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An Innovative Strategy For Secondary Side System Lay-up Using Film-Forming Amines

Dr. Ute Ramminger[1], Jörg Fandrich[1] and Dr. Andreas Drexler[1]

[1]AREVA NP GmbH, Erlangen, Germany

ABSTRACT

The major safety function of steam generators (SG) in pressurized reactors is well known as acting as a barrier between the radioactive primary side and the non-radioactive secondary side. The main reason for SG tube failure is known to be the accumulation of deposits contributing to formation of local aggressive conditions. Consequently the SG has to be kept as clean as possible and the corrosion product transport into the SG has to be minimized. In order to reach this target, plant operators are making worldwide huge efforts to protect plant systems against corrosion during standstill and outages. Especially in case of large component replacements campaigns like steam generator or fuel channel replacements which are linked to prolonged outages lay-up strategies become important.

The use of surface active agents like 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. The adherent non wettable film built by FFA acts 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 hydrophobic character while the amine group bounds to the metal.

Advantages of the FFA application for lay-up:

- Significant reduction of lay-up efforts
- Long-term stability of the protective film even in aggressive environmental conditions
- No influence on existing oxide layers
- No negative influence on plant operation and performance
- No environmental hazards of the waste water after system lay-up

Nevertheless application of film-forming amines are applied in fossil fired power plants, the requirement of nuclear power reactors are more ambitious. This paper deals with a possible lay-up application scenario in pressurized heavy water reactors. The proposed lay-up strategy will consider AREVA's experience gathered with FFA non-continuous dosing in the whole secondary side of two PWRs during power operation with the target to reduce corrosion product transport into the steam generator.

1. INTRODCUTION

World wide a number of Nuclear Power Plants are in operation with steam-water cycles based on a mixed metallurgy concept and / or a non optimal Balance-of-Plant (BoP) design. Together with limitations of the applied water chemistry treatment, these conditions can enforce the enrichment of impurities. This results in the formation of an aggressive environment that finally causes corrosion of the structural materials of the water-steam cycle. The transport of corrosion products and impurities together with hardening substances (mainly silicate) is a high risk of hard sludge formation on the top of tube sheet (TTS) area of the steam generators. This process can result in several degradation phenomena, like Denting and Outer-Diameter Stress Corrosion Cracking on affected tubes. Therefore, one of the major goals of secondary side chemistry treatment is the minimization of corrosion product formation and transport into the steam generators. A pH increase to minimize the formation of corrosion products of the steam-water cycle is sometimes not feasible due to the existing material concept.

Besides efforts to optimize the pH control strategy, the corrosion product generation can be further decreased using surface active agents like film-forming amines. The molecular film on the surface affects the corrosion susceptibility of the metal or metal oxide by either altering the anodic (oxidative) or the cathodic (reductive) reactions that are involved in corrosion processes. As a positive side effect the mobilization of existing deposits has been observed. This paper deals with the application of film-forming amines as complementary conditioning agents in the steam-water cycle of Nuclear Power Plants (NPP) with Pressurized Water Reactors (PWRs). The decision for complementing the existing secondary side water-chemistry treatment with a controlled and time limited application of film-forming amines was part of a project, which has been developed by AREVA NP GmbH and the operator of a NPP of western design to improve the conditions of steam generators. It covers the AREVA NP GmbH stepwise approach of the qualification process and the results of the application of a selected film-forming amine.

2. CHARACTERISTICS OF FILM-FORMING AMINES

Even small quantities of film-forming amines (FFA) affect the structure and hydrodynamic cavitation characteristics of the two phase flows, as well as heat transfer and mass transfer from / to the inner surfaces of the water-steam cycle. The adherent non wettable film acts 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 to and from the surface. The film reduces the rate of oxides dissolution and re-precipitation because every particle is coated and the mass transfer is inhibited due to the inner surfaces of water-steam cycle components.

The strategy of AREVA NP GmbH is to improve the existing secondary side water chemistry by the application of film-forming amines.

A possible application of FFAs seems very attractive due to the following properties:

- Formation of an adherent hydrophobic film, resistant to elevated temperatures with the amine group bond to the metal or metal-oxide.
- Decrease of the corrosion rate by inhibiting mass transfer between phase boundaries.

Even adsorbed or adhered colloidal iron-oxide deposits and ionic impurities on the surfaces can be mobilized to a variable extent. This effect has been clearly observed in field applications. FFAs are protecting the whole secondary cycle

3. FFA SELECTION CRITERIA

Considering the selection criteria of a film-forming amine or a similar chemical group of them, an intensive research was carried out by AREVA NP GmbH to get an overview of the state of the art of FFA applications.

According to this review the following requirements should be fulfilled:

- Applicable as a complement to the existing steam-water cycle chemistry treatment
- No thermal decomposition products, which may lead to side effects during normal chemistry operation
- Compatible to environment
- Prevention of impurity adsorption
- Minimization of corrosion product ingress into the SGs
- Easy to apply (dosing technology, analytical supervision)
- Exclusively pure product with well-known chemical properties and no formulation
- Easily mixable with water (solubility)

The selected FFA should also have a sufficient volatility to ensure its efficiency in all parts of the water-steam cycle, i.e. in the liquid and steam flow areas as well as the wet-steam areas.

The experimental determination of K_d (distribution coefficient) of film-forming amines normally causes many problems. For this reason AREVA NP GmbH performed theoretical calculations with the result of sufficient fit with data, that have been published (EPRI, KWU). [1], [2]

In Figure 1 the Distribution coefficients (right) and dissociation constants (left) of different amines and FFAs are shown as a function of the temperature. Considering the K_d values of the FFA it has to be taken into account that at lower temperatures the values show a higher uncertainty caused by changes of the physical properties of the solution due to the beginning aggregate formation and the solid state of the FFAs.

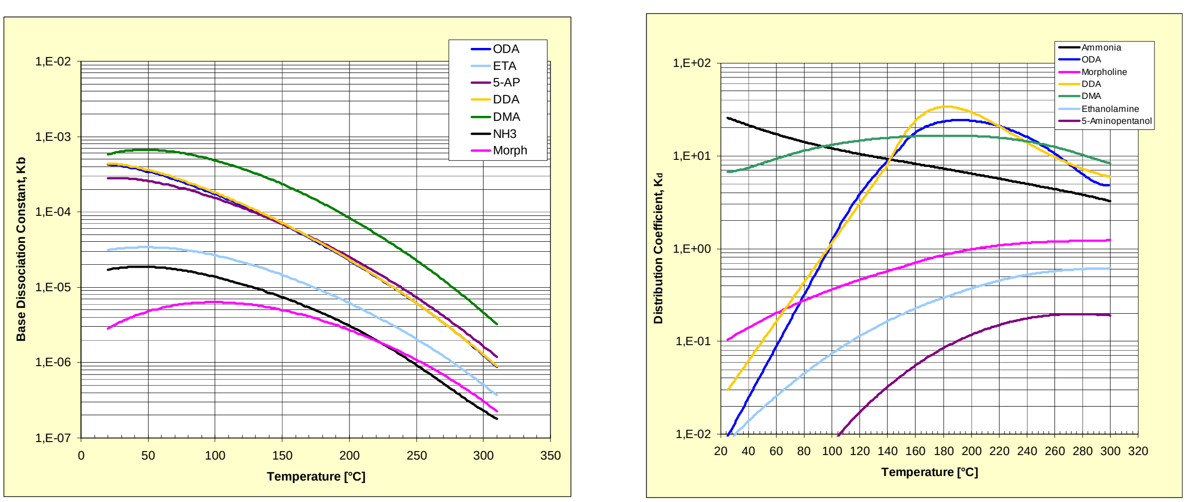


Figure 1. Dissociation constants (left) and distribution coefficients (right) of different amines as a function of temperature

The solubility of the FFA is an important characteristic, which mainly determines the feasibility of its application, i.e. dosing strategy and distribution in the liquid phase of the working medium.

The solubility of FFAs in water rises with increasing temperature, whereas the solubility at room temperature normally is very low, see Figure 2. For optimal working conditions the temperature and concentration dependency has to be taken into account whereby the presence of additional ions can also have an influence. The best conditions are in the range of the solubility curve (turbidity points). The interception point of the saturation concentration of the turbidity point gives the KRAFFT point of the colloidal solution. The critical concentration of the micelle formation (CMC) is the concentration at the KRAFFT point where the physical properties of the solution are changing due to the beginning aggregate formation.

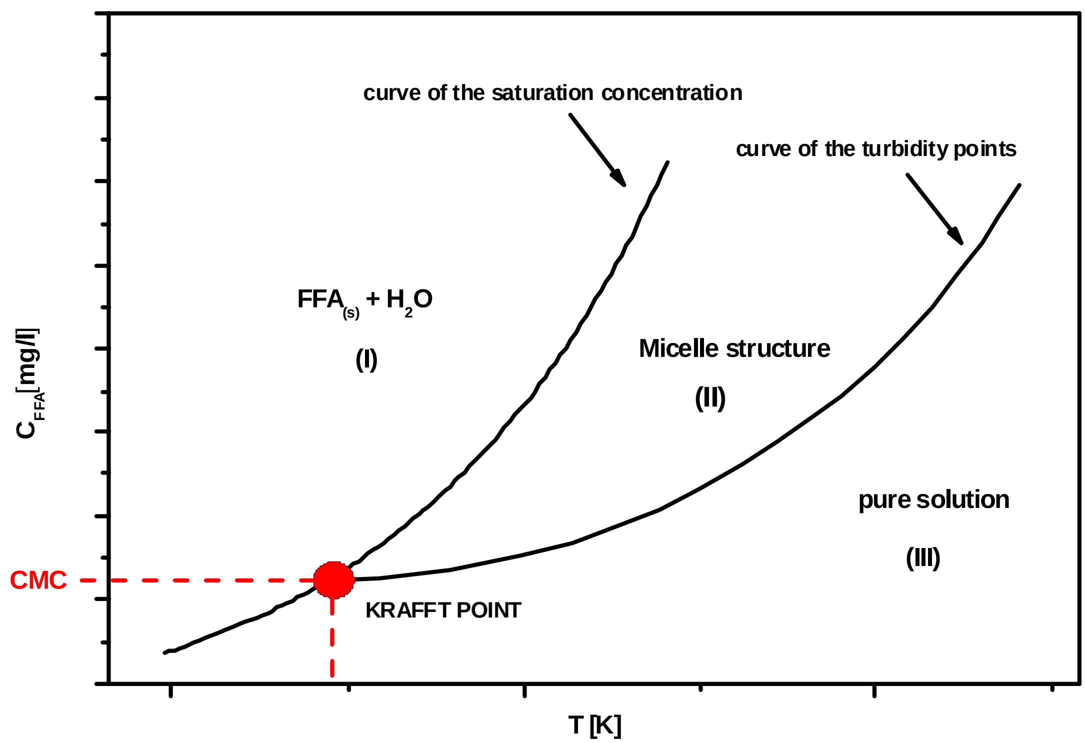


Figure 2. Schematic Phase-Diagram Water/Film-forming amine

Considering non ionic decomposition products and in some extent organic acids there is a strong controversy in the use of film-forming amines. The organic compounds are decomposing in the water-steam cycle and especially acetate and formate are enriched in the early condensate. EPRI found strong indications that these organics may contribute to LP turbine blade failure. [3]

Thermal instability of film-forming amines under typical operating conditions of the water-steam cycle of PWRs results in the formation of unwanted organic decomposition products, mainly organic acids and carbon dioxide, which can increase the risk of specification violations of the plant under normal power operation (acidic conductivity). This requirement includes also the radiation resistance of the selected film-forming amine to a given extent, i.e. typical dose rates in the secondary side of steam generators under normal power operation.

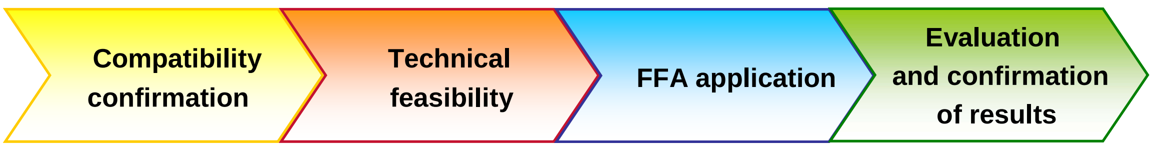
Thermal decomposition of film-forming monoamines - reaction mechanism:

1. $2\ R\text{-}NH_2 \rightarrow R_2\text{-}NH + NH_3$
2. $3\ R\text{-}NH_2 \rightarrow R_3\text{-}N + 2\ NH_3$
3. $R\text{-}NH_2 + R_2\text{-}NH \rightarrow R_3\text{-}N + NH_3$
4. $R\text{-}NH_2 \rightarrow R'\text{-}CH{=}CH_2 + NH_3$

The FFA, which has been qualified by AREVA NP GmbH is stable under the given thermal conditions and shows a good radiation resistance during power operation of a PWR (i.e. no decomposition products were detected up to a temperature of 280 °C).

4. APPLICATION APPROACH

The approach, developed by AREVA NP GmbH for the application of film-forming amines is unique and applicable for different plant designs. It consists of the following steps:



4.1 Compatibility confirmation

First of all the compatibility of the application of a selected FFA has to be confirmed by evaluation of the design, material concept and water chemistry of the pilot plant. If required, additional laboratory tests had been carried out, e.g. the influence of FFAs on plant-specific Ion Exchange Resins (IEX) and the influence on on-line monitoring devices.

The selected pilot plant consists of water-steam cycles with all-ferrous material concept. From the literature and also from fossil power plant experience, the influence of FFAs for this specific design is well known. The pilot plant applies H-AVT treatment, using Hydrazine and Ammonia for control of the pH in final feed water and sufficient reducing conditions. Therefore, the influence on Ion Exchange Resins of the SG blowdown purification system and the make-up water treatment plant (the pilot plant is performing blowdown recovery) were of essential interest.

Investigations regarding the influence of FFA on the following types of ion exchange resins (IEX) have been carried out:

- SAC (Strong acid cationic resin)
- WBA (Weak base anion resin)
- SBA (Strong base anion exchanger)
- MB (Mixed Bed)

The studies were performed in a test plant under defined conditions (demin water, pH and T, simulating also the applied secondary side chemistry) over a time span of approximately 10 weeks. The loading phase was carried out in series of down flow with a flow rate of 7….35 BV /h (3.5 l/h). The loading phase was stopped after the breakthrough of the strong cation exchange resin detected by conductivity increase after SBA. After the loading phases the resins were technically regenerated (HCl 5%, NaOH 4%) and small samples were analyzed by dye-test.

The following questions had to be answered:

- - Is there a fouling of the resins caused by the FFA?
- - Could the possible fouling film repeatedly be removed during the regeneration steps or is there an accumulation?
- - Is there an irreversible loading of the IEX?

It could be shown that the FFA was nearly completely taken up from the strong acidic cation resin (SAC) see Figure 3. A loss of cross-linking by breakage of the covalent bonds between Divinylbenzene and the Polystyrene-chain of the matrix (ageing mechanism of SAC) leveled out to a constant degree and could be removed easily by technical regeneration. The other tested resins showed similar results like the blank test (without FFA). The operating capacity was not restricted by a blocking of the functional groups.

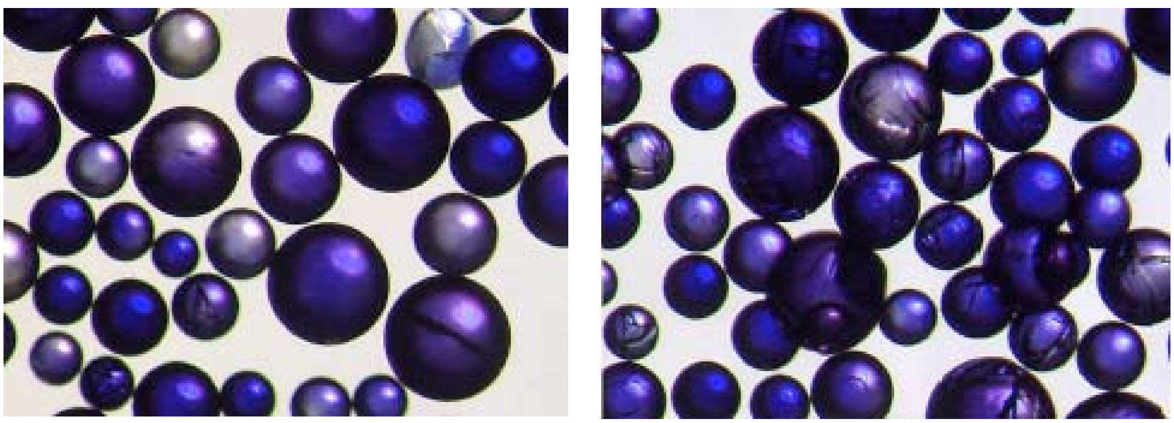


Figure 3. FFA treated IEX sample after regeneration (left) and blank test after regeneration (right)

4.2 Technical feasibility

The second step of the AREVA NP GmbH approach is the technical feasibility. In this step the dosing strategy and injection point as well as the on site monitoring procedures have to be defined and elaborated. Monitoring procedures do not only cover the monitoring process of the applied FFA, but depend also on:

- Water chemistry treatment of the water – steam cycle (H-AVT, ETA or Morpholine treatment)
- Chemistry specification for the secondary side (control and diagnostic parameters for normal power operation)
- Specific requirements from vendors of main components of the water-steam cycle (i.e. Turbine specification)

The FFA injection is applied during power operation therefore any impact on plant performance shall be excluded in advance. Furthermore, due to the mobilization effect of FFAs with respect to adsorbed corrosion products and impurities, a violation of the plant specific water chemistry specification shall be avoided in advance. For this reason a risk analysis was carried out to estimate the mobilization effect, based on a detailed plant data assessment.

Regarding the mobilization effect on strong anions like sodium, chloride, and sulphate, the cationic conductivity (CC), specific conductivity (SC) shall be monitored with special attention. The impact on the cationic conductivity of chloride, fluoride and sulphate is shown in Figure 4. Each curve assumes the absence of the other two species. The control value of the CC in final feed water (0.2 µS/cm) and the diagnostic parameter regarding the concentration in the SG bulk water is indicated by the red lines.

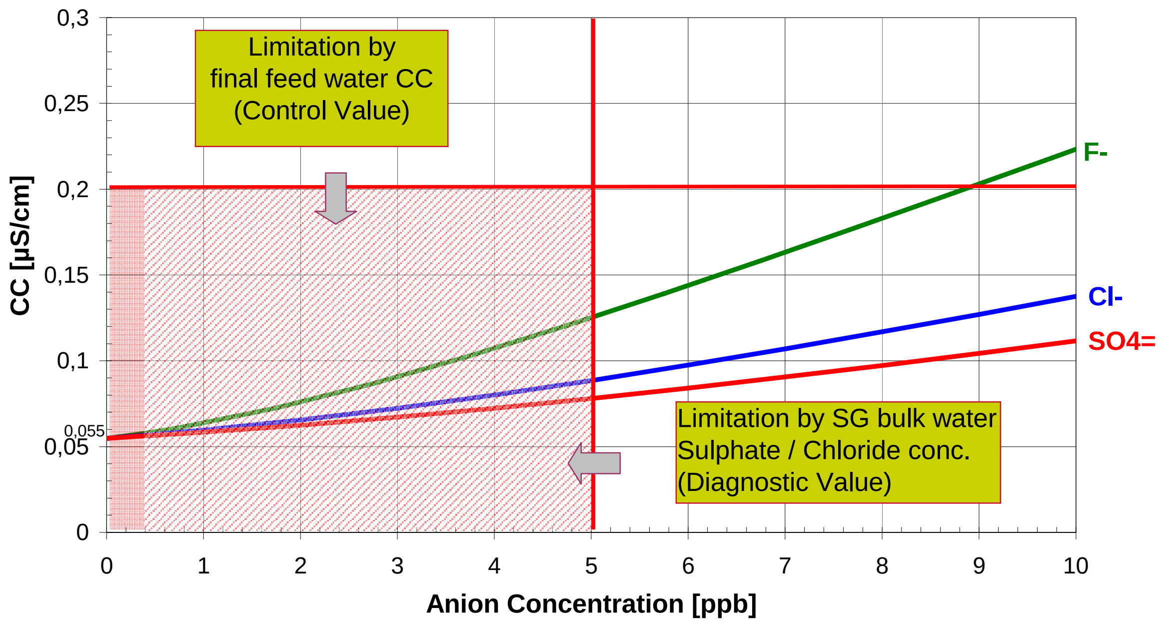


Figure 4. Cationic conductivity (CC) due to strong anions

Grab sampling and analysis will be performed in the laboratory of the NPP. On-line supervision of pH, CC and SC could be carried out by plant measurement devices.

4.3 FFA application

The FFA application on site was performed by AREVA NP GmbH experts together with the customer's operational team. The application also included the monitoring of the process and the necessary technical support.

Impact on daily plant business:

- Duration of FFA application on site about three weeks (first application)
- Treatment can be performed by small teams
- Teams can be supported by plant personnel

A visual inspection of secondary side systems and components during subsequent outage was recommended in the feasibility study to confirm the quality of the produced film.

4.4 Confirmation of results

The confirmation of results consists of the visual inspection and the data evaluation. Furthermore the AREVA NP GmbH experts will support the plant operators to follow up and evaluate the prospective SG cleanness. For maintenance the stability of the FFA film has to be monitored and, based on the observation it should be decided if a further FFA application will be necessary.

The visual inspection of the main components at the pilot plants was carried out one week after finalizing the FFA dosing and plant shut down, see Figure 5 and Figure 6. To check integrity of the adsorbed FFA film a simple test with demineralized water has been carried out. If a complete and closed FFA molecular layer was formed, the metal and metal oxide surfaces show the typical water repellency with rolling liquid drops from the surface. The adsorption layer in the condenser was completely established.

Figure 5. Condenser (left) and feed water pump steam turbine (right)

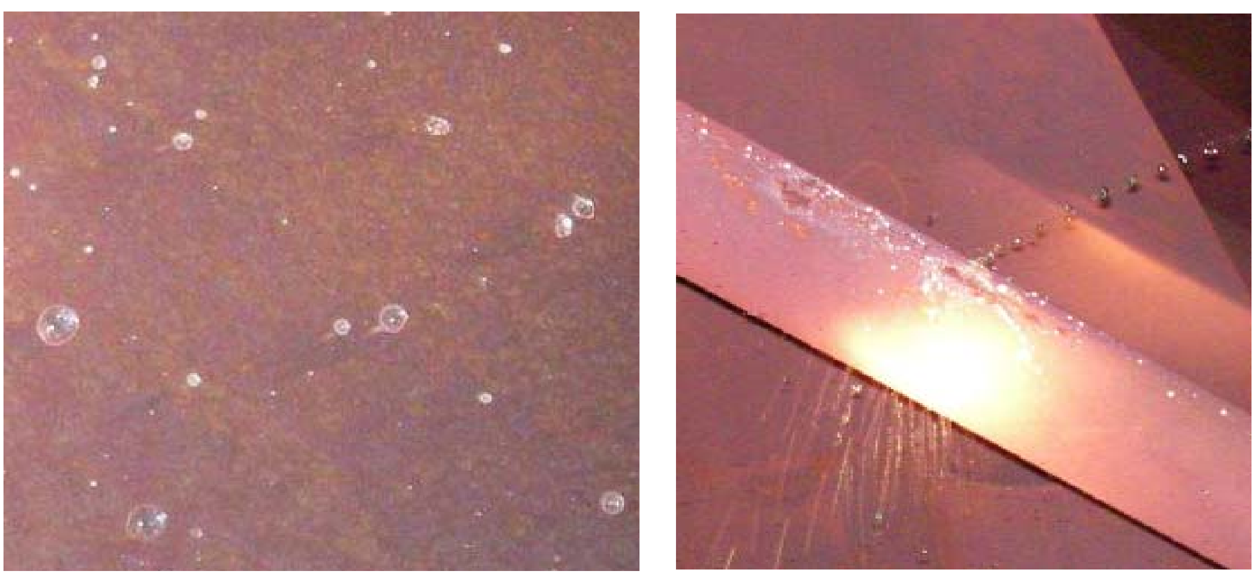


Figure 6. Condenser floor (left) and condenser component (right)

The measured iron concentrations indicated that during the FFA application and before entering the transient phase of the plant shut-down, significant amounts of iron could be mobilized and removed via the SG Blowdown. Furthermore, after re-starting the treated units, a significant decrease in the corrosion product transport into the SGs could be verified. Figure 7 shows iron filters of FW samples before and after FFA treatment.

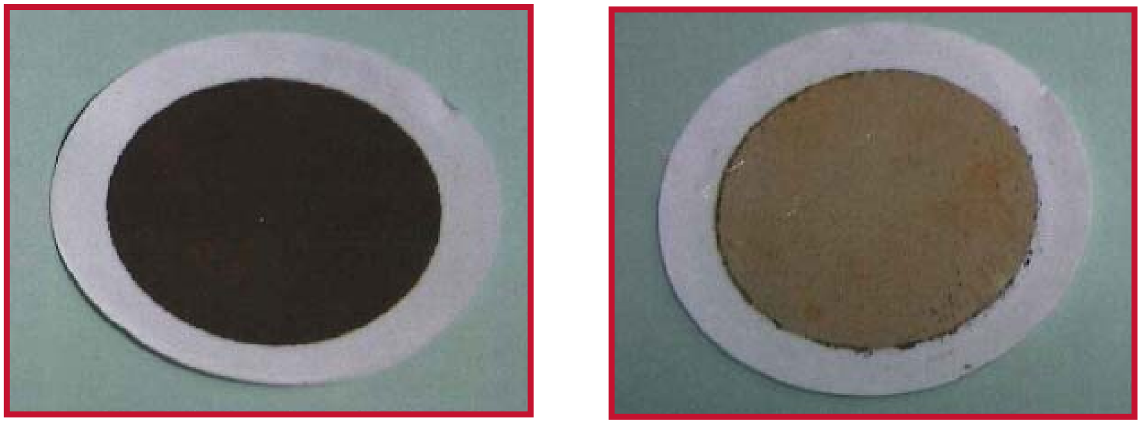


Figure 7. Fe filters before (left) and after FFA treatment (right)

Significant increase of corrosion products in the steam generator blowdown water during the FFA dosing confirmed the mobilization of detachable particles. Iron concentrations were decreased to a half than before FFA application and the significant decrease of impurity concentrations in Hideout Return (HOR) measurements by a factor up to 10 showed that even strong anions (sulphate and chloride) could be removed by the FFA.

5. AREVAS CONCEPT

Plants with a non optimal BoP design on secondary side are restricted in the use of H-AVT. A sufficiently high pH can not be established and therefore a complementary and continuous dosing of less volatile amines is necessary to avoid FAC. Self-evident the application of FFA is adaptable and desirable to other plant designs and water chemistry treatments.

As a result of the successful plant application in two units of the pilot plant, AREVA NP GmbH introduced an effective and competitive measure for the secondary side steam-water-cycle, the non-continuous and controlled dosing of a film-forming amine:

- - Significant reduction of corrosion product generation and transport into the SGs
- - Significant reduction of impurities from the inner surfaces of the water-steam cycle

Especially the reduction of the corrosion product transport into the SGs can lead to an enhancement of the heat transfer efficiency and an increase of turbine efficiency.

The first application of FFAs in the steam-water cycle of a PWR was proven to be a useful supplement to the existing water-chemistry for:

- - cleaning inner surfaces of the secondary cycle (removal of impurities)
- - protecting surfaces in the wet steam areas
- - contributing to an optimized pH control strategy

A refreshment application of FFAs in the steam-water cycle of a PWR is required in case of:

– - Iron concentration in FW is increasing

– - Change of the heat transfer characteristics of the SGs due to impurities

Furthermore AREVA NP GmbH comprises the use of film-forming amines for lay-up strategies. During outages systems and components are open to atmosphere. Wet surfaces, moisture condensation will result in general corrosion of carbon steel surfaces. Additionally localized corrosion might also occur in case of formation of anodic sites (preferentially in the presence of impurities).

Establishing a hydrophobic film on the metal surfaces, no additional measures for outage lay-up have to be taken into account. The surface film has long term stability also in aggressive environmental conditions like seawater and salted air.

6. CONCLUSIONS

The main reason for steam generator tube failure as known is caused by the accumulation of deposits contributing to the formation of local aggressive conditions. Consequently the SG has to be kept as clean as possible and the corrosion product transport into the SG has to be minimized.

Due to the promising results of the FFA application at two western type PWRs (2011, 2012), impurities from the inner surface areas of components of the water-steam cycle could be mobilized and further corrosion product ingress into the steam generators (SGs) be reduced in a significant amount.

AREVA NP GmbH consequently investigated and performed an effective complementary proceeding to the used water-steam chemistry of the secondary cycle, the completely monitored and controlled non continuous dosing of a film-forming amine.

REFERENCES

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[2] A. Drexler, V. Schneider and J. Fandrich; “Chemistry Related On-Line Monitoring of PWRs”, Power Plant Chemistry 2010, 12(12), 700-707.

[3] EPRI TR-1012630, Proceedings 2006: International Conference