistry
- Thermal performance data
  - Fouling measurements
  - Calculation of heat transfer performance

- Outage activity results
  - Visual inspections, e.g. videos and endoscopy
  - Analysis of tube sheet lancing results
  - Deposit inventory and distribution
  - Consistency of the deposits

Beside the typical inspection methods AREVA developed a deposits mapping technology based on eddy-current testing which allows a detailed analysis of the distribution and can also provide information about broached-hole opening ratios.

In a first step of the steam generator assessment appropriate measures which improve the current status or counteract on identified relevant issues are identified. These measures may be focus not only reactions on existing conditions (e.g. mechanical and/or chemical cleanings), but also proactive measures. These proactive measures can include improvements of water chemistry and also changing materials used in the water steam cycle. The principle of such an assessment is shown in Figure 1.

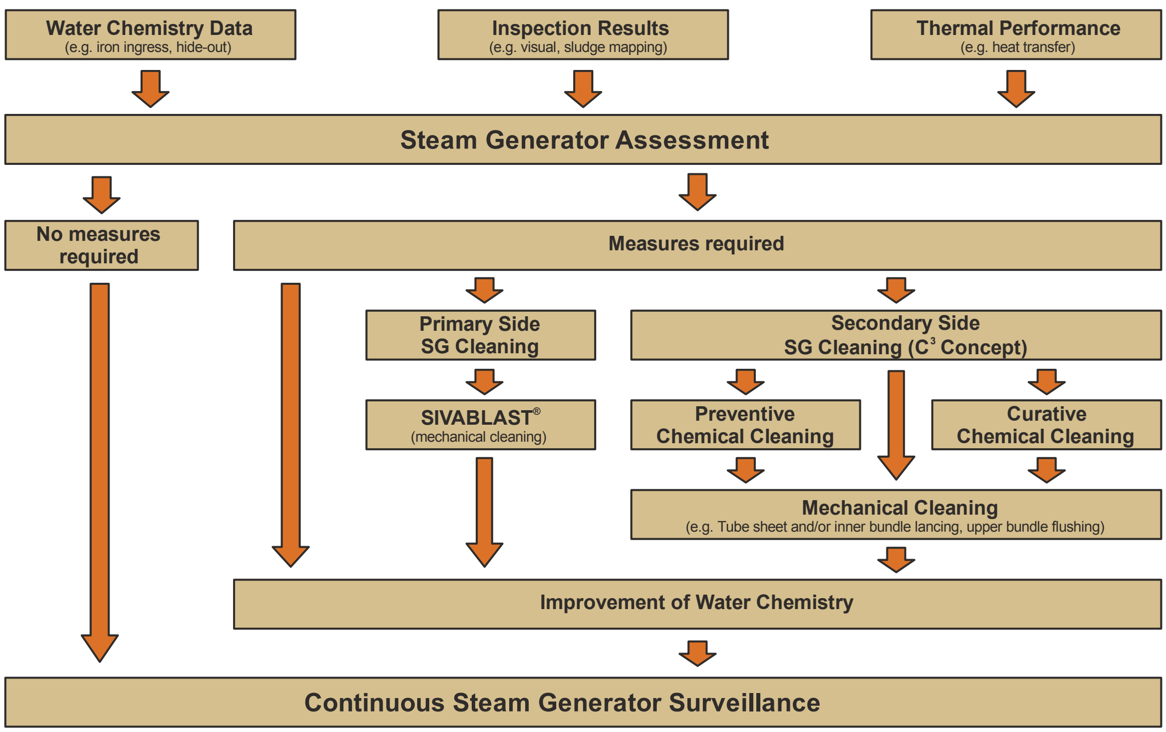

Figure 1. AREVA approach of steam generator assessment

The cleanliness management program is in principle a closed cycle process that first assesses the current SG situation and the long term trend. Application of steam generator assessment

AREVA's approach of a holistic view on all parameter influencing the steam generator status is performed by application of AREVA's Fouling Index Tool Box. It combines AREVA's international expertise with operator's plant performance information and uses an extensive range of input data. AREVA's Fouling Index Tool Box is a proven tool for German KWU-designed power plant operating with High-AVT steam-water cycle chemistry treatment. [2], [3], [4].

Currently the tool box has been successfully applied and validated to a variety of different SG model, BoP-design and water chemistry treatments [5].

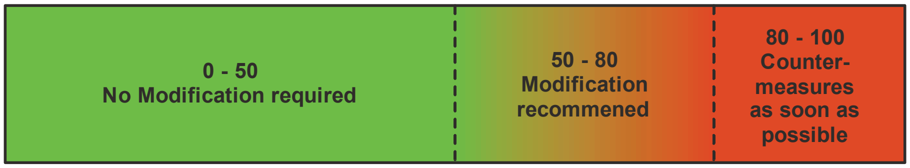

Figure 2. Range of AREVA's Fouling Index [5]

2. WATER CHEMISTRY MEASURES

2.1 Basics

The corrosion product ingress into the steam generator depends on the corrosion rate along all the water-steam cycle and during all plant operation conditions, i.e. power operation, shut-down condition (especially outages) and start-up transients.

The basic requirements to achieve minimization of the corrosion product generation are ensuring

- a high overall pH along the whole circuit for suppression of general corrosion and
- a high local pH at the liquid film of two-phase flow areas (HPT outlet, cross under lines, MSRs) for suppression of flow accelerated corrosion(FAC).

To fulfill the first requirement achieving a high overall pH within the whole secondary circuit a volatile alkalizing agent should be applied ensuring a good distribution along the steam-water cycle. But the second requirement of a high local pH in the liquid film of two-phase flow system needs a low volatile or a high amount of a volatile alkalizing agent.

The general corrosion depends on the pH(T) at operation temperature, at each location of the cycle. It has been shown that at 250°C a pH(25°C) of approximately 10 is required for minimization of corrosion [6]. In order to achieve a high pH various amines (e.g. ammonia, morpholine, ethanolamine) are applied which have different influence on pH(T) due to their dissociation constants. Additionally they will distribute along the cycle according to their different volatilities (measured by their distribution coefficients). The pH(T) at each system section is therefore a function of these two temperature-dependent parameters. The target is, that the pH(T) at all BOP systems should be as high as possible for effective suppression of general corrosion. A suitable criterion is to strive for $pH(T) - pH(T)_{neutral} > 1.0$ in feedwater.

Regarding the flow accelerated corrosion tests were performed at 180°C, at which the highest FAC rates are commonly observed [1]. The FAC rate decreases rapidly by several orders of magnitude when the measured pH(25°C) is 9.45 to 9.55 which correspondence to a pH(T) of 6.6 to 6.7. The same fundamental pH dependency was measured for a large number of materials and a wide variety of application conditions [7], [8], [9], [10]. Consequently the target is pH(T) > 6.6 in the wet-steam water phase for effective FAC suppression.

The achievement of these criterions can be evaluated and confirmed by chemical calculation using AREVA's CHEMBAL code.

2.2 Calculation of pH(T) and amine distribution using AREVA's CHEMBAL

The amine distribution depends of a complex relationship of plant-specific interrelated variables and operation conditions. To define the optimum pH control strategy for each individual case AREVA has been developed computer code CHEMBAL (Chemistry Balance). This code is able to perform detailed mass balance calculations for substances dissolved in the operation medium including especially volatile amines, enabling

- Determination of decomposition rate of hydrazine and ammonia generation rate.
- Distribution of N_2H_4, NH_3 and amines (e.g. morpholine, ETA, others) along the cycle.
- pH calculation at diverse points of the cycle, as a function of temperature.
- Calculation of specific conductivity at 25°C due to conditioning agents along the cycle.

Beside the cycle design and operation data (flow rates, temperatures, SG recirculation rate, etc.) and dosing amounts, a group of selectable variables and plant condition relevant parameters must be also entered to fit with the operation conditions subject to analysis.

One result of the CHEMBAL calculation is given in **Fehler! Verweisquelle konnte nicht gefunden werden.**. This calculation was run for a specific plant having copper-free BOP systems, high wet-steam temperature and high ammonia losses. Due to the high ammonia losses the pH(25°C) in feedwater are below 9.3 even in case of a hydrazine concentration of about 100 µg/kg. The CHEMBAL code was applied considering three different scenarios.

Case 1: Additional ammonia dosing to reach pH(25°C) = 9.98 in feedwater.

Case 2: ETA dosing to reach a pH(191°C) = 6.7 in the water phase of wet-steam.

Case 3: Additional ammonia dosing to reach pH(25°C) = 9.98 in feedwater and additional ETA dosing to reach a pH(191°C) = 6.7 in the water phase of the wet-steam

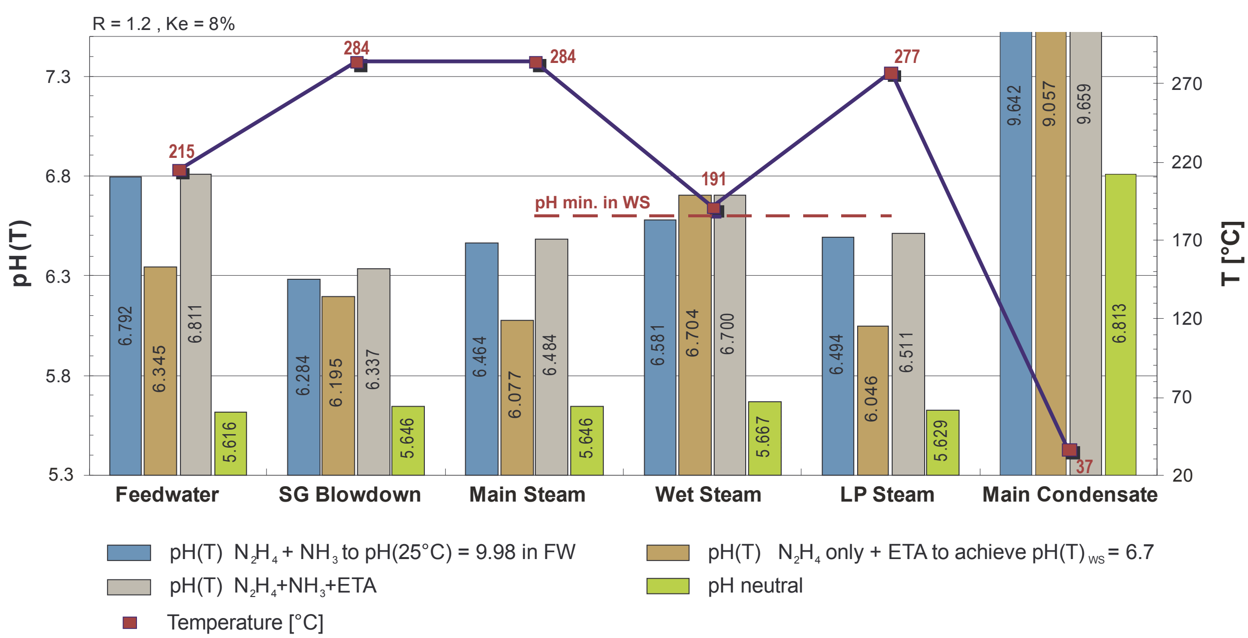

Figure 3. Calculated pH(T) in steam-water cycle systems (100 µg/kg hydrazine in feedwater and additional ammonia and/or ETA dosing)

The additional ammonia dosing (case 1) provides the necessary pH to minimize overall general corrosion ($pH(T) - pH(T)_{neutral} = 1.18$ for feedwater). Also an acceptable, although not optimum, protection in wet-steam areas is achievable ($pH(T)_{wet\text{-}steam} = 6.58$), but the required ammonia amount would be too large. In case 2 (ETA dosing instead of ammonia) the criterion regarding FAC is fulfilled ($pH(T)_{wet\text{-}steam} = 6.7$), but the overall pH(T) at all points of the steam-water cycle is lower than in the Case 1 and not satisfactory ($pH(T) - pH(T)_{neutral} = 0.73$ for feedwater). Only in case of ammonia and ethanolamine dosing, i.e. a high volatile and a lower volatile amine both requirements are fulfilled. The pH(T) in wet-steam area is 6.7 and $pH(T) - pH(T)_{neutral} = 1.19$ for feedwater.

This example clearly indicates the necessity of considering all plant specific aspects influencing the pH in the steam-water cycle, like the ammonia losses due to condenser exhaust.

2.3 Application of film-forming amine to improve corrosion behavior

Complementarily to an adequate pH strategy, an effective corresponding improvement can be introduced consisting on the application of film-forming amines in the secondary side as a very effective measure to counteract corrosion. The use of film-forming amines (FFA) has become very popular in the fossil power plant sector, showing a decrease of corrosion product generation by improving the surface conditions.

An adherent hydrophobic, temperature-resistant film is built acting as a shield that limits the access of water and hydrated species to the metal or metal oxide surface. This barrier lowers the corrosion rate by inhibiting the mass transfer between surface and solution. The hydrocarbon chain imparts a hydro-phobic character while the amine group bounds to the metal (Figure 4).

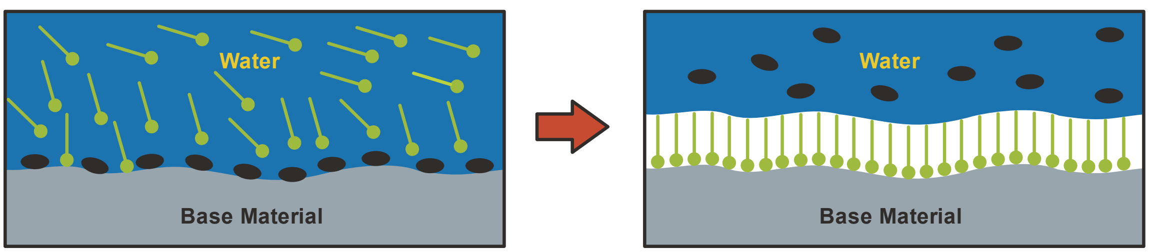

Figure 4. Principle of mobilization of adsorbed / adherent colloidal deposits (e.g. iron-oxides) and ionic impurities (e.g. chloride)

This preventative water chemistry measure is described in detail elsewhere [12]. AREVA performed successful the non-continuous FFA dosing in the whole secondary side of two PWRs during power operation with significant reduction of corrosion product generation and transport into the steam generator. A patent application is pending.

3. DEPOSIT REMOVAL MEASURES

3.1 Primary side measures

The feeder pipes of the fuel channel of CANDU Reactors are made of carbon steel. They are affected by wall thinning during operation, which causes magnetite deposition on the inner surface of the steam generator tubes. These magnetite depositions lead to change of the hydrodynamic conditions in the primary heat transport system. This can affect the reactor header inlet (RHI) temperature and could lead to a general decrease of the RHI pressure linked with a reduction of heat transfer efficiency. An example is given in Figure 5 which shows the evolution of the fouling factor of a CANDU reactor due to magnetite deposition on the inner side of steam generator tubes.

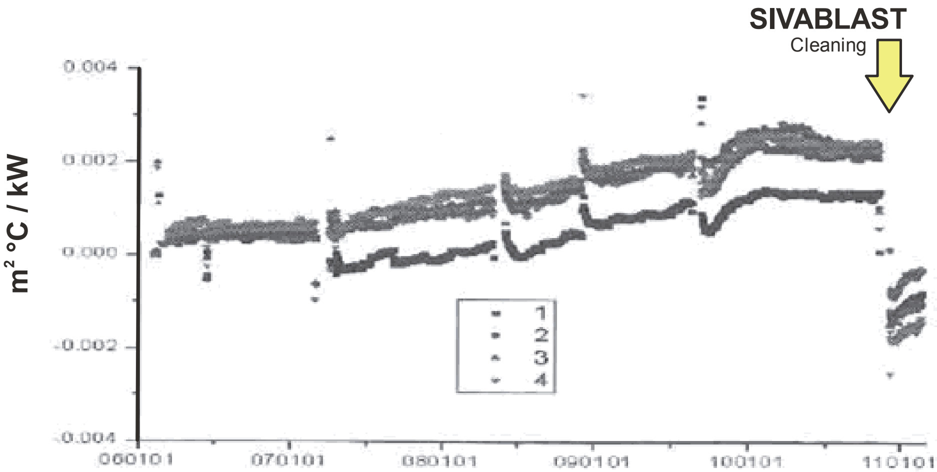

Figure 5. Evolution of fouling factor of a CANDU plant (from 2006 to 2011) due to magnetite deposition on the inner side of SG tubes [13]

Figure 5 shows also the result of the primary side cleaning as a countermeasure. Regarding the primary side cleaning of steam generators it has to be taken into account that the contamination of the magnetite is of major importance. The generated waste will be highly radioactive which is difficult to handle and store. Accordingly the generated waste volume is directly affecting the price. Furthermore not only the volume but also whether the generated waste is liquid or solid affects drastically the cost. Due to these facts AREVA developed in the mid nineties a regenerative mechanical cleaning process (SIVABLAST) that effectively removes the magnetite from the inner tube surface without negatively affecting the tube material.

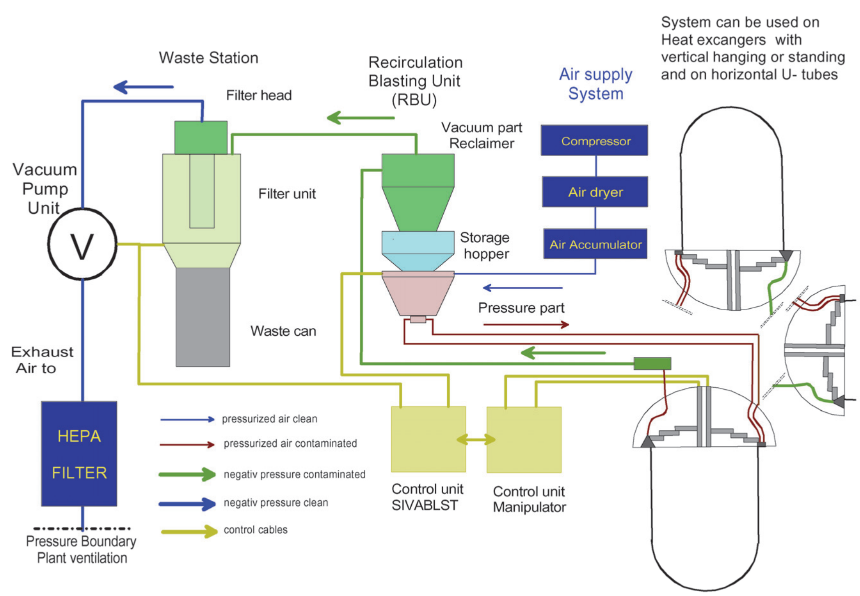

Figure 6. Outline of the SIVABLAST mechanical cleaning system

The advantage of this process in terms of waste generation is that the pure magnetite can be collected in waste drums hence the generated waste volume is the lowest possible. During the latest application in Wolsong Unit 2A only 9 drums with a total volume of 253 liter were used by removing more than 2200 kg magnetite from the steam generators [13]. A part of AREVA's SIVABLAST system is the so called "suction header", a patented device that allows a higher flow rate of the cleaning material in the tubes and enhances efficiency drastically.

The SIVABLAST technology has been successfully applied to all types of heat exchangers with straight tubes, horizontal, upright and hanging U-bend tubes with different materials including brass, carbon steel and typical SG materials like Inconel 600 and Incoloy 800.

The positive effect of this cleaning measure on the plant performance can be taken from the decrease in fouling factor as shown in Figure 5 but also reactor header inlet temperature and pressure showed significant improvement as shown in Figure 7 from the latest application at Wolsong 2.

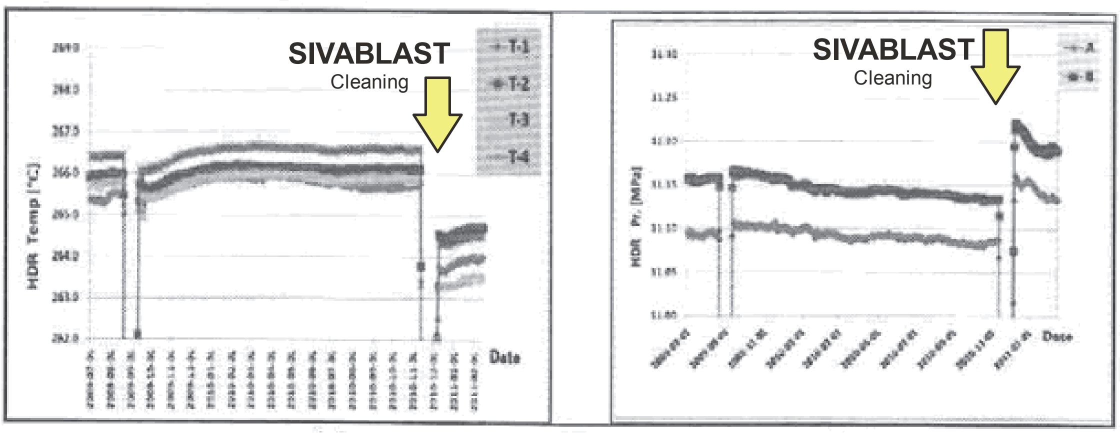

Figure 7. Evolution of reactor header inlet temperature (°C, left side) and RHI pressure (MPa, right side) [13]

In every case when SIVABLAST has been applied for the removal of magnetite deposits from the inner side of SG tubes, significant and measurable benefits have been observed. While the results vary from application to application, here are some typical observations:

- Thermal Performance: The removal of deposits invariably leads to a significant improvement in thermal performance for the SG. The end result is an observed reduction in reactor inlet header temperature (RIHT), ranging up to 4.5°C
- Flow Increase: The removal of the deposits clears a major constriction for the primary heat transport system, resulting in improved core flow in the range up 6% depending on evaluation method.
- SG Tube Inspection Quality: Magnetite deposits present a major problem for SG in-service inspection (ISI) techniques. Removal of the deposits results in improved inspecttion signal quality, duration of testing and prolonged probe life.
- Dose Rate Reduction: The removal of deposits from the SG tubes have resulted in significant reductions in the general gamma dose rate in working areas around the SGs. Localized decon factors (DF) of up to 4.6 have been observed.

3.2 Secondary side measures

Based on the steam generator assessment (Figure 1) the most suitable countermeasure is elaborated, if required at all. As an option a chemical cleaning of the steam generator might be recommended as a suitable countermeasure. Since each plant and each steam generator has its own history and particular condition it is obvious that the applied cleaning scenario should take these aspects into considerations as well as application constraints like outage schedule critical path etc. Therefore AREVA has developed the Customized Chemical cleaning Concept C^3 concept (see Figure 8). This concept comprises a variety of chemical cleaning technologies which allow tailoring the chemical cleaning exactly to the plants needs.

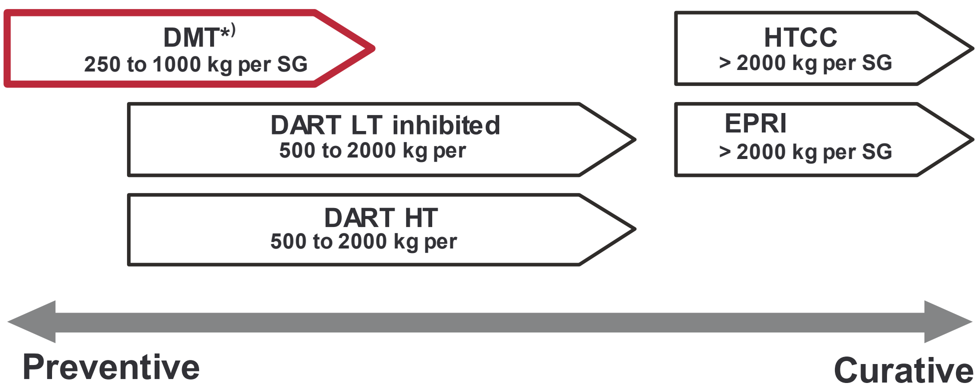

Figure 8. AREVA's customized chemical cleaning (C^3) concept for SG cleaning

Part of the AREVA C^3 concept is the proprietary DMT (Deposit Minimization Treatment) process. The DMT process utilizes an alternative cleaning agent, namely oxalic acid, in the SG chemical cleaning business, which increases the cleaning efficiency compared to the commonly used EDTA chemistry. Oxalic acid is well known and proven due to its use within the CORD® decontamination process. Besides the dissolution of the magnetite the corrosion of the base material is present as competitive reaction in any way.

In the case of applying DMT process a highly insoluble product is generated, which forms an adherent closely protective iron(II)-oxalate layer on the base metal surface and consequently prevents further corrosion.

$$Fe + H_2C_2O_4 \rightarrow FeC_2O_4 \downarrow + H_2 \uparrow$$

This intrinsic feature of the self-inhibition effect on carbon steel is an important advantage of the DMT process and ensures extremely low corrosion rates of carbon steel. The protective iron(II)-oxalate layer impedes further corrosion by steric hindrance. The layer formation within the initial phase of the chemical cleaning can be seen in Figure 9. After protection the corrosion rate is about 10 – 15 nm/h. The corrosion itself is stopped after a few µm.

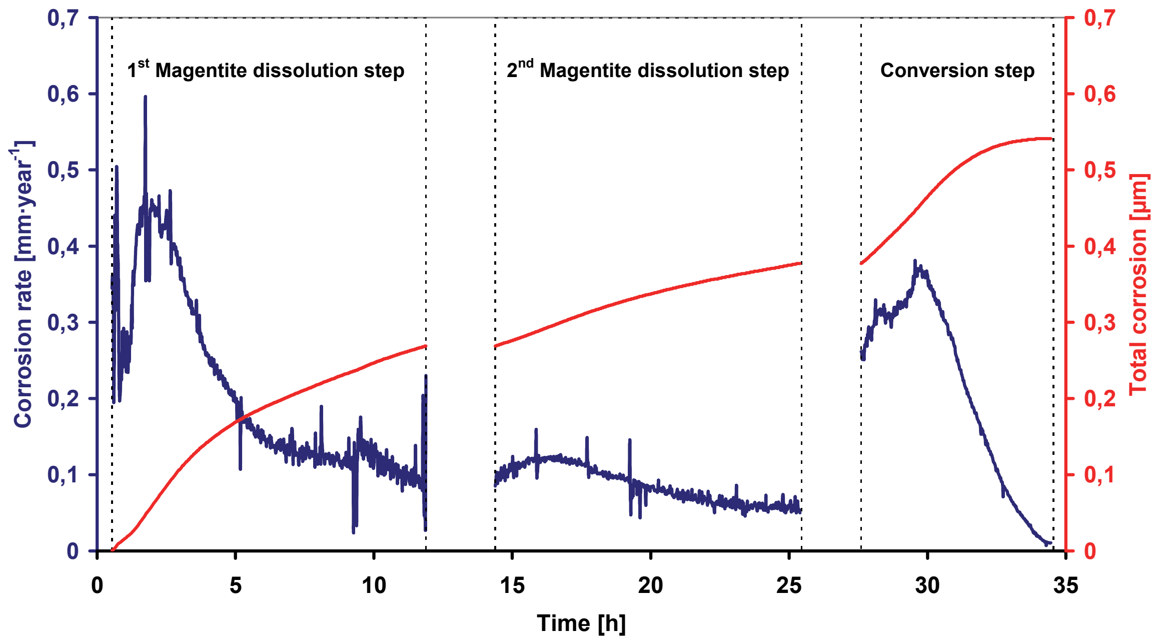

Figure 9. DMT self-inhibition effect

The DMT process was applied with excellent results in two 3-loop PWRs in the USA and three 4-loop PWR in France, confirming the excellent sludge removal capacity (Table 1) and extremely low base material corrosion. Neither selective corrosion (e.g. heat affected zone or welding) nor local corrosion phenomena were observed.

Table 1. Removed magnetite deposits of DMT field application

	DMT [kg Fe_3O_4]	Lancing [kg Fe_3O_4]	Total [kg Fe_3O_4]
Plant A	930	76	1007
Plant B	995	165	1160
Plant C	3332	415	3747
Plant D	3345	1112	4457
Plant E	2252	113	2365

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

pre DMT post DMT

Figure 10. Visual inspection results prior and after application of AREVA's DMT process

AREVA's SG maintenance cleaning process DMT

- is based on oxalic acid chemistry, which provides several advantages like high efficiency, low corrosion and abolishment of hydrazine or other CMR chemicals.
- has a field proven high magnetite removal capacity.
- has a field proven extremely low carbon steel corrosion (self-inhibiting effect) and no impact on stainless steel and nickel base alloys.
- provides an easy on-site liquid waste treatment (only clean water and solid iron oxides remain).

4. CONCLUSION

As outlined above the status of the steam generators of PWRs and CANDU® reactors is the key issue and leads to an optimization in terms of life time and thermal performance by applying a systematic cleanliness program. The major safety function of SGs is to act as a barrier between the radioactive primary side and the non-radioactive secondary side. Any degradation mechanism, which impairs this barrier function, is a significant safety concern.

Especially on the secondary side of steam generator the accumulation of deposits contributing to formation of locally aggressive conditions is known as the main reason for SG tube failure. These risks have their origin not in the steam generators, but in the steam-water cycle. Therefore in case of determination and elimination of the cause for high SG deposit load not only the steam generator itself but also the water chemistry within the whole secondary circuit has to be assessed and evaluated. Furthermore deposits on primary as well as secondary side of SG tubes reduce the heat transfer performance.

A SG cleanliness management program is therefore mandatory to ensure high plant performance regarding efficiency as well as component integrity. Such a cleanliness management program is in principle a closed cycle process that first assesses the current SG situation. In the subsequent steps appropriate measures which improve the current status or counteract on identified serious issues are identified, defined and applied. These measures include possible changes in the water chemistry and materials concept to minimize unfavourable conditions in order to reduce the effort for later remedial measures.

AREVA's integrated management program for CANDU steam generator cleanliness, follows a holistic, field-proved methodology considering all aspects influencing steam generator status.

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