

## Aspects on Chemistry in French Nuclear Power Plants

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This paper first briefly describes the primary water chemistry of PWR, how the lithium and boron concentration are selected in order to minimize their impact on deposition associated to the concentration due to heat flux and some limited boiling that may occur on the fuel elements. The main issue is axial offset anomalies and dose rates limitation. Then, this paper mainly focuses on evaporation and associated concentration process in the steam generator where a high flow of steam is produced. Thus, the hide out phenomenon is discussed, as well as its consequences on corrosion in flow restricted areas. The options and interest for amine selection in the AVT (All Volatile Treatment) of the steam-water cycle are explained, according to the physico-chemical properties of the reagents, i.e. the partition coefficient steam/liquid phases, the alkalinity evolution versus temperature. The limited content of hydrazine reducing agent to be added is also discussed so as to minimize its potential effect on Flow Assisted Corrosion of carbon steel while keeping a sufficient efficiency on the Stress Corrosion Cracking of steam generator tubing. The various options of the chemistry of the different systems are thoroughly discussed as well as their results for achieving the main objectives such as minimizing radioactive dose rates, components corrosion, operating costs and moreover increasing safety. Finally, the evaporation in cooling towers and all the associated phenomena are listed, mainly fouling due to carbonate precipitation. The remedial treatments are explained, as well as those associated with amoebae mitigation in the cooling circuit.

### 1. Introduction

Steam and liquid phases of water are present in the various circuits of a Pressurized Water Reactor (PWR) Nuclear Power Plant (NPP). High heat flux and flow rates induce important concentration process and transport of chemical in various proportions in liquid and vapour phases according to the properties of the compound and the temperature. Then, locally, some chemicals may highly concentrate due to the heat flux and hide out phenomenon. This makes the chemistry regulation of the various systems a real challenge, since it may also cope with several requirements associated to the mitigation of activity generation and transport, neutronic, material corrosion, chemical wastes, thermal performances and operating costs [1].

This paper covers the three main systems:

- the primary coolant where the heat is generated from the core and, normally, the water should remain liquid in every location, which is roughly achieved ;

- the secondary system where the high evaporation occurs in the steam generators and induces the most important concentration process and the risk of corrosion of steam generator tubing ;
- the cooling water system where large quantities of water are evaporated to minimize the heat release in the river water, with a great impact on calcium carbonate precipitation.

### 2. Primary Coolant

**2.1. Chemistry description.** The primary water of a PWR is first containing boron as boric acid in order to control the core reactivity through neutronic absorption of boron 10. Even though boric acid is weakly dissociated, particularly at high temperature, an acidic environment is unacceptable since it increases the general corrosion of materials in presence with the consequence of a too high activation and transport of corrosion products in the system.

Thus, an alkaline reagent, lithium hydroxide, is added in the water, in small quantities for reaching the slightly alkaline pH at operating temperature which minimizes the corrosion, solubility and transport of activated corrosion products.

The table 1 and 2 indicate the main radioisotopes produced by activation of corrosion products, and their half-life. Table 1 reports those obtained from activation of the base metals of the components, stainless steels or nickel base metals. Table 2 reports those obtained from activation of small quantities of elements which are present in specific components but are highly activated.

Table 1. Main isotopes from activation of base metals corrosion products in a PWR.

Stable isotope	<sup>58</sup> Ni	<sup>54</sup> Fe	<sup>58</sup> Fe	<sup>50</sup> Cr
Radioactivated isotope	<sup>58</sup> Co	<sup>54</sup> Mn	<sup>59</sup> Fe	<sup>51</sup> Cr
half-life	71 d	312 d	45 d	28 d

Table 2. Main isotopes from activation of highly activated metals in a PWR.

Stable isotope	<sup>59</sup> Co	<sup>109</sup> Ag	<sup>121</sup> Sb	<sup>123</sup> Sb
Radioactivated isotope	<sup>60</sup> Co	<sup>110m</sup> Ag	<sup>122</sup> Sb	<sup>124</sup> Sb
half-life	5.3 y	250 d	2.7 d	60d

In some countries, another alkaline reagent, potassium hydroxide [2], may be also added, as this will be discussed in § 2.3 below. Nevertheless, Lithium 7 is produced in situ from the neutronic reaction <sup>10</sup>B (n,α)<sup>7</sup>Li. Natural Li is not used since it contains a too high proportion of <sup>6</sup>Li, highly activated into undesirable tritium. Instead, a lithium enriched over 99 % of <sup>7</sup>Li is used.

Finally, hydrogen, directly added through a gas pressure or coming from radiolysis decomposition of ammonia in Eastern Europe VVER design [2] is present for counteracting the radiolysis decomposition of water into oxidizing compounds and oxygen, which are not compatible with the presence of stainless steel, sensitive to cracking corrosion at high temperature in presence of oxygen and chloride.

**2.2. Lithium-Boron concentrations selection.** The boron 10 concentration is imposed by the core characteristics and design and by the fuel burn up. Natural boron only contains about 20% of <sup>10</sup>B, the useful isotope in neutronic absorption. This means that the required total boron content starts inside the

1000-2000 ppm B range and progressively decreases along the fuel cycle while the fuel burn up increases. At the end of the fuel cycle, the boron concentration reaches a few ppm or is close to zero.

Consequently, the optimum high temperature pH<sub>300°C</sub> to be maintained requires a decreasing lithium concentration along the fuel cycle.

Calculation codes as well as feedback experience agreed to select a pH<sub>300°C</sub> of ≈ 7.2 ± 0.2 for minimizing (i) the solubility and corrosion of the surfaces of the main components in the primary system, (ii) the difference of solubility and thus of transport of radioactivated isotopes in the various parts of the system at different temperatures, typically in the 270 – 325°C range for a standard 1000MW PWR. The curve of lithium concentration according to the decrease of boron content in French units is shown on figure 1.

Lithium (mg/kg)

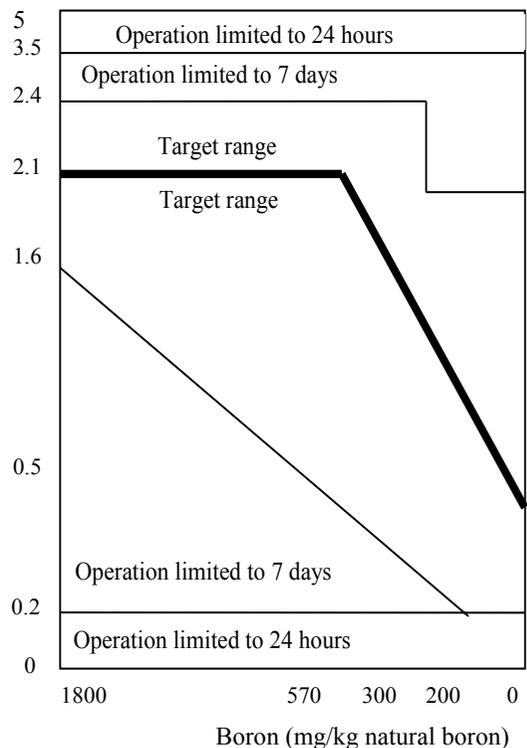


Fig. 1. Boron-Lithium curve along the fuel cycle of a French PWR.

The corresponding lithium concentration, according to boron evolution, is ranging from 5 to 10 ppm at the beginning of the fuel cycle.

A 0.5 ppm Li content with a few ppm boron are low enough not to cause any problem. But, at the beginning of the cycle, a 1300 ppm boron content for example with a lithium concentration of around 4 ppm may induce non negligible concentration and precipitation condition, even if nucleate boiling at the wall of the fuel element is avoided. Lithium concentration has to be limited for avoiding a too high local concentration on the fuel cladding, with subsequent corrosion. On the other hand, a too high boron concentration may increase the risk of precipitation with a safety concern of axial flux anomalies and inadequate control and monitoring of the core fission.

Then, in addition, such deposit will increase nucleate boiling condition which should not exist in a PWR primary system as it is the case in a BWR.

Finally, this will be an additional risk to allow other compounds to precipitate in this deposit with consequences either on corrosion, or on thermal transfer or on radioactivation.

Consequently, in most cases, lithium concentration has been limited to 2.2 ppm mainly to avoid fuel cladding corrosion, based on fuel vendor restrictions, with an insufficient  $\text{pH}_{300^\circ\text{C}}$  and non optimized control of corrosion products activation and transport.

**2.3. Remedies.** Some utilities already started to increase the lithium content up to 3.5 ppm, corresponding to a  $\text{pH}_{300^\circ\text{C}}$  at the beginning of the fuel cycle of almost 7.0, which is more or less acceptable.

But with the always increased burn up of the fuel, for longer fuel cycles, less frequent shutdown for refueling and maintenance, the boron concentration has to be higher at the beginning of the fuel cycle and the  $\text{pH}_{300^\circ\text{C}}$  is insufficient, even with 3.5 ppm Li.

Eastern Europe VVER are using potassium instead of lithium hydroxide with two main advantages :

- cost limitation by avoiding the use of enriched  $^7\text{Li}$  ;
- higher solubility of K as compared to Li, with lower risk of precipitation and axial offset anomalies.

But there are three main disadvantages of K :

- its activation ;
- its solubility and alkalinity that may induce corrosion of some components,
- the necessity to monitor K + Li for the pH control since  $^7\text{Li}$  is anyhow produced from  $^{10}\text{B}$ .

One of the way to mitigate activation of cobalt is to replace it by zinc in the surface composition. Thus, a few ppb of Zn is already added in some countries (Germany, USA,...) or considered as a key option such as in France or in Japan [3].

The best solution, already applied in some European PWR (Germany, Switzerland) is to use Enriched Boric Acid (EBA) with a higher proportion of  $^{10}\text{B}$  [4].

As an example, if only 40% of  $^{10}\text{B}$  instead of 20% in natural boron is used, the total boron concentration will be twice lower and a concentration of 2.2 ppm Li becomes satisfactory.

The benefit of such EBA use will first be on obtaining the optimum  $\text{pH}_{300^\circ\text{C}}$  at any moment, with minimized dose rates from activated corrosion products. But another interesting purpose will be the limitation of boron deposition with its consequences described above.

### 3. Secondary System

**3.1. Chemistry description.** As it is the case for the primary coolant, the secondary system (steam-water) pH must be slightly alkaline to be settled at a low corrosion value of the components in presence.

In the case of this system, the situation is more complicated for various reasons :

- several materials in presence, including stainless steel, nickel base alloy, carbon steel which is very sensitive to erosion-corrosion (also named FAC, Flow Assisted Corrosion) if the pH is not sufficient, copper alloys in some plants and which are very sensitive to corrosion in presence of ammonia or amine treatment ;
- a wide range of temperature (about  $40^\circ\text{C}$  in the condenser to  $285^\circ\text{C}$  in the steam generator) ;
- a high evaporation rate inducing a high concentration of chemicals which are not volatile ;
- steam and liquid phases in the system which requires the use of volatile alkaline reagents in order to get the alkaline environment all through the circuit.
- Some points such as the condenser where the pressure inside the circuit is lower than outside, meaning that in case of un-tightness the raw cooling water (river or sea) may enter and contaminate the secondary water.

In the early times of PWR operation (up to the mid 70's), the typical treatment was including :

- Ammonia for having a slightly alkaline pH in the whole steam-water system ;
- Phosphate addition (a mixing of  $\text{Na}_2\text{HPO}_4$  and  $\text{Na}_3\text{PO}_4$ ) for buffering the various potential contaminants, that may enter the system through the condenser.

Such a treatment was, and still is, largely applied in many fossil fired units. In the case of a PWR design, it has been observed that a constant  $\text{Na}/\text{PO}_4$  ratio of about 2.4 was hardly maintained. As a consequence of precipitation or reaction with various compounds in presence, the ratio and pH was not correctly controlled, inducing alternatively either alkaline condition and stress corrosion cracking of steam generator tubing or acidic condition and other types of corrosion such as wastage, pitting.

Then, heavy deposits were formed.

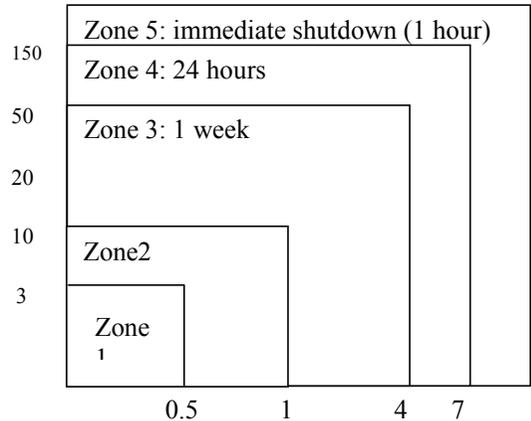
Thus, most of the manufacturers of nuclear steam supply system recommended the use of only all volatile treatment (AVT) without any phosphate addition. But, the absence of buffer implies a very high quality water in the steam generator. The corresponding chemistry specifications have been several times tightened with more and more restrictive limits to try to avoid corrosion of the steam generator tubing, particularly for most of the plant that had inappropriately selected the Alloy Inconel 600MA tubing very sensitive to stress corrosion cracking (SCC) in presence of residual stress during operation with some contaminants. Even in pure water, this 72% Ni base alloy is sensitive to SCC which is worse in alkaline conditions.

The example of chemistry applied in in French PWR at steam generator blowdown in shown on figure 2 where various zones of operation are defined with allowed duration corresponding to the water purity. Two main parameters are defined, sodium which is the main detrimental for producing alkaline condition and cation conductivity which is representative of the general purity of the water, proportional to the anions such as chloride, sulphate, organic acids, ...) in the water.

Historically, the use of ammonia as an alkalizing reagent for the whole steam-water system has been widely used since this is a widespread chemical which is also in situ produced in the system by thermal decomposition of the hydrazine reducing agent that is also added (see 3.4). Ammonia was added in a sufficient concentration to get a  $\text{pH}_{25^\circ\text{C}}$  of 9.2 in presence of copper alloys but is not any more used in this case since it has been

demonstrated that such a treatment is not acceptable for carbon steel corrosion (FAC). It is now only used in some of the plants without any copper alloys and where a  $\text{pH}_{25^\circ\text{C}} \geq 9.8$  may be applied.

Sodium ( $\mu\text{g}/\text{kg}$ )



Cation conductivity ( $\mu\text{S}/\text{cm}$ ) at  $25^\circ\text{C}$

Fig. 2. Chemistry specification at the Steam Generator Blowdown of French PWRs.

In the other cases (presence of copper alloys or some of the plants without such materials), the use of an amine (see 3.3) is preferred since it allows a higher pH at operating temperature of various parts of the system, minimizing FAC of carbon steel, production, transport and deposition of corrosion products, with two main advantages :

- less decrease of thermal transfer and power ;
- limitation of hide out phenomenon of contaminants potentially inducing corrosion of steam generator tubing (see 3.2).

**3.2. Hide out phenomenon.** The steam generator is the location for concentration of chemical impurities through two different phenomenon :

- evaporation,
- ebullioscopy rule inducing hide-out.

The first one is easy to understand and is simply associated to the fact that a high vaporization flow is taking place in the steam generator which is there for this purpose.

Most of the non volatile impurities which may induce corrosion of steam generator tubing are only slightly soluble in the vapor phase, with a ratio depending on the pressure/temperature. As a typical example, the  $K_D$  partition coefficient for sodium :

$$K_D = \frac{\text{concentration in steam}}{\text{concentration in liquid phase}}$$

is around  $10^{-4}$  in the condition of a PWR while it is about 10 times higher ( $10^{-3}$ ) for a fossil fired unit. This means that during the vaporization, a negligible part of the most deleterious impurities will leave the liquid phase. In addition, some of these chemical will also depart the steam generator into the steam via the carry over, i.e. the fraction of liquid which has not been correctly separated from the steam and which is going with the steam out of the steam generator.

Practically, this quantity may be of about 0.1% and thus the quantity of sodium contained in the liquid part going with the steam may be 10 times higher than the sodium dissolved in the steam.

But, whatever the exact number, in any case, the proportion of sodium going into the steam is marginal and the salt will concentrate in the liquid phase.

The steam generator water is deconcentrated through the blowdown with a flow rate usually in the range 0.5 to 1% of the feedwater (or steam) flow rate.

In most of the French PWRs, this value is 1% and is optimized in order :

- not to excessively concentrate the chemicals ;
- not to loose too many heat.

With such a blowdown proportion, without any other phenomenon described below, the concentration of impurities in the steam generator liquid phase would roughly be 100 times the feedwater one.

Albeit this is quite high, this would not cause any significant problem of corrosion on the steam generator tubing.

In practical, locally, in flow restricted areas, the chemicals will much more highly concentrate in relation with ebullioscopy rule which will induce hide out.

The principle of ebullioscopy and hide out is the following :

- in areas of low flow, such as crevices, sludge pile (deposits of corrosion products on the top of the tubesheet), the circulation of water is limited ;
- the steam generator tube wall on the external side is not properly cooled ;
- the tube surface temperature  $T_1$  is higher than it should be, corresponding to the boiling temperature  $T_2$  of pure water at the steam generator pressure ;

- according to ebullioscopy<sup>\*</sup>, the chemicals are able to concentrate up to a concentration  $x$  depending on  $\Delta T = T_1 - T_2$  ;
- the higher  $\Delta T$ , the higher  $x$ .

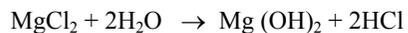
The consequence of this phenomenon is a dramatic increase of some chemicals.

The achievable concentration thus depends on the  $\Delta T$  but also on the compound solubility.

Three main cases can be encountered :

- highly soluble chemicals such as sodium hydroxide, without any solubility limit at 300°C ; pure liquid NaOH may be even observed; with a  $\Delta T$  of 20°C, a concentration of 270g/l is obtained, which is more than sufficient to create the condition for intergranular stress corrosion cracking of the steam generator tubing ;
- intermediately soluble chemicals such as sodium chloride ; at 300°C, the solubility limit is of about 30g/l, close to sea water concentration; this is also sufficient to induce corrosion like pitting ;
- low solubility chemicals such as calcium or magnesium compounds ; their consequence for corrosion is not direct since it is impossible to get high concentration and strongly alkaline medium detrimental for corrosion.

Their consequence will be, in the case of  $MgCl_2$  pollution and hydrolysis at high temperature the precipitation of  $Mg(OH)_2$  and the production of concentrable hydrochloric acid which will be able to create the corrosion :



Finally, when a pure feedwater quality is achieved, typically 0.01  $\mu g/kg$  of Na, the bulk water in the steam generator will be about 100 times higher i.e. 1 $\mu g/kg$ , due to evaporation and blowdown flow rate ratio; in low flow restricted areas (crevices, sludge) the concentration may be  $10^3$  to  $10^6$  higher.

This means that the impurities are not completely eliminated by the blowdown as they should be in ideal conditions.

<sup>\*</sup> The ebullioscopy rule is such that when a chemical is present in the water, the boiling point of the water is increased in a proportion depending on the chemical concentration. For example, at normal atmospheric pressure, boiling point of pure water is 100°C while the sea water one is around 101°C.

A fraction is kept inside the steam generator (SG), either due to local concentration or to precipitation.

The percentage of hideout rate is defined as :

$$\tau \text{ hide out} = \frac{\text{mass remaining in the SG}}{\text{mass entering the SG}} \times 100$$

Of course,  $\tau$  is very high for low solubility chemicals and lower for the highly soluble ones. For the first ones, it has been seen that there is no direct consequence on corrosion ; deposition of these compounds is a problem in case of fossil fired units with high temperature but rarely in the case of PWR since the feedwater purity must be very good at any time and the impact of these deposits on thermal transfer is quite limited.

For the soluble compounds,  $\tau$  is depending on the presence of other corrosion products coming from feedwater train metal dissolution and on the design. In case of improved design and optimum secondary water treatment with an amine,  $\tau$  is only of a few percents. In less favorable cases, it may reach 20%.

The table 3 below gives for sodium some examples of hideout rates with 2 different designs, which have been measured during specific tests in operating units [5].

Table 3. Hideout rate of various compounds.

Compound	$\tau$ hideout
Sodium :	
- efficient tube support plate design	2 – 5%
- old design with concentration in tube support plates crevices	10 – 20%
Calcium	≈ 80%
Sulfate, due to hide out in local areas + absorption on metal surfaces	≈ 90%

**3.3. Amine selection.** The main objective of the pH reagent selection is to get the conditions for the lowest possible corrosion rate of the different materials present in the whole steam-water system.

Thus, as explained in § 3.1, a volatile reagent must be selected in order to obtain the alkaline pH in the entire system. Stainless steels, sometimes used for condenser and some heaters, and always for the steam generator tubing, have a lowest generalized corrosion rate in slightly alkaline condition but can accept a rather wide range of pH. On the opposite, carbon steel, often used at least for high pressure heaters or copper alloys, mainly used in oldest condensers and some low pressure heaters or moisture separator reheater tubing, are compatible within a limited range of pH. In addition to corrosion of materials, other issues must

be considered when selecting the water treatment control agent and the pH to be used. These include:

- . corrosion transport to the steam generator, giving rise to deposits where corrosion might occur;
- . impact on condensate polisher operation or on blowdown demineralizers, if any of these;
- . low toxicity of reagent and acceptable release to the environment;
- . commercial availability and cost;
- . thermal stability and type of decomposition products;
- . required concentration for the desired pH.

Thus, existing materials as well as the presence of condensate polishers have a large impact on pH and reagent selection.

**Ammonia.** Up to the mid eighties, ammonia was mainly used since it is of easy implementation, with a long experience, known characteristics, absence of decomposition products, low cost and no adverse effect except ammonia corrosion and formation of soluble copper-ammonia complexes if pH is above 9.2 at room temperature. In addition, its use is even easier since it is the main decomposition product of hydrazine, generally added as a reducing agent. This will allow the use of a higher hydrazine content, that is favourable to obtain a reducing environment as described in § 3.4.

However, ammonia has one main disadvantage: for the maximum pH<sub>25°C</sub> which is compatible with either waste release in the environment, or resin exhaustion, or copper alloys corrosion, the high temperature operating pH is not sufficient to minimize corrosion product transport along the feed water train, coming from carbon steel generalized corrosion, and moreover to protect carbon steel components, in liquid phase, from flow assisted corrosion (FAC).

Table 4. Typical selection of pH and reagent for feedwater in the secondary system

Parameter	Typical Range	Materials - Treatment
pH <sub>25°C</sub>	9.1 to 9.3	Copper - Amine
Morpholine, ppm	4 to 6	Morpholine and Copper
Hydrazine, ppb	> 10	
pH <sub>25°C</sub>	9.5 to 9.6	No Cu - Amine
pH <sub>25°C</sub>	9.8 to 10.0	No Cu - Ammonia
Hydrazine, ppb	50- 100	No Copper

The table 4 shows the principle of selection for the pH and reagents according to the presence or not of copper alloys in the system and to the other discussed options and parameters.

In effect, in presence of copper alloy, the maximum  $\text{pH}_{25^\circ\text{C}}$  of 9.2 leads, at  $175^\circ\text{C}$  (the most sensitive temperature) to an unacceptable rate of erosion-corrosion, as demonstrated by the severe accident which occurred on a pipe in the Surry U.S. plant in 1986.

In absence of copper alloys,  $\text{pH}_{25^\circ\text{C}}$  has to be increased at least up to 9.7 and preferably to 9.8 – 10 [4] to avoid FAC and minimize corrosion product transport. However, in presence of condensate polishers permanently in operation and in hydrogen cycle only, regeneration frequency will be too high. On the other hand, in the absence of condensate polishers, a pH of 10 as applied in German units is appropriate for minimizing corrosion products transport but requires either (i) a frequent regeneration of blowdown demineraliser resins or (ii) operation of resins after exhaustion by ammonia that will decrease their efficiency for sodium elimination at such a high ammonia molar concentration.

Finally, ammonia treatment with a  $\text{pH}_{25^\circ\text{C}}$  of about 9.7 seems acceptable only for plants without copper alloys and without condensate polisher continuously in operation.

In the eighties, several alternate amines have been thoroughly investigated by various countries, mainly United Kingdom, U.S.A. and France.

**Morpholine** has been satisfactorily used in the French PWRs since 1984 in all the units with copper alloys and in most of those without copper alloys. This is acceptable since there is no condensate polishing plants. Morpholine is also used in some other countries, mainly in the USA, Ukraine.

The main objectives of that reagent selection are to protect carbon steel from erosion-corrosion and to decrease corrosion products transport.

With morpholine, a  $\text{pH}_{175^\circ\text{C}}$  of 6.8 in two phases flow can be obtained with a  $\text{pH}_{25^\circ\text{C}}$  of 9.3 while the same high temperature pH would require a room temperature of 10 with ammonia.

This can be explained by two advantages of morpholine over ammonia.

a) The evolution of morpholine dissociation constant versus temperature which is less decreasing than that of ammonia. This means that for a same  $\text{pH}_{25^\circ\text{C}}$  and the corresponding concentration of reagent, the alkalinity decrease when temperature increases is more pronounced for ammonia than for morpholine.

b) The morpholine distribution coefficient (which is close to relative volatility) between steam and water is close to 1 giving a constant concentration all over the steam - water system while with ammonia, liquid drains have a lower concentration.

The main disadvantages of morpholine are the relatively high molar concentration required, which is comparable to that of ammonia at a pH of 9.7, and the risk of increasing organic compounds content.

The consequence of the molar concentration is, like for ammonia at a high pH, observed on condensate or blowdown polishers. This is why plants with condensate polisher should not select morpholine or should by pass the treatment system most part of the time. French PWRs operating with morpholine do not have such a purification system and blowdown demineralizer cation resins are generally kept in operation after morpholine exhaustion so as to increase their life duration since the French option is not to regenerate these resins for avoiding any risk of secondary system contamination by either regeneration reagents or resin fines. In addition, nuclear grade resins are used.

The second main consequence of morpholine is the increase of organic acids, acetate and formate concentration which can be observed in some cases. The decomposition steps of morpholine, hydrolysis followed by oxidation, produces organic ions in various parts of the secondary system of operating PWRs. It has been shown that the highest organic acid concentrations have been observed in presence of oil or grease pollution, and particularly with significant air ingress at the condenser level, confirming the oxidation step in morpholine decomposition. Even though laboratory studies and operating experience feedback never revealed any corrosion of steam generator tubing associated with pure organic acid content observed in operating units, their concentration should be as low as possible for keeping a low cation conductivity which is the key on line monitor for secondary system overall contamination.

**Ethanolamine (ETA)** is an alternate amine, sponsored by EPRI [6] and is largely used in the USA and an increasing number of countries with PWR units. The main advantage of ETA is the lower molar concentration needed, as compared to morpholine, to get the target pH at operating temperature.

Consequently, the load on condensate polisher or blowdown demineraliser resin will be lower with a beneficial effect on one or several of the following parameters : (i) operating cost, (ii) run length of cation resin in hydrogen form, (iii) reduced frequency of resin regeneration, (iv) better possibility of increasing hydrazine concentration for the time of operation with ammonia elimination on cation resin in H form as compared to resin exhausted with morpholine, (v) nitrogen compounds release into the environment, which is nowadays of always increased concern.

The relative volatility of about 0.6 for ETA, instead of 1 for morpholine, will not give a constant concentration along the different parts of the steam-water system with a possibility of having some portion of copper alloy components with a too high ETA concentration and an increased corrosion. On 2 phases (steam + liquid) parts of the system, the liquid phase that may be affected by FAC will have a higher concentration of alkaline reagent with ETA and thus will be more efficiently protected against corrosion.

Another important advantage of ETA is its higher thermal stability inducing a lower concentration of organic acids than with morpholine in some cases even though it is not a key issue with morpholine.

Finally, ETA is a good selection when condensate polisher are continuously used.

**3.4. Hydrazine.** A reducing environment in the secondary side of steam generators is of utmost concern for trying to minimise occurrence and progression of intergranular stress corrosion cracking of Alloy 600 tubing, which is the main secondary side degradation of steam generator tubing in most of the western countries.

The main reductive reagent used in PWR units is the hydrazine ( $N_2H_4$ ) which may react with oxygen and has the advantage of having its excess thermally decomposed into ammonia, an acceptable reagent of the system.

One largely used hydrazine concentration is around 100  $\mu\text{g}/\text{kg}$  as recommended by many organisations.

However, hydrazine addition is not the way to solve air ingress into the condenser, which has to be strictly searched by plant staff, since it has been shown that hydrazine added in the condensate water does not react significantly with oxygen.

Furthermore, for plants with copper alloys, hydrazine must not be increased in a too large

proportion if ammonia resulting from its thermal decomposition is not eliminated by condensate polisher operating continuously in hydrogen form.

In addition, the drawbacks of high hydrazine concentration with ammonia elimination by condensate polisher are the operating costs, the release of wastes to the environment associated with resin regeneration and the potential detrimental influence on flow assisted corrosion of carbon steels associated to the highly reducing environment which is not favourable for a stable iron oxide on the carbon steel surface.

EDF studied the influence of the feedwater hydrazine concentration (25, 100 and 200  $\mu\text{g}/\text{kg}$ ) on the suspended solids reducing properties and on the redox potential, in order to optimize the hydrazine content with respect to minimizing SG tubing IGA/SCC. From these tests, it was proved that increasing hydrazine above 100  $\mu\text{g}/\text{kg}$  was not relevant [7]. Moreover, an increase in the feedwater hydrazine concentration would lead to an increase of operating costs (reagent costs, SG blowdown resins replaced more often); it may also have a negative influence on carbon steels erosion-corrosion and increase the risks for sulfates to be reduced into sulfides and finally may have an environmental impact.

In EDF units, hydrazine recommended concentration in absence of copper alloys is in the range 50 to 100  $\mu\text{g}/\text{kg}$ . In the presence of copper alloys in the secondary system, the value is settled in order to cope with the maximum admissible pH.

#### 4. Closed Cooling Water System

**4.1. Objective.** Although the circuit was designed to avoid scaling and acid treatment was settled for sites with a scaling risk, scaling is encountered and evolving on some French Nuclear Power Plants (NPP) with closed cooling towers. Scaling is the direct consequence of precipitation of calcium carbonate due to :

- increase of concentration in the system by a factor of  $\approx 1.5$  in relation to evaporation of water in the cooling tower ;
- decrease of solubility with a slightly higher temperature.

Scaling is increasing on some NPP and not only in those where a potential risk was originally identified.

Furthermore, condenser and cooling towers scaling is a potential source of power limitation and maintenance costs in NPP cooled by river water without any pre-treatment of this water.

Unavailability of the NPP, tower structures degradation with time, as well as chemicals and thermal releases growth are the consequences of scaling. These are the reasons why it is important to bring responses to scaling problems in order to win in efficiency on the economical (power rate, availability, maintenance) and environmental point of view.

**4.2. Fouling phenomenon.** As it was known before NPP construction that scaling problems could appear on French cooling towers, loop tests were carried out with the upstream river in order to define the water ability to deposit scale on condenser tubes and cooling towers.

These tests allowed to distinguish two types of NPP whether or not a risk of scaling existed whatever the conception of the closed cooling system. For those where the risk was present, an acid injection facility was settled.

This acid injection is based on some key parameters such as outlet condenser temperature, total alkalinity of the river water and calcium concentration. Then, in order to remain under a limit of alkalinity in the installation, a level of sulfuric or hydrochloric acid is added.

For those where the risk was less important, specifications and operating conditions were determined to avoid scaling. If those specifications were met, no scaling problems should have been encountered.

Injection had been optimized in order to limit the quantity used and the subsequent impact to the environment. Therefore, different theories were implemented, which were specific of each NPP. If those models are correct and the corresponding criteria applied, no scaling problems should occur.

Scaling origins in cooling towers are linked to:

- The water quality evolution along the time.
- The water quality depends also on whether the river flow rate is supported by water from a dam; and on the industrial release which have evolved along time.
- The operating issues (eg unusual warm periods with thermal releases limitation which did not allow a sufficient make up and blowdown flow rate).
- The replacement of the brass tubing condenser by copper and zinc free materials.
- The biological treatment for elimination of Amoeba (*Naegleria Fowleri*) which may develop in the closed cooling system. This

treatment is alkaline so it could favour carbonate calcium crystals formation.

- The chemical release regulation; indeed new environmental constraints have been introduced by the Regulator, mainly for sulphate with an impact on acidic treatment.
- The presence of sludge and suspended solids from the river water probably enhance the deposit weight and has a consequence on the scaling rate,
- If the packing is designed to be very thermal efficient, the water film can be evaporated which enhances the scaling rate.

**4.3. Amoebae.** New issues are encountered with the presence of *Naegleria Fowleri* Amoeba (Nf) and its sanitary consequences. As a countermeasure, chlorination being almost forbidden in French NPP system, monochlorination is used to decrease the Nf level below 100 in the river downstream the NPP.

Such treatments are carried out in some French NPP during the warm season.

As indicated, it may have some consequences on the acidification treatment for carbonate solubilisation.

## 5. Conclusions

The chemistry regulation and control in the various systems of a PWR Nuclear Power Plant is a key and difficult work that needs to cover several aspects.

The first and main one is the corrosion mitigation of the various materials in presence in order to bring the correct answer to components duration, plant availability and safety, radioactive dose rates.

However, the other important objectives, operating costs and low impact on the environment, become more and more crucial.

The physico-chemical situation of the various systems are facing phenomena related to high temperature, heat flux and vaporization.

Thus, for the primary system, the efforts focus on the lithium concentration adjustment able :

- to reach a sufficient alkaline condition for minimizing corrosion products activation and transport ;
- to avoid the fuel cladding corrosion ;
- to mitigate any unacceptable deposition that would affect the axial offset anomalies.

The use of enriched Boron 10 for decreasing total boron concentration is an interesting but expensive approach.

For the secondary system, the presence of potential contaminants, mainly coming from the condenser and which may highly concentrate in the steam generator, particularly in flow restricted areas where the hideout phenomenon is occurring, is the difficult point which may create the condition for the stress corrosion cracking of sensitive steam generator tubing, when it is Alloy 600.

Then, the pH regulation is adjusted to the chemical properties of the alkaline reagent and the materials of the secondary system. More and more frequently, as an alternative way to ammonia treatment at pH<sub>25°C</sub> of 10, an amine is injected. Morpholine, with a partition coefficient of 1, is largely used in France while ethanolamine is the preferred reagent in the USA and several other countries.

Finally, the condenser cooling system needs to be treated in many cases when there is a cooling tower since calcium carbonate may precipitate and produce high amounts of fouling in the cooling tower packing or on the condenser tubing.

The situation in this circuit is also complicated with the need to eliminate the proliferation of amoebae during the warm season.

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