Operational Experience with Zinc Injection at Angra 2

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The paper gives an overview of the influence of zinc injection on primary coolant chemistry trends and the evolution of radiation fields at the reactor coolant system (RCS) of Angra 2 after the first three operation cycles. Angra 2 is a Siemens-designed four-loop 1300 MW_e class PWR which went commercial in 2000. The stellite inventory in the reactor pressure vessel (RPV) of Angra 2 is similar to that of other units of the same plant generation. The plant is operated with modified B/Li chemistry. Zinc injection for minimization of future build-up of radiation fields at the RCS was started two days after first criticality. After three operation cycles with zinc injection, the Fe concentration level of Angra 2 is at the lower end of the data band typical of Siemens plants. This indicates RCS oxide layers with good protective properties. The RCS dose rates at Angra 2 are in the range of dose rates of the subsequent Convoy and pre-Convoy plant generations and approx. one third of that of sister units operated with modified B/Li chemistry. With few exceptions, stellites in the RPV of Convoy and pre-Convoy plants could be substituted by Co-free wear-resistant materials.

Introduction

The dose rate at the reactor coolant systems of older-vintage Siemens plants is due primarily to the radionuclide Co-60. The main source of the cobalt and hence Co-60 are internals and wear-resistant hardfacings (stellites) in the RPV. Cobalt-free substitute materials have therefore been systematically implemented for the internals in Siemens pre-Convoy and Convoy plants. The success of this measure can be seen in Figure 1. Compared to older Siemens plant generations, pre-Convoy and Convoy plants are characterized by extremely low annual collective doses.

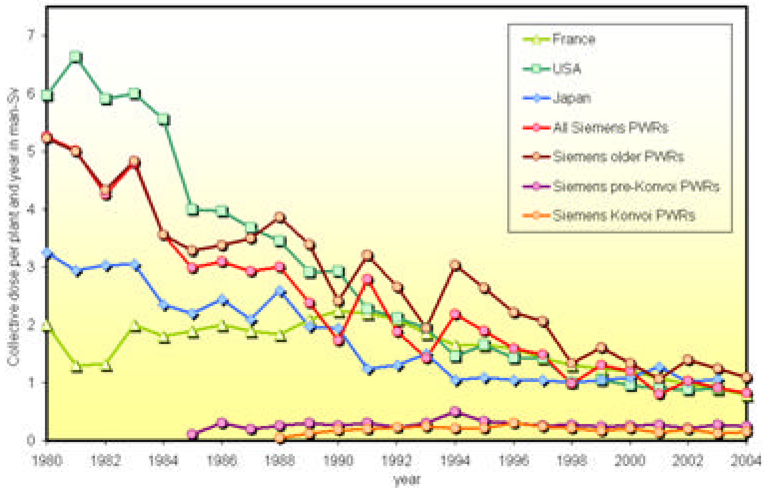

Figure 1: Average annual collective doses at PWR plants around the world

The Angra 2 PWR plant is closely comparable to four-loop 1300 MW class Siemens PWR plants which went commercial in the early 80-ties. As many cobalt alloys as possible were replaced at the Angra 2 plant before initial startup, e.g. stellited parts of the reactor coolant pump impellers and diffusers. This replacement had also been performed in the early 1990s at other Siemens PWR plants. It did not, however, have the expected effect on RCS dose rates. The stellites in the RPV play a much more significant role as far as the contribution to RCS dose rate from Co-60 is concerned. However, no further material substitution was implemented for the RPV internals of Angra 2, so that in this regard the plant still corresponds to the status of plants built prior to the pre-Convoy plants.

Dissolved zinc in primary coolant has a positive effect on the formation of the oxide layers on stainless steel, nickel-base alloys and also cobalt-base alloys. Thinner protective layers are formed which provide a greater degree of protection, release fewer corrosion products into the coolant and pick up less Co-60 and Co-58. At the recommendation of Framatome ANP, the operator of Angra 2 introduced zinc injection during the initial startup phase to minimize the formation of Co-60 depots as well as the buildup of high dose rates at Angra 2's reactor coolant system.
Zinc injection for radiation field control at Siemens-designed PWR plants was qualified and implemented in collaboration between the German PWR operators, represented by VGB and by Siemens/KWU, now Framatome ANP. In order that the results from the VGB project could be used also for Angra 2, it was agreed that ETN would become a participant in the project and would supply the other participants with the chemical and radiochemical data including dose rate data from Angra 2.

This report presents the results obtained with zinc injection at Angra 2 up to and including the third refueling outage. The effectiveness of zinc injection in Angra 2 is investigated and assessed based on comparative values from the initial years of operation at other Siemens PWRs; namely reactor coolant chemistry as well as dose rate and radionuclide deposition in the RCS.

Preparations for Zinc Injection at Angra 2

Evaluation of compatibility of the method with the overall plant confirmed that no differences existed between Angra 2 and the zinc injection demonstration plants as regards core design and RCPs, etc., and that plant compatibility was verified by the operating experience obtained to date.

The following was specified with respect to the application of the method at Angra 2:
- Use of same zinc injection concept as that employed at other Siemens plants; i.e. injection of zinc acetate by chemical injection system
- Injection of zinc depleted in Zn-64 (< 5 at.% Zn-64)
- Reactor coolant zinc analyses by graphite-tube atomic absorption spectrometry (AAS); frequency of analysis for Zn and Fe initially once per day, for Ni and Cr once per week; monitoring of reactor coolant activity
- Quantity of zinc initially injected: 25 g/day; then to be adjusted to reach targeted zinc concentration of 5 ppb in reactor coolant.
- Zinc injection was begun during start of Phase D, power tests, two days after first criticality of the plant on July 16, 2000.

Results

Primary Coolant Chemistry Data
Primary coolant Zn concentration data of the first three cycles of Angra 2 including power testing are shown in Figure 2. Zn could be detected already at the start of Zn injection. The target concentration of 5 ppb Zn was achieved ~ 4 weeks after start of injection. The average Zn concentration in cycles 1 to 3 was 4 ppb Zn.

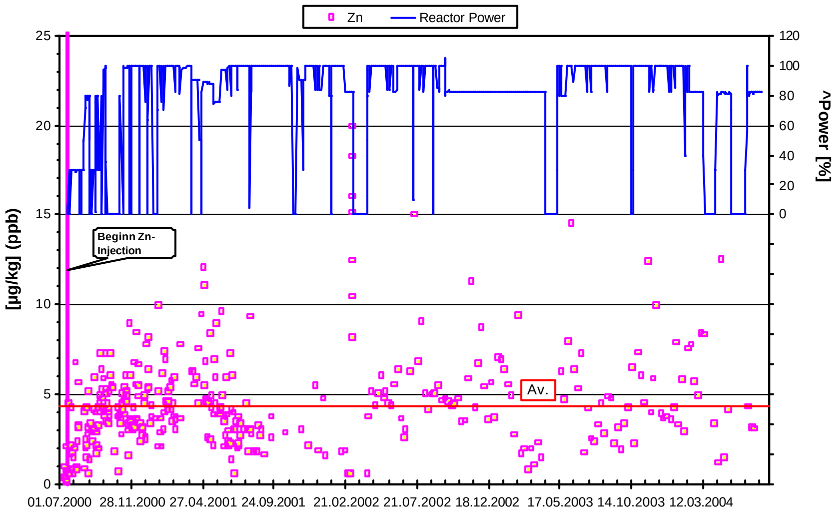

Figure 2: Primary coolant Zn concentration data of the first three cycles of Angra 2 including power testing

The concentration of Fe in primary coolant is shown in Figure 3. If the measurement results performed with the AAS graphite furnace technique are taken as relevant, the Fe concentration lies in the range between the limit of detection of the method (0.15 ppb Fe) and ~2.0 ppb Fe. The average value of the last two cycles was 1.2 ppb Fe, that is, at the lower end of the range typical of Siemens PWR plants.

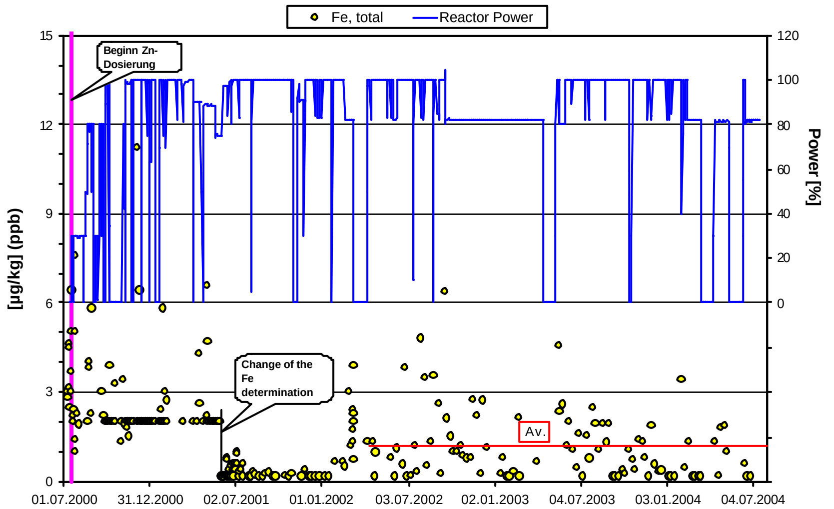

Figure 3: Concentration of Fe in primary coolant of Angra 2 in the first three cycles

Primary coolant Co-58 and Co-60 data of Angra 2 are plotted in Figure 4. The Co-60 level in Angra 2 ranges between the levels of Convoy plants and four-loop sister plants with stellites in the RPV. The presence of Zn results in

- a decrease in Co and hence Co-60 release of RPV internals and therefore a general decrease in the primary coolant Co and Co-60 levels, and
- a decrease in Co and Co-60 incorporation in RCS surface oxide layers, and correspondingly an increase in the Co-60 concentration level of primary coolant.

In spite of the lower Co-60 pickup by RCS surfaces, the content of Co-60 in the coolant of Angra 2 is lower than that of its sister plants. This indicates that the cobalt release of RPV internals of Angra 2 must be also low.

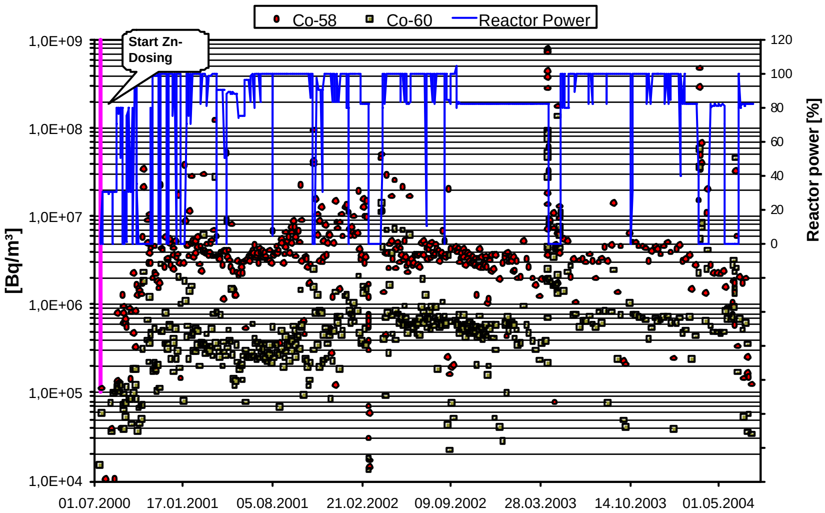

Figure 4: Primary coolant Co-58 and Co-60 activity data of Angra 2 of the first three cycles

RCS Surface Activity Values and Contact Dose Rates

Co-60 surface activity data of Angra 2 and of other Siemens PWRs are plotted in Figure 5 (hot leg) and Figure 6 (cold leg). Plants with coordinated B/Li chemistry, pH(300°C) 6.9, for the first few fuel cycles are marked "coord.", plants with modified B/Li chemistry, pH(300°C) 6.9(BOC) to 7.4(EOC), "mod.". The Co-60 surface activity level of Angra 2 at the third refuelling outage still is in the range of data of Convoy and pre-Convoy plants. Percentage contribution of Co-60 to total dose rate at Angra 2 is in the range 60 – 80 %. Co-60 contribution at sister plants is > 90%.

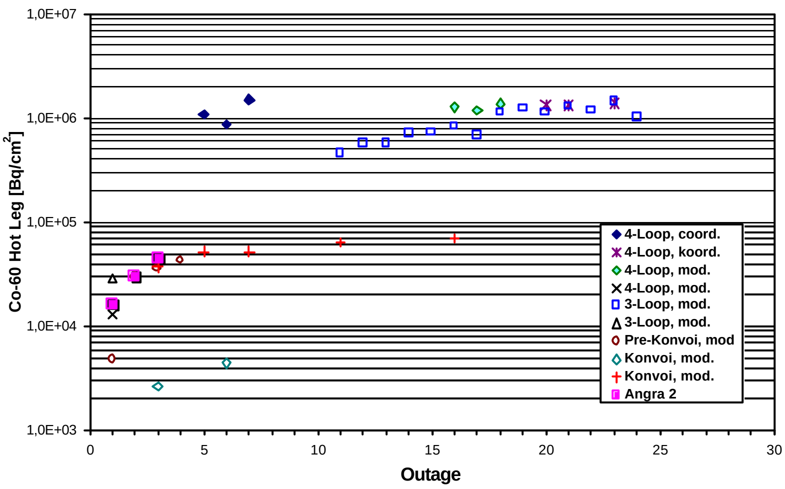

Figure 5: Co-60 RCS hot leg surface activity data of Siemens plants

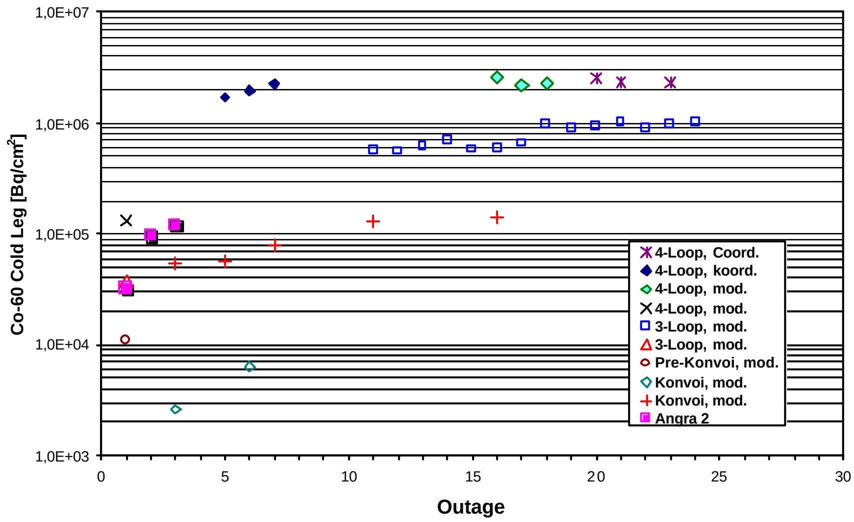

Figure 6: Co-60 RCS cold leg surface activity data of Siemens plants

Contact dose rates at primary system piping of Angra 2 and of other Siemens plants are plotted in Figure 7 (hot leg piping) and Figure 8 (cross-over piping). Data show that the RCS dose rate levels at Angra 2 and at pre-Convoy and Convoy plants are in the same range. The RCS dose rate level of sister plants with mod. B/Li chemistry is ~ three times higher than that of Angra 2.

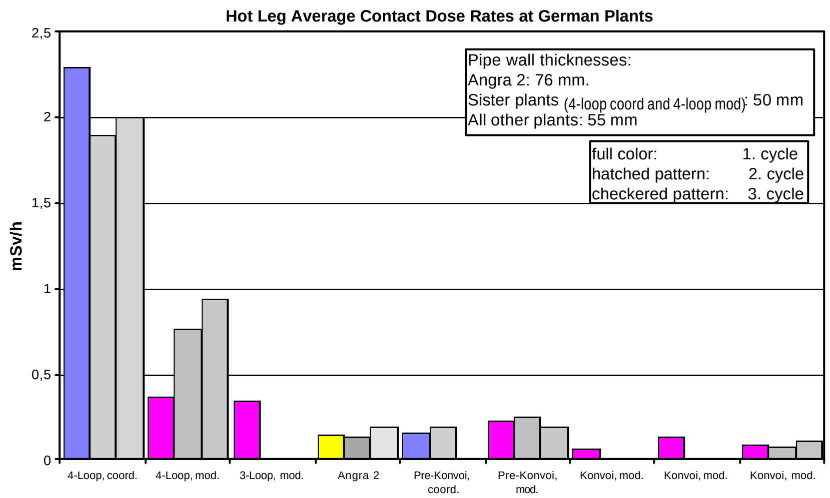

Figure 7: Hot leg piping average contact dose rates at Angra-2 and other Siemens PWRs

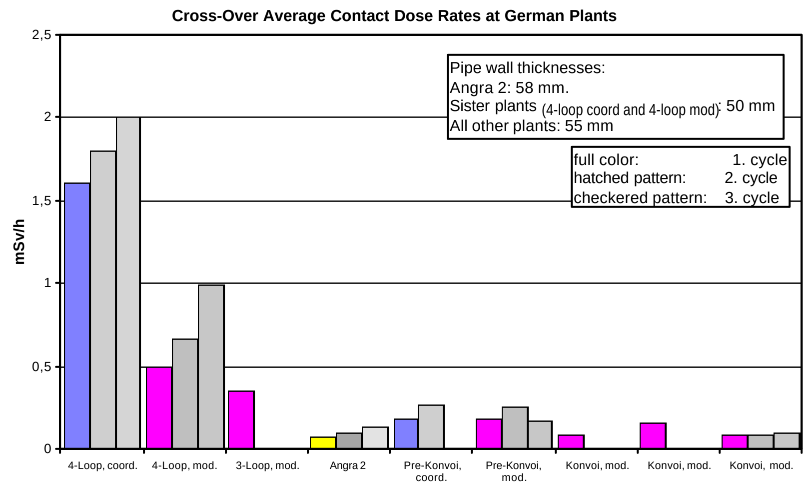

Figure 8: Cross-over piping average contact dose rates of Angra-2 and other Siemens PWRs

Dose rates in the steam generator (SG) channel heads of Siemens plants are plotted in Figure 9. The values for Angra 2 in third outage lie in the range of those of the pre-Convoy and Convoy plants. Contrary to the case of old plants without Zn injection, the dose rate in the SG channel heads of Angra 2 has decreased in the period from 1st to 3rd outage.

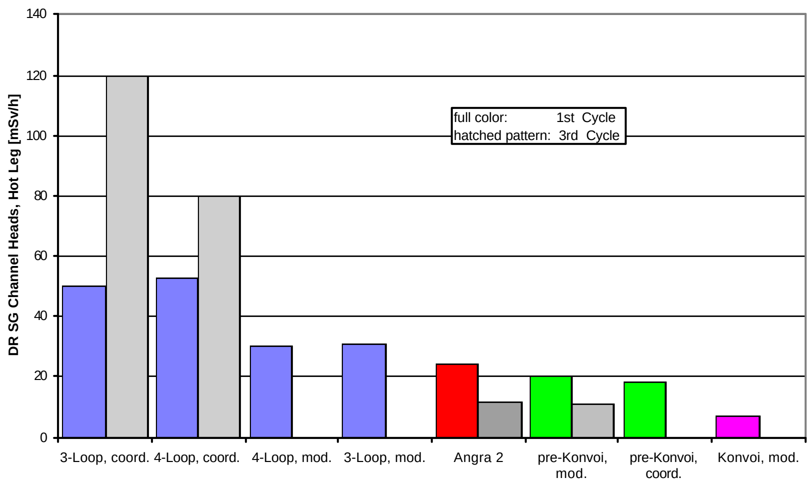

Figure 9: Dose rate in SG channel head of Siemens PWRs, hot leg first and third outage

Summary and Conclusions

Zn injection was started two days after first criticality of Angra 2. Zn injection resulted in the expected formation of high quality and stable protective layers. The corrosion product concentration of primary coolant has been in the range of the detection limit of the applied measurement techniques. After the third operation cycle, Co-60 surface activity values and RCS contact dose rates of Angra 2 are in the range of pre-Convoy and Convoy plants, that is, in the range of plants with stellite substitute materials in the RPV. Contact dose rates are also in the range of that of the Convoy plants and at least three times lower than values of sister plants of Angra 2 with similar primary system material concept.