OVERVIEW OF ACTIVITIES FOR THE REDUCTION OF DOSE RATES IN SWISS BOILING WATER REACTORS

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Abstract

Since March 1990, zinc has been added to the reactor water of the boiling water reactor (BWR) Leibstadt (KKL) and, since January 1991, iron has been added to the BWR Mühleberg (KKM). These changes in reactor water chemistry were accompanied by a comprehensive R & D programme. This paper covers three selected topics: a) the statistical analysis of KKL reactor water data before and after zinc addition; b) the analysis of the KKL reactor water during the 1991 annual shutdown; c) laboratory autoclave tests to clarify the role of water additives on the cobalt deposition on austenitic steel surfaces.

1 Introduction

Two General Electric (GE) boiling water reactors are in operation in Switzerland: Mühleberg (KKM, 320 MW, 1972), with a brass condenser and, since 1986, a new recirculation system; Leibstadt (KKL, 942 MW, 1984), with a titanium condenser since 1985. A major problem is the activity build-up in the recirculation system mainly due to Co-60, leading to a high local dose rate and enhanced radiation exposure of the personnel during maintenance.

Following good experience in Japanese reactors, KKM, since January 1991, has added 0.65 ppb Fe-III as oxalate to the feedwater to maintain a ratio of 0.24 between II-valent cations (Zn + Ni + Cu [1/4]) and III-valent Fe.

Qualitatively following a GE recommendation, KKL, since March 1990, has added 0.4 ppb Zn to the feedwater using a passive system.

Table 1 summarizes the tendencies in both plants. It should be noted that, in spite of the dose rate at the recirculation loops, both plants achieved a reduction in the collective annual dose to the personnel by organizational measures.

This interesting development in the Swiss BWR's led to a comprehensive R & D programme by the Swiss Authorities (HSK), the BWR operators, the Swiss Federal Institute of Technology (ETH, Zürich) and the principal investigator, the Paul Scherrer Institute (PSI), following three selected themes:

- Statistical analysis of KKL reactor water data over the last few years,
- KKL reactor water analysis during the annual shut-down,
- Autoclave tests to clarify the role of water additives on the Co-60 deposition on steel surfaces.

Table 1: Trends in Swiss BWR's since 1989 for the average dose rate at the recirculation loops (mSv/h) and the collective annual dose (Person-Sv).

	1989	1990	1991
KKM (Fe addition since January 1991)			
Average dose rate (%)	100	113	133
Collective annual dose (%)	100	58	55
KKL (Zn addition since March 1990)			
Average dose rate (%) 100	86	80	
Collective annual dose (%)	100	89	98

2 Statistical Analysis of KKL Reactor Water Data

2.1 Procedure

KKL analyzes the corrosion products of the reactor water once a week completely: Undissolved impurities (> 0.45 μm filter) Cr, Fe, Cu, Ti, Ni; dissolved impurities (< 0.45 μm filter) Cr, Fe, Cu, Ti, Ni, (Zn), SiO_2. Seventy weekly data sets were available before March 1990 – no Zn addition – and 70 sets after March 1990 – *with Zn addition.*

The aim of the statistical analysis was to correlate the Co-60 activity with other analyzed influencing factors x_i. Since the basic physico-chemical processes are mostly unknown, linear regression was chosen as a first approach:

$$\text{Co-60} = a_o + \sum_i a_i x_i \qquad (1)$$

Each data set represents a point (Co-60 activity) in multi-dimensional space. The parameter a_i can be calculated so that the squared sum of the rectangular distances of the points to the plane is a minimum.

From the weekly data sets – no Zn/with Zn – the arithmetic mean and the deviation σ_i is calculated for Co-60 and the influencing factors x_i. This reference data set is similar to the annual average reactor water quality. Following this, a particular influencing factor x_i is varied by $\pm\sigma_i$ and the effect on the Co-60 activity calculated, keeping the other influencing factors x_i from the reference data set constant. The deviation from the mean Co-60 activity, expressed in percentage and calculated for one specific influencing factor, is a measure

Table 2: Statistical analysis of KKL reactor water data before and after Zn addition; effect of water impurities on the Co-60 activity expressed in % deviation from the mean Co-60 activity.

	No Zn (eqn. (2))		With Zn (eqn. (3))	
	Reference (ppb)	Effect on Co-60	Reference (ppb)	Effect on Co-60
Cr	1.7 ± 0.9	+	2.9 ± 1.5	– –
Fe	1.7 ± 1.0	– –	2.0 ± 0.5	+ +
Cu	0.11 ± 0.07	–	0.07 ± 0.03	0
Ni	0.09 ± 0.03	+	0.22 ± 0.09	– –
SiO_2	118 ± 45	–	146 ± 47	0
Zn			2.2 ± 0.6	–
Co-60 (Bq/ml)	13.7 ± 5.9		7.4 ± 3.7	

0 Small effect on Co-60 activity (± 10%)

– Reducing effect on Co-60 activity, – moderate (10 to 30%), – – strong (> 30%)

+ Increasing effect on Co-60 activity, + moderate (10 to 30%), + + strong (> 30%)

Table 3: KKL reactor water analysis during the 1991 shutdown

	OPERATION	POWER REDUCTION		HOT STANDBY	COOL-DOWN	SHUT-DOWN
	Control with recirculation pumps			Control rods inserted		
POWER/COOL-DOWN	72 %	56 %	24 %	0 %	10°/hr	10°/hr
TIME		–12 hr	–6 hr	0 hr	+ 11 hr	+ 30 hr
TEMP.,PRESSURE	270°C, 70 bar	270°C, 70 bar	270°C, 70 bar	270°C, 70 bar	160°C, 10 bar	30°C, 1 bar
PARTICLES > 1μm	$10^{+3} - 10^{+4}$/ml		10 x	50 x	> 50 x	20 x
OXYGEN						
- O_2	230 ppb	180 ppb	160 ppb	30 ppb	30 ppb	> 1000 ppb
- H_2O_2	0 ppb	0 ppb	0 ppb	0 ppb	10 ppb	3500 ppb
Co-60 ACTIVITY						
- total	2×10^{-4} μCi/ml	1.5 x	1.5 x	2 x	12 x	25 x
- dissolved	5×10^{-5} μCi/ml	4 x	4 x	2 x	12 x	20 x
- diss./total	0.25	0.7	0.7	0.25	0.25	0.2
Zn-65 ACTIVITY						
- total	4×10^{-3} μCi/ml	1.5 x	8 x	11 x	20 x	16 x
- dissolved	7×10^{-4} μCi/ml	2.9 x	29 x	43 x	86 x	86 x
- diss./total	0.2	0.3	0.7	0.7	0.8	0.9

of the effect of this particular influencing factor. If the spread between the maximum and the minimum Co-60 value is large, then the influencing factor is of importance.

2.2 Example

The application of the statistical analysis will be illustrated using the above-mentioned KKL data sets in a highly simplified form – considering only the total concentration of the elements without differencing between undissolved/dissolved – to demonstrate the effect of Zn addition.

$$\text{Co-60} = a_0 + a_1 \cdot \text{Cr} + a_2 \cdot \text{Fe} + a_3 \cdot \text{Cu} + a_4 \cdot \text{Ni} + a_5 \cdot \text{SiO}_2 \quad (2)$$

$$\text{Co-60} = \ldots\ldots\ldots\ldots + a_6 \cdot \text{Zn} \quad (3)$$

Table 2 shows that the Zn addition to the KKL reactor water represents a strong intervention in the water chemistry. Considering specifically the Co-60 activity before and after Zn addition:

- Cu and SiO_2 have negligible effects, in both cases.
- Fe changes sign; strong reducing effect without Zn, strong decreasing effect with Zn. Therefore, a further Fe increase by a combined Fe/Zn addition appears inadvisable.
- Cr and Ni also change sign; moderate increasing effect without Zn, strong decreasing effect with Zn.

Considering the method and the conclusions of the statistical reactor water analysis, it should be noted that:

- The method is purely phenomenon oriented without consideration for the basic physico-chemical processes.

- The results refer to the Co-60 activity in the reactor water only, and up to now cannot be extrapolated to the Co-60 build-up on austenitic surfaces.
- The statements made refer to the KKL-specific water chemistry (see Table 2). Water chemistry data sets from other BWR's are presently being analyzed to see to what extent the KKL results are of general significance.

3 KKL Reactor Water Analysis during the 1991 Shut-down

The annual KKL shut-down between 24–26 July, 1991, was followed by an extensive analytical program. Reactor water samples were taken from a line tied to the pressure side of the recirculation pump. This line was cooled to 30°C and the length of about 30 m caused a delay in sampling of 15 to 30 min. The main parameters followed were:

- Particle concentration > 1 μm size by an on-line POLYTEC counter (POLYTEC, D-7517 Waldbronn, Germany).
- Oxygen by an ORBISPHERE probe (ORBISPHERE Laboratories, Neuchâtel, Switzerland) and H_2O_2 by photometry in samples taken at regular intervals.
- Total γ-activity (Cr-51, Co-58, Fe- 59, Co-60, Zn-65) in samples taken every 30 min.
- γ-activity of particles (> 0.45 μm filter) and in solution (< 0.45 μm filter) in the above-mentioned samples after filtration.

Table 3 summarizes selected data measured during 6 periods in the shut-down. Compared to the initial period of normal operation at 72% power, the following phenomena can be observed:

- Already at −6 hr (24% power) the total Zn-65 activity increases by a factor of 8, mainly because of more dissolved Zn-65. The total Zn-65 remains high over the rest of the shut-down.
- Also at −6 hr, the particle concentration increases by a factor of 10. A further, dramatic increase, by a factor of 50, occurs at 0 hr (full control rod insertion).
- An important point is at +11 hr (160°C, 10 bar), where H_2O_2 is first measured (10 ppb). In the following cooling period the amount of H_2O_2 increases to 3500 ppb.
- Also at +11 hr, parallel to the occurrence of H_2O_2, the total Co-60 activity increases by a factor of 12. The ratio dissolved/total Co-60 remains constant. The large concentration of crud particles seems little influence on the Co-60 activity in the reactor water.

Since most of the Co-60 activity is liberated late in the shut-down (after +11 hr, 160°C, 10 bar), the relationship to the occurrence of H_2O_2 should be clarified. Also, from the operator's point of view, it would be important to know whether to include a halting period at 160°C to purify the reactor water or, on the contrary, to aim to reach room temperature as quickly as possible, e.g. at a rate of 25°C/h, to avoid Co-60 discharge.

4 Laboratory Investigation: The Influence of Water Additives on the Cobalt Deposition

Four heated stainless steel autoclaves (40 mm internal diameter, 310 mm length) were run in parallel at simulated BWR conditions (Fig. 1).

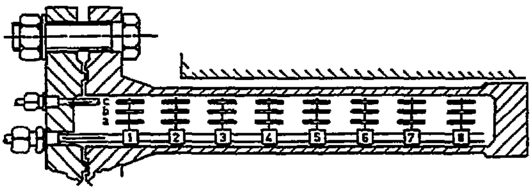

Figure 1: Laboratory autoclave with test samples (numbers indicate the stack, letters the stack position)

The autoclave water was purified by demineralization, deionization, decomposition of organic carbon, degassing and oxygen adjustment. The water quality was controlled by on-line conductivity and oxygen concentration measurements. Additives such as cobalt, iron, and zinc were injected into the water by high-pressure pumps at the inlet to each autoclave. The linear water velocity in the autoclave was adjusted to 1.1×10^{-4} m/s – a very slow flow, approaching natural convection, leading to a stagnant film of up to 2.5 mm thickness on the test samples. At the autoclave outlet, the Co-58 activity and the oxygen concentration were 1% to 10% of those at the inlet. After a 300 hr exposure period, the test samples were removed and the deposited activity measured by γ-spectroscopy. It was noted that the Co-58 activity decreased in a linear fashion from stacks 8 to 5 and remained about constant from stacks 4 to 1. Any comparison should therefore be based on steel samples from corresponding stacks and positions in the 4 autoclaves.

Figure 2 shows, as an example, the Co-58 activity on steel samples in corresponding positions in the autoclaves: Reference; Co-58 only (autoclave 1); 1.5 ppb Zn (autoclave 2); 20 ppb Zn (autoclave 3); 20 ppb Fe (autoclave 4).

The results are consistent and the effect of water additives on the Co-58 build-up can be expressed qualitatively as follows:

- 20 ppb Zn > Reference > 20 ppb Fe > 1.5 ppb Zn
- Co-58 builds up linearly with time. Even after 1800 hours no saturation is in sight.

Table 4 summarizes test conditions and results. Excluding arbitrarily the initial 300 hr period and using the average values for stack 8 to 1, the Co-58 build-up is as follows:

20 ppb Zn	>	Reference	>	20 ppb Fe	>	1.5 ppb Zn
107 to 135%		100%		64 to 77%		47 to 69%

Table 4: Co-58 activity measured on steel samples in autoclaves after 300, 600, 900, 1200, 1500, 1800 hr exposure time in simulated BWR reactor water with Zn or Fe addition

Exposure time (hr)	300			600			900		
Average for stacks (No.)	8 − 1	8 − 5	5 − 2	8 − 1	8 − 5	5 − 2	8 − 1	8 − 5	5 − 2
(A) Reference (KBq)	5.1	6.5	4.0	8.4	11.3	5.9	11.1	14.8	7.9
(B) 1.5 ppb Zn (% of A)	82	61	93	67	49	81	69	54	81
(C) 20 ppb Zn (% of A)	62	67	61	127	123	150	135	127	163
(D) 20 ppb Fe (% of A)	67	56	80	67	56	82	77	67	92

Exposure time (hr)	1200			1500			1800		
Average for stacks (No.)	8 − 1	8 − 5	5 − 2	8 − 1	8 − 5	5 − 2	8 − 1	8 − 5	5 − 2
(A) Reference (KBq)	15.4	19.9	11.4	21.6	27.9	16.7	27.3	35.2	21.5
(B) 1.5 ppb Zn (% of A)	62	53	68	49	42	52	47	42	50
(C) 20 ppb Zn (% of A)	129	125	146	111	104	121	107	99	118
(D) 20 ppb Fe (% of A)	75	68	86	69	62	75	64	58	72

- Autoclave water conductivity < 0.1μS/cm, flowrate 1.1 x 10^{-4}m/s, 1400 ppb O_2, 290°C, 110 bar
- 316 NG steel samples, as delivered; dimensions: 20 × 20 × 2 mm
- Average values for stacks 8 to 1, 8 to 5, 5 to 2 (position(a), Fig. 1)
- (A) Reference Co-58 only, 0.02 ppt Co, 1.3 Bq/ml Co-58
- (B) Reference A + 1.5 ppb Zn-65 (zinc chloride), 1.3 Bq/ml Zn-65
- (C) Solution B + 18.5 ppb Zn inactive (zinc acetate), 20 ppb Zn (total)
- (D) Reference A + 20 ppb Fe (Fe-III acetate)

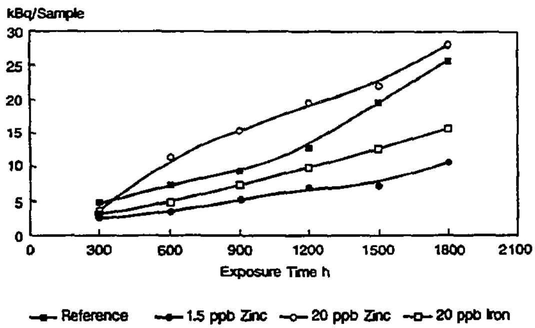

Figure 2: Co-58 activity measured on steel samples in stack 5, position (a), after different exposure times (test conditions as described in Table 4)

- The test results are consistent. Maximum % values are reached after 900 hours and minimum values after 1800 hours. No extrapolation for the development over longer exposure times can be made.

- Not addressed here are further test results for the effect of surface treatment, the oxide layer thickness, the Zn-65/Co-58 ratio, and the in-depth profile for Zn, Fe, Co, and oxygen.

- The tests were made at slow water flow. In a new set-up, the effect of high flow rates will be addressed.

For the two BWR's in Switzerland, these preliminary results are of interest since they provide at least an indication of the effect of Zn (KKL) or Fe (KKM) additions to the reactor water.

5 Summary

Since March 1990, Zn has been added to the reactor water at the BWR Leibstadt (KKL). This change in water chemistry was accompanied by a comprehensive research programme:

- **Statistical water analysis** was applied to the weekly reactor water data sets before and after Zn addition. This purely phenomenon-oriented approach relates to the Co-60 activity in the reactor water only and, as of now, cannot be extended to the Co-60 build-up on austenitic steel surfaces. The statistical analysis is of interest since it considers not only the effect of Zn but also the role of other impurities in the reactor water.

Zn has a moderate reducing effect on the Co-60 activity in the reactor water. Cu and SiO_2 can be neglected. The role of other impurities is strongly affected. In particular, Fe changes sign; without Zn it has a strong reducing effect, with Zn a strong increasing effect. Cr and Ni also change sign; without Zn they have a moderate increasing effect, with Zn a strong reducing effect. Other BWR data sets have to be analyzed to see whether these KKL-specific statements are of general significance.

- **The reactor water analysis during the annual 1991 shut-down** allowed the observation of the following phenomena:

  Already at 24% power the total Zn-65 activity increases by a factor of 8, mainly because of dissolved Zn-65. At 0% power (full control rod insertion) the crud particle concentration ($> 1\mu m$ size) increases by a factor of 50. An important point in the cool-down period is at 160°C, 10 bar, where H_2O_2 is first measured and, at the same time, the total Co-60 activity has increased by a factor of 12. It is not clear how the plant cooldown procedure should be modified to take these effects into account.

- **Laboratory autoclave tests** were made with different water additives and austenitic steel samples at simulated BWR conditions.

  After 6 time periods, each of 300 hours, the Co-58 build-up (%) on steel samples exposed to different water additives (ppb) was measured. The results are consistent and can be summarized as follows:

20 ppb Zn	>	Ref.	>	20 ppb Fe	>	1.5 ppb Zn
107 to 135%		100%		64 to 77%		47 to 69%

  Results have to be considered as preliminary because:

  a) They were obtained at very slow flow rate,
  b) Even after 1800 hours, saturation of cobalt build-up was not reached. Nevertheless, for the two Swiss BWR's, they provide at least an indication of the effect of additives in the reactor water.

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