Experiences with Zinc Injection at Obrigheim Nuclear Power Plant

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1. Introduction/Background

Obrigheim Nuclear Power Plant (KWO) went on-line in October 1968. The Siemens-built PWR (pressurized water reactor) plant has a rated capacity of 350 MW. In addition to having a positive effect on the economic rating, over 30 years of reliable, problem-free operation (with a 82% availability rating) have also been important in terms of the radiation exposure received by plant personnel. In spite of its good operating results, the plant's role as a demonstration facility necessitated continuous modification to take account of new findings and experiences in order to reduce personnel radiation exposure (Figure 1). To this end, in addition to the implementation of administrative measures, shielding, in particular, was improved, and a number of different components were decontaminated. Mechanical filters were also installed in the coolant purification system, and the reactor water chemistry regime was modified (LiOH and H2 injection) to prevent fuel damage and improve corrosion behavior of primary system components. The effects of these measures can be observed in trends in personnel radiation exposure over time, and in the dose rate histories of key primary system components (Figure 2). It was established at a relatively early stage that the active corrosion product cobalt-60 (Co-60) is the principal contributor to personnel radiation exposure. For this reason, the improvement measures described would be expected to have only limited effect. Since 1991, the initially marked drop in dose rate at key primary system components has leveled off, or even increased slightly (Figure 2). To enable further reduction in dose rate, it is necessary to reduce the source of Co-60 activity. This was previously only possible by replacing components surface-coated with materials containing cobalt. Injection of zinc into the reactor coolant to reduce cobalt levels on primary system surfaces represents a low-cost alternative to this method, and is therefore being investigated at Obrigheim.

2. Activity Sources and Activity Transport

The surfaces concerned are stellited to increase the wear-resistance of components subjected to high levels of mechanical stress. Stellite is an alloy which contains up to 60% cobalt. In addition to being used for various valve surfaces, stellited components (for example latches on control rod drive rods) were also installed at locations inside the reactor neutron field in nuclear power plants (Figure 3). The reliability and service life of the parts concerned is increased as a result. As a result of the physical stresses acting on the components, activated Co-60 particles are released from the stellited surfaces in the reactor core area into the reactor coolant, forming part of the colloidal/ionic activity in the coolant (Figure 4). The contaminated coolant entrains the active nuclides and deposits them in the oxide layers present on primary system surfaces. It is via this mechanism that activity generated inside the reactor neutron field is transported to parts of the primary system (for example steam generators, loops) which have to be accessible to outage personnel following shutdown of the plant. The activity deposited in the oxide layers is a principal radiation source, and determines dose rate distribution in the plant (Figure 5).

3. Zinc Injection

As a result of experience obtained at BWR (boiling water reactor) plants and in laboratory investigations based on simulation of PWR reactor coolant systems, it was established that deposition of radioactive nuclides in oxide layers on component surfaces is strongly dependent on the coolant chemistry. This applies in particular to cobalt under PWR service conditions. For this reason, zinc has recently been injected into the reactor coolant of some PWR plants (Biblis A and B, Obrigheim, Palisades) to reduce dose rate. This technique has been used in BWRs for some time, and occurs naturally in BWR plants with brass condensers.

Due to the base materials used in the manufacture of primary system components, the oxide layer at component surfaces comprises mainly Fe/Ni/Cr spinels (Figure 6). The lattice of spinel oxide phases incorporates cations with different valencies at tetrahedral and octahedral sites. The Co and Zn ions, with a valency of two, occupy tetrahedral sites. As a result of the greater stability of the spinel containing Zn ions in comparison with the cobalt-containing spinel, zinc injection initially reduces the incorporation of Co and favors the incorporation of Zn into the spinels. In the next stage of the equilibrium process, the active nuclides Co-60 and Co-58 are displaced from the oxide layer into the coolant. Activity released into the coolant is removed via filters. In this way, activity levels at component surfaces, and hence the source of radiation exposure for outage personnel, are reduced.

In addition to the effect described above, zinc injection is also expected to reduce the metal release rate from stellites containing cobalt in the reactor neutron field. This effect of zinc injection, whereby oxide layers are stabilized, has been utilized as a means of influencing crack propagation in the presence of mechanical stresses. Zinc injection programs of this type are currently under way in the USA at Farley 1 and 2 and Diablo Canyon 1 and 2. The zinc concentration in the coolant at these plants is approximately 30 ppb. Excessively high zinc concentrations ($\geq$ 50 ppb) can lead to formation of deposits on fuel cladding (Farley 2, USA, 11th operating cycle).

The target zinc concentration in the reactor coolant depends on the desired effect of the operation. If the aim is to reduce stress corrosion cracking in nickel-based alloys in primary system components (for example steam generator tubes made from I-600), a concentration of at least 30 - 50 ppb zinc is necessary. A concentration of 5 ppb is considered sufficient to enable reduction of radiation levels.

4. Zinc Injection at Obrigheim

Zinc injection represents a cost-effective alternative to currently available options for reducing radiation exposure, such as

- replacement of stellite surfaces
- decontamination of reactor coolant systems.

As part of the VGB (German Technical Association of Large Power Plant Operators) research project '*Gewinnung von grundlegenden Erkenntnissen über den Aktivitätsaufbau in LWR-Anlagen*' ('Basic research into activity buildup in LWR plants'), therefore, zinc was injected into the reactor coolant to reduce radiation exposure at two plants, Obrigheim and Biblis B. Given the potential for negative effects on fuel assembly behavior at zinc concentrations of 50 ppb, the compatibility of this operation with the fuel condition was to be examined and verified, in particular, in addition to investigating the effect of injection on radiation levels. Activity deposits on primary system surfaces in contact with reactor water were measured during outages between operating cycles in which zinc injection was performed .The zinc injection program at Obrigheim began on February 12, 1998, in the 28th operating cycle.

The natural isotopic mixture of zinc contains 48.6% Zn-64. The radioactive nuclide Zn-65 ($E\gamma$ = 1.1 MeV) is formed through a (n, γ) reaction with thermal neutrons. To avoid diminishing the expected dose-reduction effect of zinc injection, zinc depleted in Zn-64 (to less than 5%) is used.

In line with the aim of the injection program, which is to reduce the dose rate at primary system components, the target zinc concentration was fixed at 5 ppb in the reactor coolant. Zinc is injected in the form of zinc acetate. The solution containing zinc, which is injected using a piston pump via the surge tanks on the suction side of the high-pressure pumps, reaches the primary system downstream of the coolant outlet from the reactor (Figure 7). The first major primary system surfaces to be impacted are therefore those of the tubes of the two steam generators.

4.1 Behavior of Zinc in Reactor Coolant

At the start of the zinc injection program, the injection rate was approximately 1 g Zn/h. In contrast to previous zinc injection programs at Farley (USA) and Biblis B, a high zinc concentration of 67 ppb was measured in the reactor coolant only around 18 hours after the start of injection, which subsequently fell to values close to the detection limit a few hours later. At Farley and Biblis B, the presence of zinc in the coolant could only be detected 30 - 50 days after the start of injection. Approximately 2 weeks after the start of injection, the zinc concentration rose continuously to 9 ppb. Reducing the injection rate enabled zinc concentration to be set at approximately 5 ppb. The corresponding injection rate was approximately 0.2 g/h (Figure 8). A total of 1.5 kg of zinc was injected into the reactor coolant in the 28th operating cycle. Zinc injection was continued following the 1998 outage. A total of 1.1 kg of zinc was injected during the 29th cycle. During the second operating cycle of the zinc injection program, the zinc concentration rose to almost 10 ppb at increasing pH (6.9 $\rightarrow$ 7.4) and at a constant injection rate. By modifying the reduction of the injection rate it was possible to re-establish the target concentration of 5 ppb. No negative effects on plant behavior occurred as a result. Zinc injection is being continued in the current (30th) operating cycle. A total of approximately 3 kg of zinc has now been injected into the primary system at Obrigheim. In contrast to the start of the zinc injection program in the 28th operating cycle, an increase in zinc concentration in the reactor coolant was detected immediately on re-commencement of injection following the two outages. However, zinc concentration in the primary system did not fall to a value below the detection limit of 0.1 ppb after interruption of injection during the 29th operating cycle .

To increase the dose-reduction effect of zinc injection, and investigate the behavior of activation products, the zinc concentration in the primary system is to be increased to 10 ppb during the current cycle. As, according to theoretical predictions, the oxide layers on primary system surfaces should have become saturated as a result of the quantity of zinc already injected, accounting in respect of the amount of zinc injected is particularly important (Figure 10). In this connection, it should be taken into consideration that between 50 and 100 mg of zinc is removed from the primary system per hour as a result of the cleanup rate.

4.2 Behavior of Corrosion Products in Reactor Coolant

At the start of zinc injection, the colloidal fraction of coolant activity (> 3 μm) rose by approximately a factor of two. Although the behavior of colloidal corrosion products is significantly influenced by a change in power (automatic turbine tester - ATT) two days after the start of zinc injection, the reaction to zinc injection can be clearly identified. As the 28th operating cycle continues, the concentration of colloidal activity falls to values comparable to those measured before the start of zinc injection (Figure 4).

The increase in the ionic fraction of the corrosion products in the primary system occurred approximately seven days later. The activity concentrations of the radionuclides Co-58, Co-60 increased by almost a factor of 10 (Figure 4). Sb-122, Sb-125 and Ag-110m were not affected by zinc injection. This is to be expected in accordance with the model described above, as Sb and Ag ions cannot be incorporated into the spinel lattice.

The time history of colloidal and ionic coolant activity in the second and (so far) in the third cycle of the zinc injection program (the 29th and 30th operating cycles) is in agreement with the observations made in the 28th cycle. In accordance with the theory applied, the ionic corrosion products fraction, in particular, reacts to the presence of zinc in the reactor coolant. In addition to the period following the start of zinc injection (second half of the 28th cycle), this is strongly marked after the temporary interruption of injection during the 29th cycle (Figure 9).

In addition to the above-mentioned radionuclides, the behavior over time of the inactive corrosion products Fe, Cr, Ni and Co was investigated. The behavior of Fe concentration, as a reactor water chemistry monitoring parameter, is particularly important. Shortly after the start of injection, Fe concentration rose briefly to 8 ppb, subsequently falling, in the same way as zinc concentration, immediately to values comparable to those measured before zinc injection started (0.5 ppb). Fe concentration also rose simultaneously with the increase in ionic active corrosion products, leveling off at values around 2 ppb. While Ni displayed only a considerably attenuated reaction to the increased zinc concentration in the reactor coolant, no impact was observed on the inactive chromium and cobalt content.

4.3 Influence of Zinc Injection on Activity Deposition on Primary System Surfaces

Given the interaction (described above) of zinc in the reactor coolant with oxide layers on primary system components, the next logical step is to determine the activity deposits on the surfaces concerned. Surface activity measurements were therefore carried out by the CEA and the operator of KWO following the first and second operating cycles with zinc injection (during the 98 and 99 outages). The measurements involved deriving the nuclide-specific activity deposition from the energy-dependent photon flux at a geometrically precise distance from the surface being examined by means of adapted shielding calculations. This method does not enable distinguishing between wipeable and adherent surface activity. To obtain data on wipeable surface activity, even in plant sections which are difficult to access, "smear test specimens" were subjected to examination by gamma spectrometry, and compared with corresponding measurements from previous years.

4.3.1 Determining Surface Activity from Photon Flux

The surface activities determined by the CEA and the operator of KWO are compared with measurements performed by the CEA and ABB before the start of zinc injection. The difference in assessment of background radiation interference at the measuring location by ABB and the CEA, as well as the different methods for calculating the shielding effect, explain the differences, some of them significant, in the results obtained by the CEA and ABB prior to the introduction of zinc injection (Table 1). The measurements carried out by the operator of KWO used the CEA shielding model, but do not take into account a correction factor for the changing ambient influences due to radiation interference. In addition to the different analysis methods described, the plant condition at the time of measurement should also be taken into consideration in assessing the measuring results obtained. The activity content in the reactor coolant, for example, depends on the point of time in the shutdown process and will, together with thermal parameters and the coolant fill level of components, influence the measuring result . Given this context, the measurements performed a few hours after the power reduction should be considered more significant than the measurements carried out at a later stage.

The results for the cold leg upstream of the pump and for the hot leg in both the CEA and Obrigheim measurements after the first cycle during which it was implemented (the 28th operating cycle) show that the zinc injection operation has had a positive effect (Figure 10) on all of the nuclides investigated (Co-58, Co-60, Mn-54, Fe-59). Measurements of surface activity after the first zinc injection cycle for the other primary system components investigated show no significant influence.

Due to the longer exposure time surface activity after the second zinc injection cycle (the 29th operating cycle) is important in enabling assessment of the intended effect of the operation described (i.e. dose rate reduction). Comparison of the CEA measurements before and after zinc injection shows a mean decrease of Co-60 activity deposition on 'cold-leg' primary system components (cold leg upstream and downstream of pump, and SG cold leg) of 0.64 GBq/m², while the corresponding reduction in Co-58 content was 1.6 GBq/m². However, the CEA measuring results for 'hot-leg' primary system surfaces (hot leg including SG hot leg) show a slight increase in specific Co-60 surface activity of approximately 0.1 GBq/m².

All measurements of surface activity performed prior to zinc injection show greater deposition on 'cold-leg' primary system surfaces compared with the corresponding values for 'hot-leg' surfaces. These observations are confirmed by dose rate measurements.

The larger deposits on the surfaces of 'cold-leg' primary system components are clearly affected most by the mobilization of the activity contained in the oxide layers. The activity increases at 'hot-leg' surfaces observed in some cases could be due to the fact that, because of the low initial level of the deposited activity, the values still lay within the range of measuring uncertainty after the previous operating period during which zinc was injected.

4.3.2 Determination of Wipeable Surface Activity

During the 1999 outage, both steam generators were opened on the primary side to enable inspection of the tubes. Smear test specimens were taken from the channel heads of both steam generators, and subjected to examination by gamma spectrometry (Figure 11, 12). In accordance with the results of the dose rate measurements, cold-leg contamination is significantly higher than hot-leg contamination. Steam generator 2 was decontaminated before the subsequent access. As the taking of smear test specimens from the channel heads is difficult to reproduce given the boundary conditions, additional smear test specimens were taken from the hot-leg and cold-leg manway-cover seals of steam generator 2 (Figure 13). The specimens of removable contamination taken from the cold side once again show significantly higher values than the hot-side specimens.

In contrast to the measuring results described, significantly higher dose rates were measured on the hot-leg manway-cover seals than on the cold-leg manway-cover seals of the two steam generators. The cause of this is being determined via a special project for investigating oxide layer buildup.

4.3.3 Influence of Zinc Injection on Dose Rate

In addition to release of activity from the oxide layers, zinc injection also leads to mobilization and transfer of activity to particular points in the primary system. As the investigations into surface activity described above show, there will be locations in the primary system and connected systems at which a decrease in dose rate is expected, as well as points at which the dose rate may increase. The behavior of the activity deposited (described above) shows that even an observed increase in dose rate, particularly in low dose rate areas, does not necessarily call into question the effectiveness of zinc injection. In view of this fact, it is currently very difficult to derive a percentage value for mean dose rate reduction from the measuring results obtained. In addition to these effects, which are to be expected under ideal measuring conditions, a number of interference conditions (such as positioning of dose rate measuring instruments, individual readout precision, instrument precision, background radiation, etc.) have to be taken into consideration.

To examine the influence of zinc injection on dose rate, it would appear to be sufficient to track the time history of this measured variable (Figure 2). However, in view of the mobilization of activity and the only minor effect of zinc injection, to be expected given the short exposure time, it is very difficult to make a reliable statement using this method. For this reason, a simple statistical process is applied in which the dose rates before and after zinc injection are compared. Only the plus or minus sign in respect of dose rate change is used to test the effectiveness of zinc injection ('plus-minus test').

Using this statistical plus-minus test, it is determined that zinc injection has no dose-reduction effect, with respect to the analysis of routinely measured dose rates at the 'reference points', assuming an error probability of 5%.

On shutdown of the plant, and during the outage, solid-state dosimeters were used to measure the dose rate at the reactor coolant piping over a period of several hours. To reduce the interference effect of background radiation, the dosimeters were placed behind special shielding. These measurements have been carried out since 1995, enabling a total of 58 measurements to be compared for the above-mentioned plus-minus test. As in the analysis of the ‘reference points’, the measuring results before and after zinc injection were compared (Figure 14). In contrast to the dose rates at the ‘reference points’ determined using normal service instruments, the plus-minus test highlights a dose reduction (with an error probability < 5%) as a result of zinc injection with these measurements, which are more reliable given their reproducibility.

In addition to the ‘reference points’ and the special measurements using shielded dosimeters, measurements carried out as part of the primary-side steam generator inspection were also incorporated into the statistical analysis process. According to the analysis, the effect of zinc injection on the two steam generators is different. A dose reduction as a result of zinc injection is observed in steam generator 1 both in the analysis of measuring records and in the plus-minus test. In the case of steam generator 2, however, no reduction in dose rate is observed. The cause of this behavior has yet to be explained.

5. Summary Assessment of Zinc Injection After Two Cycles

Unlike at Farley and Biblis B, the presence of zinc could be detected very rapidly in the reactor coolant on commencement of the zinc injection program in the 28th operating cycle. The start of zinc injection led to an immediate increase in colloidal corrosion products, and, approximately 7 days later, an increase in ionic corrosion products to an equilibrium value greater by around a factor of 10. This value then varied only slightly in the subsequent period of operation.

The distribution of activity deposits on primary system surfaces was in accordance with the dose rate measurements. Both greater activity deposits and greater activity decrease as a result of zinc injection were determined for cold surfaces. A clear reduction in dose rate is difficult to establish using normal service instruments as a result of the mobilization of activity and the short exposure time of the surfaces. Special measurements carried out over a long period, of considerable value thanks to their reproducibility, showed a reduction in dose rate which was clearly attributable to zinc injection.

Analysis of all the measuring results (358) used in these investigations on the basis of a simple statistical process showed a dose-reduction effect of zinc injection, although with an error probability of 20%.

At first sight, these results certainly do not appear spectacular; they will have scarcely any significant influence on applied dose in the short term. In the medium-term, however, we expect a significant reduction in dose rate at the primary system. Moreover, renewed deposition of Co isotopes is counteracted by the behavior of zinc in the coolant, and the associated saturation of oxide layers, as described above.

Appendix

Table 1
Figures 1 - 14