

Chemistry Optimisation of a PWR nuclear power plant

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One of the main objectives for the plant operator of a Nuclear Power Plant is to protect the Steam Generators (SG) during the lifetime of the plant by ensuring a safe and reliable operation. The SGs serve as an important barrier to prevent the spread of contamination out of the primary circuit. On the other hand impurities are accumulated within the SGs leading to extreme chemical and physical conditions.

The application of an optimized water chemistry treatment of the secondary side is essential to ensure a good performance of the steam generators.

Preservar los Generadores de Vapor (GV) de una central PWR es quizás la tarea más importante a la que se enfrentan el explotador para asegurar que la operación de la misma se realiza de la forma más segura, fiable y responsable posible.

Los GV son la barrera que se para la parte convencional de la central de aquella más problemática donde se producen las reacciones nucleares, pero además son el fondo de saco donde se acumulan y se concentran todos los impurezas que circulan por el circuito estando, por tanto, sometidos a la presencia de contaminantes en condiciones físicas de trabajo extremas.

Aplicar una buena química en el circuito secundario es vital para asegurar un buen funcionamiento de los GV durante la vida útil de la misma.

INTRODUCTION

CNA (Central Nuclear de Almaraz) operates two units of Westinghouse design. It started its commercial operation in 1981 (Unit 1) resp. 1984 (Unit 2). Since the first operating years, AVT chemistry has been applied within the water steam cycle. This chemistry treatment was mainly characterized by a mean feed water pH of approximately 9.0 due to the mixed metallurgy design of the secondary side (mainly condenser).

Shortly before steam generator replacement, the copper components had been removed from the water-steam cycle, resulting in an increase of the pH in feed water to approx. 9.8. With the first occurrence of some degradation phenomena in the replacement steam generators, the operator started to search for chemistry optimization measures to overcome those issues and to return to optimum performance of the steam generators.

Main achievements of this optimization plan were the introduction of a mixed amine treatment, introducing Ethanolamine as a complement to the applied H-AVT treatment as well as the temporary use of Film Forming Amines shortly before outage of the units.

While Ethanolamine was introduced to optimize the pH at operating temperature in the two phase flow areas, the filming amines have been introduced to optimize the existing lay-up strategy of the secondary side of the units.

The objective of this paper is to present the rationales of this optimization concept and the achieved results during application since 2011.

RATIONALES OF CHEMISTRY OPTIMIZATION

The applied H-AVT Chemistry uses Hydrazine and Ammonia as the only conditioning agents within the water-steam cycle. Hydrazine is responsible to ensure sufficient reducing conditions. Optimum concentration of Hydrazine in feed water is around 100 ppb, resulting in an optimum redox potential of < 400 mV. Due to

- thermal decomposition
 - catalytic decomposition (in the presence of corrosion products)
- of Hydrazine, Ammonia is produced which ensures a sufficient pH (25°C) of approx. 9.8 in feed water (resulting Ammonia concentration: 5 - 10 ppm). CNA chemists have to deal with a specific issue related to the condenser. To ensure a sufficient vacuum in



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the condenser, both condenser exhaust pumps have to be operated at maximum level. These results in a decrease of the Ammonia concentration within the water phase of the early condensates, increasing the risk of flow accelerated corrosion (FAC) in these areas. Therefore CNA adds additional Ammonia via a separate dosing system to the secondary cycle.

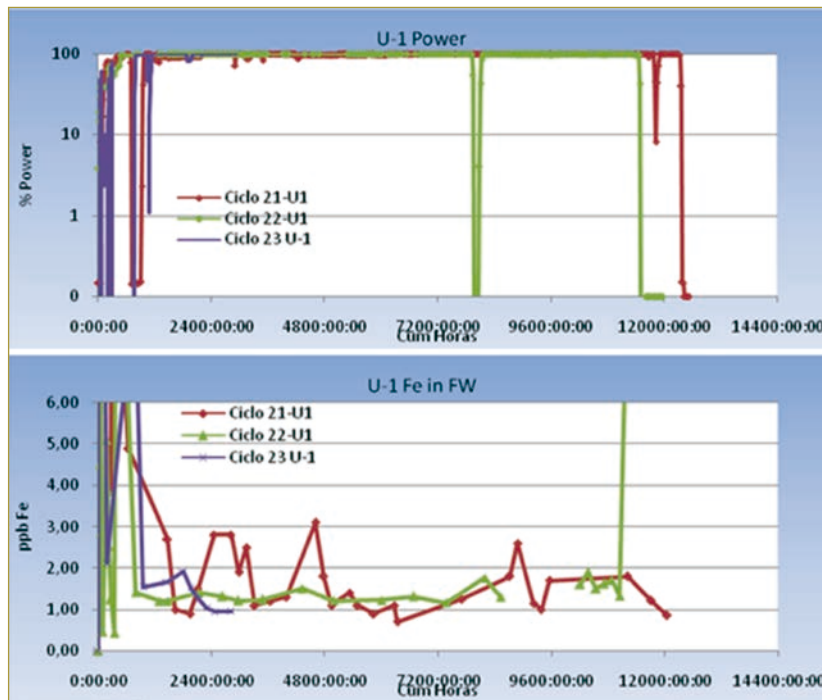
It could be shown that even this additional amount of Ammonia was not



Condenser floor.



Feed water pipe.



sufficient to reach the target pH(T) in the water films of the two phase flow areas of approx.. pH(T neutral) +1 = 6.5. This resulted in an unchanged level of iron transport into the steam generators.

CNA together with AREVA GmbH developed a strategy to introduce a less volatile alkalinizing agent to counteract this FAC risk. According to the international operating experience it has been decided to use Ethanol-

amine (ETA) for this purpose. This mixed amine treatment started in 2013 by addition of an ETA concentration of 3 ppm in feed water. It could be observed, that the ETA addition showed several positive effects regarding:

- increase of the pH(25 °C) in the SG bulk water up to 10.1 and
- reaching the target pH(T) in the two phase flow areas.

One of the main achievements was the dramatic reduction of the iron transport into the SGs. This has lowered also the risk of enrichment of corrosive impurities in the sludge areas of the SGs.

To minimize the corrosion product transport especially during transient operation (startup /shutdown), further improvements had been applied. For the first time on a Western type PWR, CNA has applied film forming amines as a further complement to the existing water chemistry of the secondary side. These film forming amines (FFA) establish a protective hydrophobic mono-molecular layer on the inner surfaces of the secondary side components, preventing the adsorption of any impurities and therefore minimize general corrosion of the components. Furthermore, FFA is a valuable complement to the existing lay-up strategy of CNA for subsequent outages.

Both improvements of the water chemistry treatment resulted in decrease of the iron concentration down to <1 ppb in feed water.

CONCLUSION

To overcome several degradation phenomena during operation of the replacement steam generators, CAN together with AREVA GmbH developed an innovative concept of improving the water steam cycle chemistry. Main results of the introduction of ETA (mixed amine treatment) and FFA are:

- Significant reduction of iron transport into the steam generator. This is complemented by preventing the enrichment of aggressive impurities within the SGs.
- Achievement of the optimum pH(T) targets in the water films of the two phase flow areas to minimize the risk of FAC.
- Strict fulfilment of the EPRI guidelines for secondary side chemistry instead of using the more relaxed AREVA guidelines for Replacement Steam Generator operation
- Optimized lay-up preparation of the water steam cycle for outages
- Improved start/shutdown chemistry

Taking these positive achievements into account, it can be considered that these water chemistry improvements might act as main contributors helping to stop the degradation phenomena of the steam generators bringing them back to optimum performance.■