

INFLUENCE OF IMPURITIES ON CORROSION PRODUCTS BEHAVIOR IN FEEDWATER CONDITIONS

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ABSTRACT

Fouling and tube support plate (TSP) blockage in steam generators are major problems in the secondary circuit of pressurized water reactors plants. The identification of deposit formation mechanisms contributes to limit these phenomena. Although the deposit is mainly composed by magnetite, some impurities, in particular aluminum and silicon, may lead to its consolidation. This paper presents the results of tests performed in a specific experimental device named FORTRAND. The aim of these tests was to evaluate the impact of the presence of impurities (Al, Si) on iron behavior in the secondary circuit feedwater conditions. Tests were performed in single phase flow at 150 L/h and 220°C in a morpholine/ammonia/hydrazine medium. The injection of aluminum and silicon separately presents no influence on speciation of these species and iron species in the loop, as well in the bulk as in the oxide layer. But the injection of both species at the same time induces both a slight increase in wt% of Al in oxides layer formed on carbon steel tubes and an increase of the Al concentration in solution. Other tests need to be conducted in order to improve the knowledge of the interaction between Al, Si and iron species.

INTRODUCTION

Limiting fouling and TSP blockage in steam generators (SG) represents a major issue in terms of performance of pressurised water reactor (PWR) power plants. These phenomena affect the heat transfer at tube surfaces. Corrosion products deposits are formed in the feedwater system of the secondary circuit mainly by flow accelerated corrosion (Chexal et. al., 1998). Reducing the source term generated by this type of degradation is one way of limiting fouling and blockage in SGs. A specific test loop, called "FORTRAND", was built at EDF R&D to study the formation and transport of deposits on pipes representative of the feedwater system of secondary circuit in PWR power plants. A test section, made in carbon steel and operating at high temperature, contains removable segments that are characterized after each test. Corrosion products are reproduced inside the device under nominal operating conditions of the feedwater system of the secondary circuit

(Delaunay et. al., 2011). Characterizations confirm the presence of magnetite after tests performed at 220°C with deaerated water conditioned by ammonia and hydrazine as in the secondary circuit medium. To improve the understanding of products formation, tests were performed in FORTRAND to follow the evolution with time of the carbon steel tubes behavior under standard secondary feedwater system physico-chemical conditions (Delaunay et. al., 2012). Many physico-chemical parameters may have an influence on the oxide behavior. The growth of oxide related to corrosion depends on chemical, hydrodynamic and metallurgic conditions (Chexal et. al., 1998). Evolution of deposits is influenced by deposition-re-entrainment of particles, precipitation-dissolution of species, and structural reorganization of the deposit. Two impurities in particular, present in the secondary circuit may affect the oxide behavior. This paper presents the results of changes in the deposit formed in conditions representative of the feedwater system and simulated in the FORTRAND loop versus impurities presence (Al, Si, Al and Si).

Experimental conditions are first described with the operation of the experimental device. Tests performed successively with aluminum, silica and both impurities for equivalent duration are then described. Analyzes of chemical composition of sampling performed during tests allow to follow the behavior of aluminum and silica. Scanning Electron Microscopy (SEM) and desquamation were used to analyse the oxides layers formed during these tests. Thanks to the weighing of segments before and after tests, iron release in solution was also quantified. These observations on the effect of aluminum and silica on corrosion products behavior are finally discussed.

EXPERIMENTAL

Description of the loop

The FORTRAND loop is dedicated to study the formation and transport of deposits in the feedwater system in pressurized water reactors. The loop includes a test section working in a single-phase flow and made of carbon steel, as in the pipes of the feedback system located between the condenser and the steam generator of PWR. The test section can be heated up to 250°C (Fig. 1).

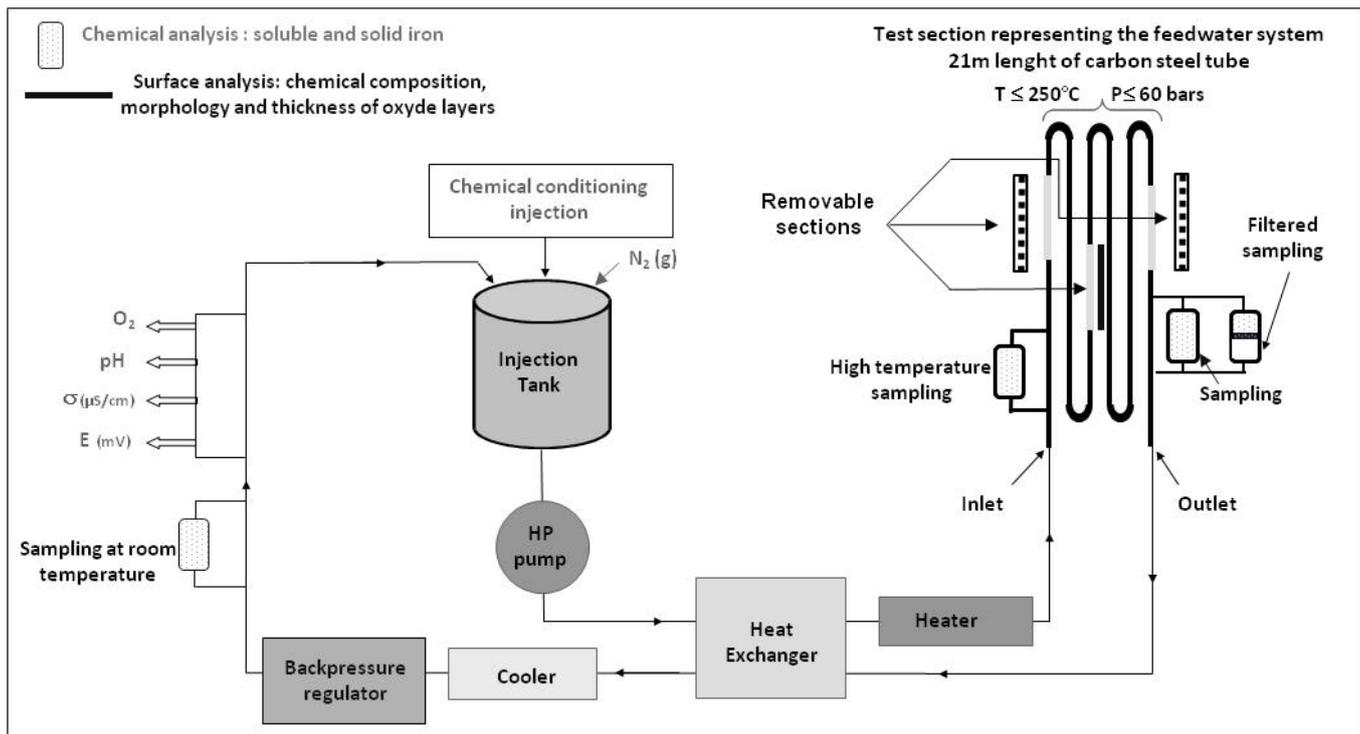


Fig. 1 Scheme of FORTRAND loop.

The other part of the circuit made in stainless steel is composed by functional elements (injection tank, HP pump, heat exchanger, heater, cooler, backpressure regulator). In this part of the loop, several chemical parameters are measured at room temperature during the test: pH, conductivity, redox potential and dissolved oxygen.

The high pressure test section (HP part) includes three removable segments (length 50 cm). The removable segments located at the inlet and at the outlet of the test section are each composed of ten segments 5 cm length (Fig.2). This configuration allows analyzing the chemical composition, morphology and thickness of deposits after the test by SEM and chemical analyses.

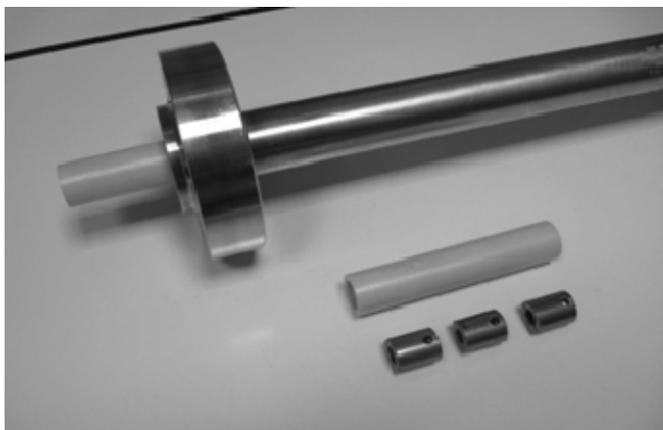


Fig. 2 Removable segments at the inlet and the outlet of the FORTRAND loop test section.

In the high pressure part of the test section, the Reynolds number varies between 3.3×10^4 and 5×10^4 when the temperature increases from 150°C to 250°C . In the low pressure part of the loop, the Reynolds number is in the range between 7.4×10^3 and 8.3×10^3 for temperatures varying between 25°C and 30°C .

Experimental procedure

In each test, the low-pressure section of the circuit is set up, the injection tank containing 70 L of demineralized water (18.2 MΩ). Continuous nitrogen flow is then used to eliminate oxygen. When the oxygen concentration is lower than 0.02 ppb, the high-pressure circuit is connected. Then, the heater is started with a progressive increase to the test temperature. The chemical conditioning products are injected into the injection tank in the deoxygenated conditions. The compounds, which are stable at high temperature, are injected before the increase of temperature while other products, like hydrazine and morpholine, are added once the test temperature is reached.

Chemical parameters are controlled in two ways: in the outlet of the injection tank and in the outlet of the test section. All parameters, measured at room temperature, are registered continuously.

During all the test duration, periodic samplings are made at room temperature and at test temperature, in the inlet and the outlet of the test section to evaluate soluble and solid iron.

At the end of each run, the temperature is lowered down to the room temperature value. All the solution is emptied and the test section is flushed by demineralized and deoxygenated water. The removable segments are withdrawn and changed. Then the sections are kept under a nitrogen gas atmosphere.

Test conditions

To simulate the environment specific to the feed water of the secondary circuit of PWR plants demineralised and deaerated water is used to prepare the solutions. This study was done at low pH conditioning, $\text{pH}_{25^\circ\text{C}}=9.2$, theoretically fixed by 5 ppm concentration of morpholine and less than 300 ppb of ammonia. Morpholine was injected at the beginning of the test. The solution was also conditioned with hydrazine throughout the duration of the test to control the redox potential and to reduce oxygen. Semi-continuous injection maintained a concentration of 15 ppb ± 5 ppb. The regulation of the pH during these tests depended on the thermal decomposition of hydrazine into ammonia. Considering this parameter, the ammonia concentration of the solution was adjusted by an injection. Monitoring the conductivity to determine the increase of the ammonia concentration during the tests was more sensitive than the variation of pH. The pH was measured on samples taken in the laboratory with an uncertainty of 0.1 pH units. Amine concentrations were verified by ionic chromatography. Tests are performed at the highest temperature reached in the feedwater of the secondary circuit of PWR plants, i.e., 220°C. The pressure reaches 50 bars. The flow rate reaches $0.82 \text{ m}\cdot\text{s}^{-1}$ inside the test section.

Carbon steel used in the test section is NF A 49-210 whose chemical composition in weight % is as follows: C<0.18%, Si<0.35%, Mn<0.75, P<0.04 and S<0.04%. The stainless steel used in the cold part is AISI 316L with the following chemical composition: 17% Cr; 12% Ni; 2% Mo.

Removable segments analysis

The difference in weight of the segments before and after the tests showed the weight of iron corroded during the test that was released into the solution. After each test, one segment was prepared for SEM analysis and cut into two half tubes, one part was used for the microstructure observation and the other part was covered by aluminum paper, coated and polished to observe the thickness of the surface oxide layer. Scanning electron microscopy observations were performed with a high resolution microscope GEMINI LEO 1530. Samples surfaces were analyzed by secondary electron imaging and by energy dispersive X-ray spectrometry (EDX). Another segment of each test was submitted to desquamation according to standard ISO 8407 January 2010, so as to quantify the oxide layer present on the surface of the tubes after test. The outer part of the tube was coated with a varnish. The solution attacked the oxide existing on the inside of the tube. The tubes were then weighed after each 10-minute desquamation. The weight loss was due to dissolution of the

total oxide present on the surface. A multi-elementary analysis of the desquamation solution was done by ICP-AES to determine the oxide layer chemical composition. Tests on reference tubes established that the surface oxide was eliminated in one 10-minute desquamation. The steel itself was then attacked. Therefore, in this study we will consider that the loss of weight after one desquamation corresponds to the oxide present on the tube surface. This result provided an estimate of the weight of oxidized iron forming the oxide layer bonded to the surface. These two combined data helped to estimate the total quantity of corroded iron during the test.

Chemical analysis

Periodic samples are stabilized under glove box by an acid. They are then analyzed by ICP-AES to know total concentration of aluminum and silicon in the samples.

Performed tests

Three experiments were carried-out with injections of impurities: the first one with three injections of aluminum, the second with silicon injection only, and the last one with both aluminum and silicon. Table 1 summarizes these tests conditions.

Table 1. Test conditions.

Test n°	Duration (hours)	Total Injected Concentration	
		[Al]i (ppb)	[Si]i (ppb)
1	443	325	/
2	500	/	100
3	344	1000	1000

For each test, twenty removable segments are installed in the test section of FORTRAND loop. Three carbon steel segments are in recipes conditions and the others correspond to different materials. Indeed segment in titanium and in Inconel are installed in the test section during all duration of the three tests.

RESULTS

Chemical conditioning monitoring

The concentration of morpholine during the tests was between 5 and 6 ppm ± 0.5 ppm. Conductivity increased uniformly during the tests. The increase in conductivity corresponds to an increase in ammonia (28 ppb per day). This result is consistent with the calculation of the ammonia concentration resulting from the decomposition of hydrazine based on semi-continuous injection. This set value was adjusted from the hydrazine concentration measured by spectrophotometry supported by the measurement of the in-situ oxidation-reduction potential.

Monitoring of the pH at ambient temperature did not show even a slight increase due to the increase in the ammonia concentration. The pH remained between 9.2 ± 0.2 pH units during the test. These data were stable and confirmed control of the chemistry in the loop. The chemical analyses indicated that the concentration in ammonia was 100 ppb at the beginning of the test and tended towards 350 ppb regardless of the test duration. The uncertainty on the ammonia analysis was 50 ppb. Therefore, these results provided guidance but they appeared to agree with the expected concentrations during the tests. Dissolved oxygen was measured and its concentration always remained less than 0.5 ppb. The electrochemical potential measured at 25°C was correlated to the hydrazine concentration and was equal to $-50 \text{ mV/Ag/AgCl} \pm 30 \text{ mV}$ throughout the tests. The ultra-pure solution circulates in the loop without any polishing. The following of iron with times indicates:

- Concentration of dissolved iron about 3 ppb in test section,
- Concentration of particulate iron about 20 ppb in the test section.

Species in solution

Thermodynamic predictions. Predictions of speciation were performed by MULTEQ code developed by EPRI (Chemworks, 2012). The cold part composed of stainless steel tubes has well known chemical properties due to the continuous measurements of chemical parameters. The temperature varied between 24°C and 29°C, and the redox potential was around $0 \pm 0.2 \text{ mV/SHE}$. Solubility of aluminum is very low at $\text{pH}_{25^\circ\text{C}}$ between 9.2 and 9.4, see in Table 2. The solubility of silicon is more important for these conditions, around 900 ppb (Table 2). At 220°C, in the test section, the solubility of these species is higher especially for aluminum, Table 2. All silicon should be soluble and aluminum dissolved species should reach a concentration of 200 ppb in solution.

Table 2. Solubility of Alumina and Silicium in FORTRAND loop physico-chemical conditions according to MULTEQ calculations.

Source : MULTEQ	T (°C)	pH _T	Injected concentration (ppb)		Dissolved concentration (ppb)	
			[Al]	[Si]	[Al]	[Si]
			25	9.2	325	/
9.4	325	/		15	/	
9.2	/	100		/	100	
9.4		100			100	
9.2	1000	1000		7	860	
9.4	1000	1000		15	955	
220	6.2		325		200	
				100		100
			1000	1000	200	1000

During the tests, the fluid continuously circulates from the cold to the hot section of the loop and vice-versa. Thermodynamics predict that an important part of injected aluminum precipitates in the cold part, only few concentration of some ppb stay in solution. That's why the injection of impurities, aluminum as silicon, was made at the inlet of the test section at 220°C. Silicon stays mainly in dissolved form according to thermodynamic prediction.

Following of species in solution during the tests. Figure 3 presents the concentration of aluminum versus time during test 1 (with injection of aluminum only). At each arrow, an injection of 100 ppb of aluminum was carried out. Total concentration of aluminum quickly reaches only between ten and twenty ppb which corresponds to the dissolved aluminum amount according to thermodynamic predictions.

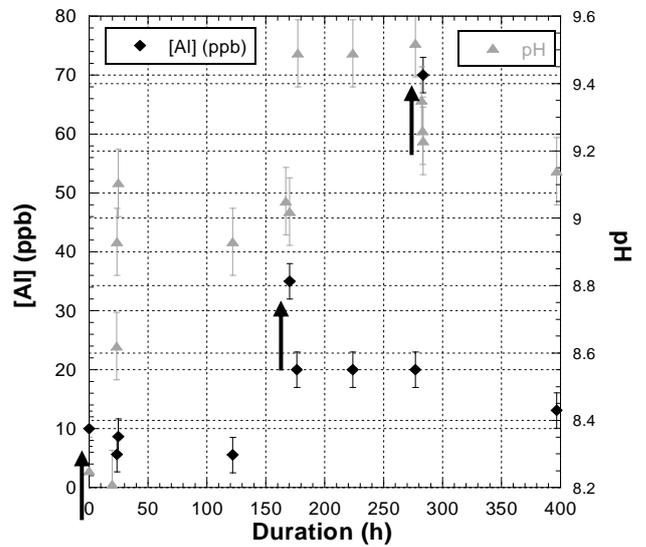


Fig. 3 Aluminum and pH variation versus time in the Fortrand loop, test 1, $\text{pH}_{25^\circ\text{C}} = 9.2$.

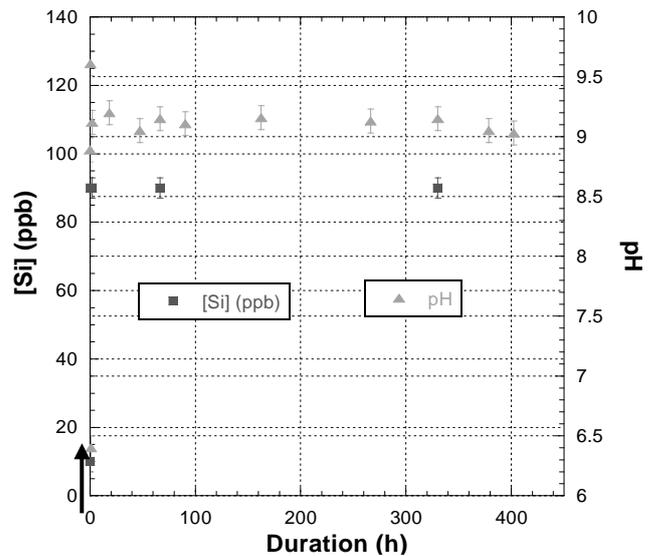


Fig. 4 Silicon and pH variation versus time in the FORTRAND loop, test 2, $\text{pH}_{25^\circ\text{C}} = 9.2$.

Evolution of silicon concentration versus time during test 2 is presented in figure 4. All injected silicon stays in solution. Thermodynamic calculation indicates that the limit of silicon solubility is about 900 ppb, so the injected silicon (about 100 ppb) stays in solution. The results are in accordance with thermodynamic predictions.

During the test with the both species, aluminum and silicon, the amount of silicon present in the solution is the same as the injected amount. According to the thermodynamic predictions, all silicon is in soluble form in these conditions of temperature and pH. The concentration of aluminum reaches between 100 ppb and 200 ppb (Fig. 5) whereas dissolved aluminum predicted in these conditions should be of about 15 ppb at 25°C (Table 2).

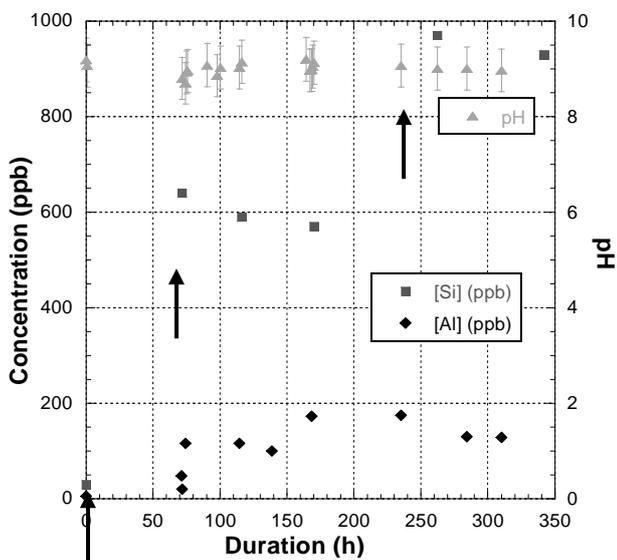


Fig. 5 Silicon, aluminum and pH variation versus time in the FORTRAND loop during test 3, $\text{pH}_{25^\circ\text{C}}=9.2$.

Oxidation of the tubes during the tests

To improve understanding of corrosion products formation, transport, and deposit, tests were performed in FORTRAND to follow the evolution of the carbon steel tubes behavior under secondary feedwater system physico-chemical conditionsⁱⁱⁱ. The results of previous tests performed in the FORTRAND loop are presented in figure 6. The aim of this campaign was to follow the deposit formation under conditions representative of the feedwater system. These tests were carried out in the same basic conditions of the last test performed with an injection of aluminium, silicon or both, i.e. $T^\circ\text{C} = 220^\circ\text{C}$, pH imposed by morpholine at 9.2 at 25°C and hydrazine semi-continuous injection to maintain redox potential. The obtained results show a slightly increase of tubes corrosion up to 400 h of test in accordance with general corrosion rate and then an important increase of both iron release in the solution and quantity of oxide on the surface with the test duration.

The following of corrosion during the tests with aluminium and silicon injection are presented in figure 6 (rounds) in comparison with the results of the previous tests (triangles). The iron quantity in the oxide layer formed during the tests (in blue Fig. 6) is in the same magnitude than tests without impurities injection. The iron released in the solution during test 3 (with both Al and Si) follows the curve of the previous test. Moreover in the test 1 (with Al) and the test 2 (with Si) more important quantity of iron is lost in solution. That's why the quantity of total oxidized iron is higher than the corroded iron expected thanks to previous tests performed versus time.

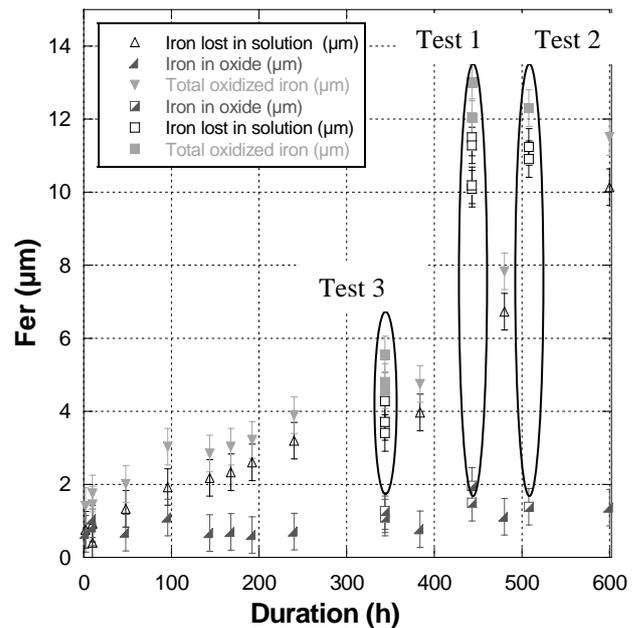


Fig. 6 Corrosion monitoring of the base metal depending on the test duration.

Chemical composition of the surface oxide

Table 3 presents the evolution of the weight of major chemical species in the oxide layers for each test. Three tubes are analyzed by desquamation for the test n°3, two for the test n°1 and one for the test n°2. The composition of oxide layer in standard physico-chemical conditions carried out in the last campaign on FORTRAND loopⁱⁱⁱ are indicated in Table 3, at 480 h and 960 h. The oxide layer is predominantly composed of iron but other species are also present in the oxide, in particular zinc and phosphorus.

No change in weight percentage of silicon is observed between tests with Si injection or without. Moreover weight percent of aluminum slightly increase in the oxide present after tests with aluminum and silica injection. This observation is not identical to that of test n°1 with only aluminum injection where aluminum weight percent stay about 0.10% as in the test without any injection.

Table. 3 Evolution of chemical composition of the oxide layer with time and injection of Al and Si (weight %).

Test n°	Duration (h)	%Fe	%Al	%Si	%Zn	%P	%Mo	%Ni
3	344	96.42	0.57	0.21	1.33	0.56	0.14	0.18
3	344	96.69	0.45	0.22	1.21	0.51	0.15	0.17
3	344	96.44	0.58	0.20	1.35	0.56	0.14	0.16
1	443	96.74	0.20	0.23	0.70	0.31	0.86	0.13
1	443	97.46	0.13	0.21	0.48	0.22	0.70	0.07
/	480	96.70	0.12	0.19	1.01	0.75	0.35	0.16
2	508	97.28	0.06	0.33	0.53	0.28	0.62	0.15
/	960	98.04	0.10	0.24	0.23	0.16	0.29	0.19

DISCUSSION

Although iron is often the prevalent element identified in the analyzed deposited, aluminum and silicon were also largely observed in deposits some time in more important quantity than iron (Little and Brown, 2012). These species are suspected to act as binding species and play an important role in the formation and consolidation of collars at the tubes-tubes sheets (Varrin, 1996). In order to determine the action of silicon and aluminum in the feedwater system conditions, tests were performed in the FORTRAND loop which allows reproducing physico-chemical conditions of feedwater system. The operating of this device present an important constraint: the solution circulates in loop with a refreshing and reheating. The speciation of aluminum and silicon are impacted by the residence time at 25°C for this species. It should be noted that this part of the loop made in stainless steel is covered by an important layer of goethite (Delaunay et al., 2011).

The results of tests with aluminum injection present a total concentration of aluminum in flow which tends to 20 ppb. This concentration corresponds to the concentration of dissolved species according to the thermodynamic calculation thanks to MULTEQ. Tests show that thermodynamic equilibrium seems to be quickly reached in these conditions but the oxide layer present on the carbon steel does not show an increase in Al wt%. Aluminum precipitates probably in the cold part of the FORTRAND loop, which is consistent with MULTEQ calculations. During the test with silicon injection only, all the silicon stays in solution. The injected concentration is less than solubility of this species. But no sorption or change in oxide composition is observed in this test versus time contrary to the literature results. Indeed all studies on sorption of silicon on magnetite agree that maximum of sorption occurs at basic pH between 9 and 11. Jordan studied concentrations lower than solubility concentration (10^{-4} M) at 25°C, he shows that 10% of silicon is sorbed at pH equal to 9 (Jordan et al., 2007). Identical results were presented by Yang for more important initial concentration, between 10^{-4} M and 10^{-3} M (Yang et al., 2008). According to Philippini works, between pH 7.6 and 9.5 at 25°C, sorption

of silicon on magnetite reaches 22% with 2 g.L⁻¹ of magnetite and $4.7 \cdot 10^{-5}$ M of silicon (Philippini et al., 2006). The tests made with goethite shows 100% of silicon sorbed at pH 9.2 (1g.L⁻¹ of magnetite and 10^{-4} mol.L⁻¹ of silicon) (Philippini et al., 2006). The analyses of sampling during each test allowed estimating a concentration of particulate iron of about 20 ppb. This concentration is very low to induce observed sorption of silicon during the tests. Moreover all tubes surface is covered with iron oxide layer, magnetite in the test section, goethite in the section at room temperature. As no attenuation of silicon concentration was observed during test 2, we could suppose that sorption on tube surface should be prevent by the hydrodynamics near the wall. The results of these two tests (n°1 and n°2) are consistent with thermodynamic predictions: no interaction between magnetite, present on carbon steel surfaces and silicon or aluminum. The last test aimed to determine the influence of both aluminum and silicon in solution. Their interactions may formed alumino-silicate, and influence the behavior of corrosion products. In the conditions of the FORTRAND loop, no silicon was sorbed or incorporated in the iron oxide. Its concentration stayed stable after each injection during test n°3 while aluminum had a different behavior with presence of silicon in the loop. Indeed, the aluminum concentration in solution is largely higher than the solubility of this species at 25°C. Interactions with silicon may explain this observation, alumino-silicates stay in solution instead of aluminum alone which precipitates. The analyses of oxide layer present on the tubes surface after the test present a slightly increase in aluminum wt % without corresponding silicon wt % increase. The transport of aluminum in test section at 220°C could be favored by silicon presence and formation of alumino-silicates complex whereas aluminum alone precipitates in the section at room temperature. The change in temperature and pH may influence speciation of these species and cause precipitation of a part of aluminum. Moreover, this observation needs to be confirmed by other tests. All these results seems to indicate that in the feedwater physico-chemical conditions, simulated in the FORTRAND loop, formation, transport and deposition are lightly influenced by the presence of aluminum, silicon or both. No sorption is observed on magnetite formed on tubes carbon steel surfaces. The speciation of aluminum and silicon follows the thermodynamic predictions in the conditions of FORTRAND loop. Other tests with higher impurities concentration, with different test duration allow improving the study of aluminum and silicon influence on corrosion products behavior.

CONCLUSIONS

Interactions between major corrosion products, magnetite, and some impurities, aluminum and silicon, are incriminated in the formation of hard sludge in steam generators. In order to determine their behavior in feedwater system physico-chemical conditions, experiments were performed in a specific loop FORTRAND which allows to reproduce chemical conditioning of secondary

circuit and to study physico-chemical parameters influence. Measurements and samplings made during tests are used to control chemistry. Characterization of removable tubes carried out after tests conducts to quantify corrosion during the tests. Three tests were performed to estimate the influence of aluminum and silicon on iron oxide in feedwater conditions.

Speciation of aluminum and silicon, injected separately in two different tests, are in accordance with the thermodynamics predictions. No specific reaction with iron is observed: neither co-precipitation nor sorption. During test with injection of both aluminum and silicon, more aluminum was present in solution than in test without silicon. The formation of alumino silicates may be at the origin of this observation. In this tests the wt% of Al in oxide layers on the carbon steel tube is higher than in oxide formed in the other tests but wt % of Si is the same regardless the test performed. The retention of aluminum content in solution thanks to silicon should induce this increase. This last test confirms the impact of the presence of both species on iron behavior in feedwater physico-chemical conditions. More tests with different parameters (concentration, duration) could improve this observation. Analyze of particles which circulate in the loop during tests should allow to determine speciation of alumino-silicate. Some tests should also be conducted in order to follow the influence of temperature on alumino-silicates behavior in secondary circuit chemical conditions. The final objective is the knowledge of alumino-silicate impact to avoid formation of hard sludge in steam generators.

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