Feedback from Stainless Steels Corrosion related Issues during Maintenance Operation in Sodium Fast Reactor: SCC in caustic solution and Intergranular Corrosion by Acid Solution

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Abstract. Stainless steels are widely used in Sodium Fast Reactor and exhibit a very satisfactory feedback regarding their behavior in contact with high purity sodium.

The French past experience with Phenix and Superphenix Nuclear Power Plants (NPP) confirmed this trend but it also highlighted that utilities have to take care at material susceptibility to different corrosion mechanisms during maintenance operations: Stress Corrosion Cracking (SCC) induced by caustic solution and InterGranular Attack (IGA) induced by acid solution used during maintenance operation.

Presently, an overview of these mechanisms, the feedback and lessons learned from Phenix operation and maintenance operation are presented as well as the present opportunity to investigate and characterize materials coming from the Phenix dismantlement. Finally, the precautions for ASTRID design and future operation are highlighted.

Key Words: Stainless Steel, Maintenance, Stress Corrosion Cracking, Intergranular Attack.

1. Introduction

In the scope of structural materials studies for ASTRID (Advanced Sodium Technological Reactor for Industrial Demonstration) prototype [1], the feedback obtained through design and operation of Phenix (PX) [2-3] and SuperPhenix (SPX) [4] NPP but also through the associated R&D studies is large and valuable. In this context, it has been shown that stainless steels are widely used in SFR and this choice is confirmed as relevant. These alloys present a very satisfactory feedback regarding their behaviour when in contact with high purity sodium.

In this paper, the authors want to highlight that, in front of these good properties in pure sodium, utilities have nevertheless to take care at material susceptibility to different corrosion mechanisms during maintenance operations that happens before or after their use in liquid sodium: Stress Corrosion Cracking (SCC) induced by caustic solution and InterGranular Attack (IGA) induced by acid solution during the maintenance operation.

After an overview of these two mechanisms, the feedback and lessons learned mainly from PX will be presented. Moreover, the opportunity of materials investigations on components with PX and SPX dismantling [5-6] will allow us to confirm that solutions and preventive measures put in place during reactors maintenance operations were relevant. In conclusion, the precautions for ASTRID are highlighted.

2. Overview of corrosion mechanisms during SFR maintenance operations

The corrosion risks [7] appear if some conditions related to material factors, operating conditions and chemical environment are simultaneously met (*see FIG.1.*). Consequently, the chance to get such a corrosion issue remains low but sufficient to be studied as highlighted by PX and SPX feedback. During the operation and maintenance, some of these parameters are well known and managed, while some of them cannot be controlled. This is why, solutions and preventive measures have to be put in place regarding design rules and/or operating procedures.

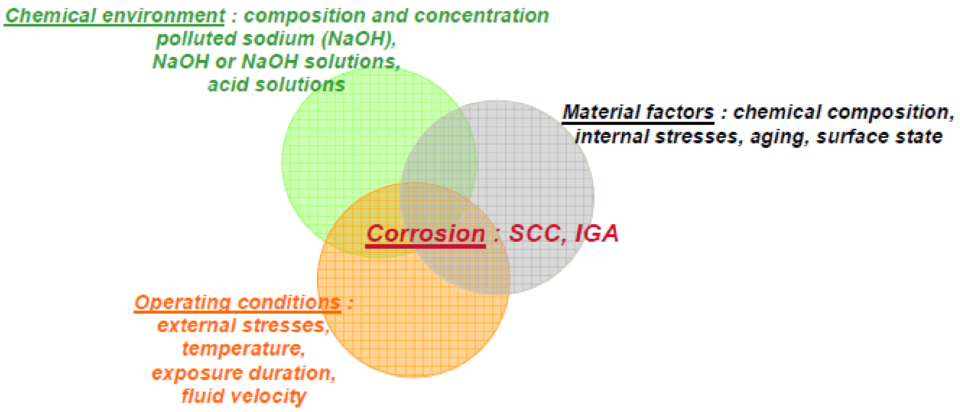


FIG.1. Schematic view highlighting conditions necessary for corrosion [7]

Hereafter, the two main corrosion issues for stainless steels during maintenance operation are described: SCC induced by caustic solution and IGA induced by acid solution. It will be noted that other corrosion issues that could occurred during normal operation or accidental ones are not addressed in this paper.

2.1. Stress Corrosion cracking induced by caustic solution

During maintenance operation at ambient temperature and for components where the liquid metal was emptied, sodium residue might come in contact with moist air leading to the formation of sodium hydroxide and aqueous sodium hydroxide.

The existence of this aqueous phase will be dependent of temperature and water partial pressure. Its formation cannot occur as the temperature increases since the equilibrium water pressure should be too high. So, aqueous caustic solution can only be formed during shutdown or maintenance at ambient temperature. The operating issue refers to the moment when the component are pre heated at 180-200°C during the filling procedure.

Indeed, regarding the different parameters mentioned on *FIG.1*, risk of SCC induced by caustic solution can appear on a component as these 3 following conditions are reached simultaneously:

- Presence of concentrated aqueous sodium hydroxide
- Presence of stress (even at low level): residual or operating ones
- Holding during a sufficient time in temperature range of risk for the material of interest.

Previously, experimental investigations have been performed in order to determine, for different materials families, the area of caustic SCC sensibility as a function of temperature and NaOH concentration [8]. As shown on the Hoffman diagram (*see FIG.2*), the risk of SCC for austenitic stainless steel ranges from about 120°C to 200°C in terms of temperature and from about 30% to 80% for the caustic solution concentration. These values are both higher than for carbon steels.

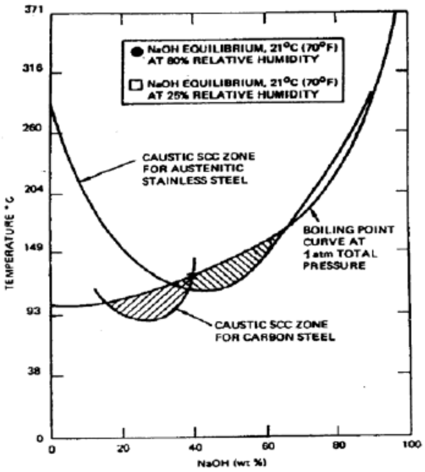
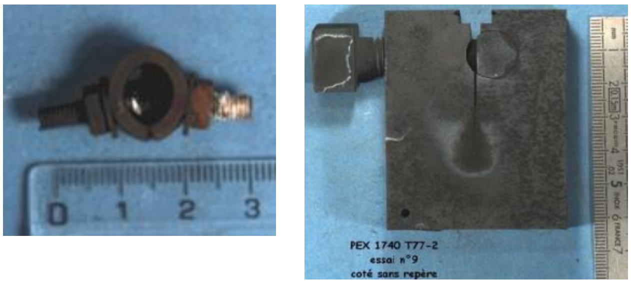


FIG.2. Caustic Stress Corrosion cracking zones for different steels (Hoffman diagram) [8]

The tests performed on pre-stressed specimens have shown that cracks can arise in some ten hours [8-9]. Different types of cracks have also been observed (intergranular or intragranular propagation ways) depending of stress level and/or NaOH concentration. The SCC could be due to a dissolution-passivation mechanism but the actual weight of different parameters such as the microstructure, the chemical composition variation in a same material family does not seem to have a significant effect. Nevertheless, this last point was not largely studied.

In order to define the domain of caustic SCC sensitivity for a material, pre-stressed specimens have to be exposed to aqueous sodium hydroxide in a specific device as presented in *FIG.3.*, for example. Temperature and solution concentration have to be varied across specified ranges. On one hand, the evaluation of the SCC sensibility can be assessed through C-Ring specimen (*see FIG.4a.*) and the other hand, measurement of corrosion cracks rate can be determine with test performed on specific WOL (Wedge Opening Loading) specimens (*see FIG.4.b*).

FIG.3. EDF R&D device for tests in aqueous sodium hydroxide



a) C-Ring specimen b) WOL specimen

FIG. 4. Specimens used for corrosion test (example on ferritic steel)

2.2. Intergranular attack

Intergranular attack of stainless steel is observed when a sensitized material is exposed to an oxidizing and/or acid environment. It may concern base metal and welds. Material degradation happens only when these two conditions are met together. As the use of oxidizing environment is necessary to achieve specific operation such as decontamination of the component before repair/maintenance, it is critical to assess when the material is in a sensitized state.

As stainless steel is exposed to high temperature (> 400°C), enriched chromium carbides precipitation appears as mentioned in a Time-Temperature-Precipitation diagram - TTP (*see FIG.5.*). Due to preferential precipitation at grain boundaries, chromium depletion zones occurs locally, meaning that locally the material lost its stainless behavior if the Cr depletion is high enough. In such case, the material is said "sensibilized". A localized intergranular corrosion which can result into a severe grains decohesion in some cases, can be observed *when the material is in contact with an oxidizing and/or acid environment* (*see FIG.6.*). Nevertheless, on the long term if the component remains in temperature, the chromium diffusion from the bulk to the depleted zones would be effective enough to increase the chromium content locally and suppressing the sensitized effect.

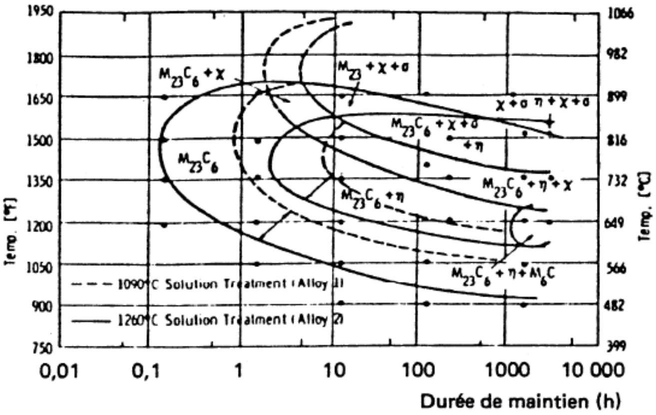


FIG.5. Time-Temperature-Precipitation diagram for 316L [10]

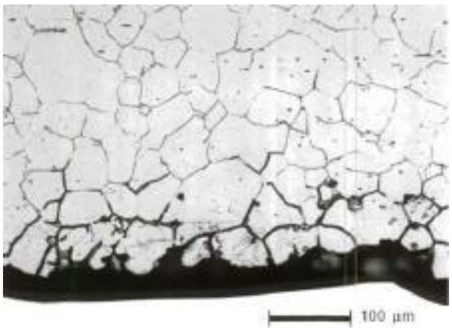


FIG. 6. Intergranular attack of 316L stainless steel after standard corrosion test

This sensitized area is defined by “Time-Temperature-Sensitization” diagram (TTS) – *(see FIG. 7.)* where the domain of interest is experimentally determined by standard accelerated corrosion test in specific medium (ISO 3651-2 regarding test in sulfuric acid copper sulfate boiling solution / Strauss test) on different heat treated specimens. It must be noticed that this standard conditions could be considered more severe that the conditions encountered in an industrial scope. This diagram shows the duration required for an isothermal sensitization. .As observed on *FIG.7.*, the carbon content plays a significant role on the time/temperature position of the sensitized area. Another parameters regarding the chemical composition and the fabrication route can also play a less significant role on the sensitized area location. Otherwise, the TTS diagram does not give relevant information on the sensitization during welding or slow cooling. By this way, the austenitic stainless steels optimization for SFR application deals with the diminution of carbon content mainly to prevent the sensitization during fabrication and start-up of reactor (forming, heat treatment, welding, …..) when elevated heat temperatures can be reached. The RCC-MRx grade 316L(N) [11] – low carbon nitrogen stabilized austenitic stainless steel – optimized for SFR application results mainly from a compromise between the mechanical properties at high temperature (creep, ageing,…) and the intergranular corrosion resistance.

Nevertheless, if it is a great interest to avoid materials sensitization during fabrication and start-up process, as illustrated in *FIG.8.* on a 316L TTS diagram, regarding in service long term operation until 60 years and SFR’s elevated nominal temperature, many components will cross this sensitization area. For example, at a temperature of 500°C, it is reached after a duration of around 50 000 h until more than 200 000 h. At a lower temperature this sensitized domain is shifted toward longer times (*for example see circled area in FIG.8.*).

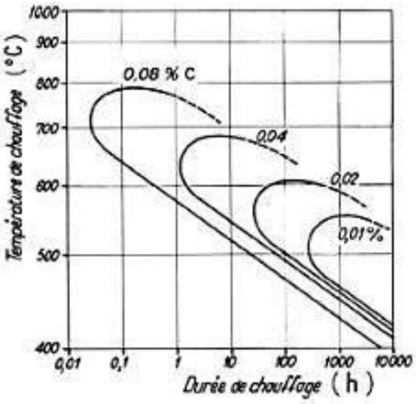


FIG.7. TTS diagram for 18-10 stainless steel grade highlighted the carbon content effect – result obtained after standard corrosion test

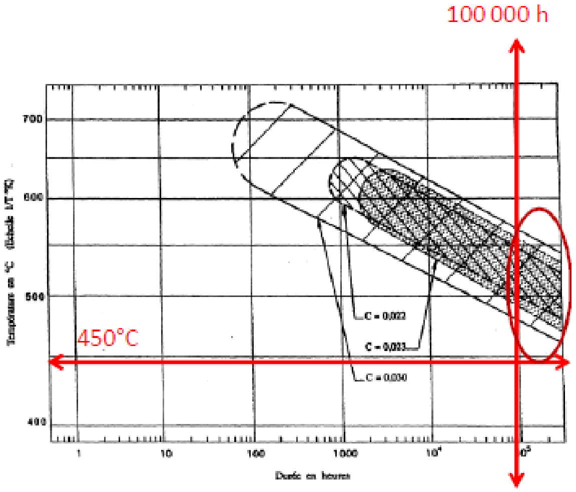


FIG.8. TTS diagram for 316L stainless steel with different carbon content.

Regarding nominal operating conditions, no detrimental effect is expected as sodium coolant is a reducing medium.

During the maintenance operation, acid solution can be used for surface cleaning and/or decontamination, so plants operators need to know if the material is sensitized or not. Only to that condition, efficient maintenance procedure could be done. In addition, some improvements in the design are expected to prevent any retention of moisture or air inlet during maintenance. This is considered as key elements to avoid intergranular attack on sensitized material. Complementary, more understanding to obtain accurate TTS diagram will be developed (linked with precise chemical composition for base material and welded joints, chemical environment …) to narrow down the maintenance conditions. In a larger scope than maintenance operation, the effect of sensitization on the other corrosion mechanisms (general corrosion in sodium, SCC) should also be studied through experimental program.

3. Feedback and lesson learned from Phenix and Superphenix experience

During its 35 years of successful operation, Phenix NPP was connected for 130 000 h to the grid. If some difficulties were encountered, they were all overcome and feedback from these enables to make improvements (design versus thermo-mechanical loads, fabrication versus relieved stress cracking for AISI 321 ….) [12]. These improvements dealt first with Phenix components evolution but also for Superphenix ones and presently, this feedback would be valuable for ASTRID conception. In fact, 32 sodium leaks were noted over the 35 years of operation for Phenix and 5 for Superphenix (15 000 h connected to the grid). In a general manner, the quantities of sodium released were small. The analysis of the causes and localizations of these leaks shows that, if the major cause (~45%) is related to design and severe thermo-mechanical stresses, corrosion by aqueous sodium hydroxide is the third occurrence (~10%) [2]. Finally, knowledge was acquired regarding the feasibility of inspection, cleaning, reparability and re-used of removable components. From this, it was learned a lot on materials susceptibility to IGA and SCC induced by caustic solution and causes evolutions in operating procedures and/or design rules.

3.1. Feedback regarding SCC in caustic environment

The caustic SCC problems were usually observed following maintenance operations and two examples are highlighted hereafter.

One SCC degradation deals with sodium hydroxide retention in a blind hole after cleaning operation (valve support flange on a primary pump in AISI 304 grade). Ramified transgranular cracks were observed in the area of the blind hole (FIG.9.)

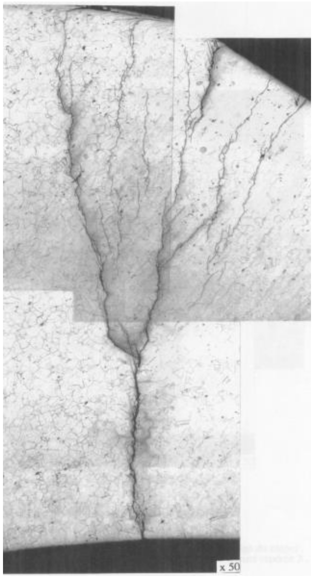


FIG.9. Cracks in the area of the blind hole – AISI 304

Another one was the consequence of accidental air ingress during maintenance on secondary circuit. In this last case, SCC was observed on the upper part of the heat exchanger tubes (AISI 316L) as during reparation, the drained heat exchanger was maintained at shutdown temperature. The SCC of the upper part of tubes has been attributed to a sufficient stress level inside the tubes and exposition within the SCC temperature range.

Phenix 5th sodium-water reaction was also due to SCC (soda accumulation during SG modules washing prior to their repair in 2002).

Moreover, the SCC risk can also be observed during cleaning procedure of the sodium residues. In fact, during the process, sodium elimination is performed by injecting water which produces sodium hydroxide solution. As sodium/water reaction is very exothermic, locally an increase of temperature can be observed. So procedure has to keep margin with respect to temperature increase.

The risk can occur either during preheating (before in sodium immersion, or before in-filling with sodium for circuits) or later during operating again in sodium (case of the 5th sodium-water reaction).

Before preheating a sodium circuit after repair, a stringent procedure (scavenging operations with several parameters monitoring) has to be followed. This procedure has been adjusted by CEA for Phenix.

3.2. Which improvement to manage SCC in caustic environment

In order to manage this issue, one of the three parameters which must be simultaneously present must be suppressed: either the stress, or the temperature or the aqueous sodium hydroxide concentration.

The component temperature and/or the existence of aqueous sodium hydroxide were the two levers used to manage this risk. In practice, design rules and operating procedures were affected because of the following recommendation.

How to avoid a possible damaging environment [7]?

- Avoid aqueous hydroxide formation by design and draining options. By this way, no more retention of solution could be observed, and more widely avoid ingress of wet air. In practice, the draining efficiency was increased by suppressing blind holes and by adding other design improvements to eliminate any liquid metal retentions.
- Check as well as possible that potentially damaging solution is not present when crossing the temperature threshold of the SCC risk area. For this, efficient cleaning procedures are required together with the use of dry inert gas to sweep off any air ingresses and to eliminate any aqueous phases. Particular attention will be paid regarding operation.
- Regarding the washing procedure, care has to be taken to eliminate thick sodium retention, by the use, for instance, of mechanical removal for sodium residues to keep safety margin with respect to the SCC risk.

Finally, regarding compatibility with environment, appropriate design contribute to limit degradation but even more, optimized operating procedures had to be defined.

As a conclusion, all the removable components (primary and secondary pumps, intermediate heat-exchanger and modules of steam generator) were dismounted, cleaned decontaminated, inspected and repaired (if requested) and, the most important, satisfactory re-used in reactor [3]. The demonstration of this feasibility is a high valuable feedback regarding SFRs operation.

3.3: Feedback regarding IGA degradation

In fact, the issue of IGA arises on sensitized stainless steels when exposed to an oxidant environment. As previously mentioned, for SFR, during normal operation, no IGA risk are feared. Nevertheless, aggressive environment can be reached during maintenance or dismantling operations as acid solutions are used.

Another point can also be underlined, regarding fabrication operation and start-up tests where an oxidizing environment could also be observed. To prevent IGA during these periods, low carbon stainless steel has been chosen to move the sensitized area to a longer duration and lower temperature. This point has been, for example, very useful regarding weldments to avoid sensitization of Heat Affected Zone (HAZ). Nevertheless, regarding long time life duration expected for present projects (until 60 years), TTP diagrams show that it will be not possible for components in contact with sodium to avoid the sensitization area which can appear after long term operation for hot structures. Due to lifetime extension for present projects, it could be asked if the historical best compromise between sensitization area location and mechanical properties has to be modified with respect to present project.

Regarding PX feedback, as an example we highlight the destruction of the anti-vibration belts of an IHX, at Phenix in 1984, during its decontamination. This issue was due to a change in the composition of the acid bath.

As previously mentioned, PX and SPX dismantling will allow us to confirm that solutions and preventive measures put in place during reactors maintenance operations were relevant. For example, investigations planned on one IHX might check that the used procedure was relevant for the maintenance of a potentially sensitized component. Then, it has been successfully in operation for a significant period. Investigation will have to prove that no grains decohesions are present due to acid solution used.

3.4 : How to avoid IGA degradation ?

The major parameter concerns the material sensitization state and it is important to be able to evaluate if the material could be or not in a sensitized state. TTS diagram can help the plant operator to obtain this information provided that accuracy is good enough.

So, for maintenance operation, the surface treatment has to be adapted to the material sensitization state.

The decontamination process used for PX and SPX component was a mixture of sulfuric acid and phosphoric acid at 55°C. Phosphoric acid is more convenient in decontamination procedure as it is less aggressive in intergranular attack of the sensitized zones compared to sulfuric acid. Nevertheless, its use has been reduced in order to minimize the phosphate release into the river. Some optimized compositions were found in order to perform efficient decontamination that allows the repair of the components and the re-use in the NPP [7].

4. Conclusion

PX and SPX NPP feedback confirms that stainless steel materials, mainly 316L grades, are a relevant choice for components in contact with high purity sodium. Indeed, such choice is confirmed for the present ASTRID project. Nevertheless, this feedback has also highlighted that utilities have to take care at material susceptibility to different corrosion mechanisms (SCC induced by caustic solution and IGA induced by acid solution) during maintenance operation.

With respect to the feedback and occurrence exposed in this paper, it was shown that particular care has to be taken into account during design step to avoid hydroxide formation and favour draining option. PX and SPX maintenance operations have made it possible to develop and successfully used adapted procedures for washing and decontamination of components. Presently, regarding long term lifetime requested for ASTRID project, it could be relevant to obtain more accuracy on TTS diagram.

The knowledge acquired on the feasibility of inspection, cleaning, reparability and successful re-used of removable components give valuable feedback to be confident for maintenance operations.

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