

울진 3호기 잠복방출시험을 이용한 물비 조절방안

김유환, 서영남, 이상섭, 김은기, 피용준*

원자로설계개발단, 한국전력기술 (주)

*울진 3,4호기 원자력발전소, 한국전력공사

Molar Ratio Control Scheme Based on Hideout Return Test for Ulchin Nuclear Power Plant Unit 3

Y.H.Kim, Y.N.Suh, S.S.Lee, E.K.Kim, and Y.J.Pi*

NSSS Engineering & Development, KOPEC

*Ulchin Nuclear Power Plant Units 3&4, KEPCO

1. Introduction

Corrosion of steam generator tubes is the major issue affecting selection of secondary water chemistry parameters. The objective of secondary side water chemistry control is to minimize corrosion damage and to thereby maximize the reliability and economic performance of the secondary system. To achieve this objective, the water chemistry has to be compatible with all parts of the system including steam generators.

Steam generator bulk water impurities can be concentrated due to localized boiling processes on clean tube surfaces and within shallow oxide deposits on the tubes. However all of chemistry parameters controlled during normal operation are based on steam generator bulk water samples. Molar ratio control (MRC) is a control strategy that adjusts the bulk water chemistry, the ratio of highly soluble cation and anion, such that the solution that is developed in the flow restricted regions is near neutral. The EPRI's secondary water chemistry guidelines^[1] introduced MRC as a possible approach for reducing IGA/SCC growth rates of steam generator tubing.

The purpose of this paper is to evaluate the relationship between a bulk water chemistry and a crevice chemistry using the chemWORKs #2 Spread Sheet for Molar Ratio Index (MRI)^[2] and MULTEQ Code^[3] for the crevice pH, and recommend the appropriate method to maintain MRI as close to a value of 1 as possible based on the hideout return test data of SG A and B during the 1st outage of UCN 3.

2. Hideout Return Mechanism

When an accumulated inventory is released as shown in Fig.1, the following describes the process. The mass balance for accumulated inventory "A" is given by :

$$\frac{dA}{dt} = -\alpha_A A \quad (1)$$

$$A_t = A_0 \cdot e^{-\alpha_A t} \quad (2)$$

where,

α_A = rate constant for release of A, hours⁻¹

A_0 = original stored inventory of A from hideout, g

A_t = amount of stored inventory of A at time t, g

t = time of release, hours

and,

$$M \cdot \frac{dC_b}{dt} = 10^6 \alpha_A A_t - Q_b C_b \quad (3)$$

$$C_b = 10^6 \alpha_A \left[\frac{\frac{A_0}{M}}{\frac{Q_b}{M} - \alpha_A} (e^{-\alpha_A t} - e^{-\frac{Q_b}{M} t}) \right] - C_{b0} e^{-\frac{Q_b}{M} t} \quad (4)$$

where,

Q_b = blowdown rate, kg/hr

C_{b0} = original concentration of A in steam generator at the beginning of transient, $\mu\text{g/kg}$ or ppb

C_b = concentration of released material to steam generator from previously accumulated inventory A_0 at time t, $\mu\text{g/kg}$ or ppb

M = mass of water in steam generator, kg

t = time, hours

The integrated return over a period of time is

$$R = A_0 [1 - e^{-\alpha_A t}] + R_0 \quad (5)$$

where,

R = integrated return at the end of interval t, g

R_0 = initial inventory in SG at the beginning of interval, g

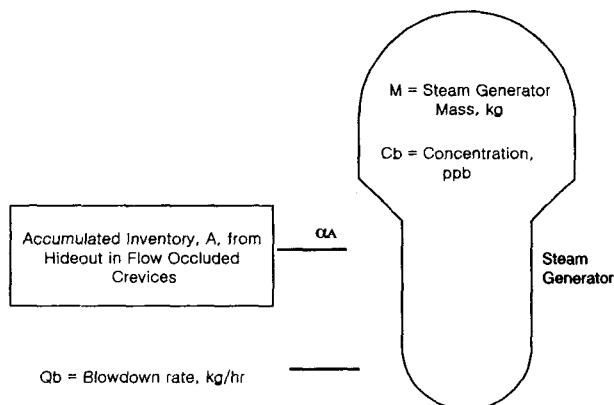


Fig. 1. Schematic diagram for mass balance in steam generator

3. Results

3-1. Evaluating Hideout Return (HOR) Data

3-1-1 Sampling for Hideout Return Test

A hideout return data was sampled at three phases : power reduction phase, 0 % power and hot conditions, and cooldown phase, respectively. Table 1 shows the sampling phases and times for HOR test.

Table 1. Sampling phases and times for HOR test^[4]

No.	Sampling Phases	Sampling Times
1	Power Reduction	81%, 50%, 30% and 15%
2	0% Power and Hot conditions	0%, +0.5 hr, +1 hr, +1.5 hr, +2 hr, +3 hr, +4 hr, +5 hr, +6 hr, +7 hr, +8 hr, +11 hr, +14 hr, +22 hr
3	Cooldown	+25 hr, +34 hr until blowdown is terminated

3-1-2 Hideout Return Data

Fig.2 shows sodium, potassium, calcium, chloride, and sulfate as a percent of the maximum integrated return. This reveals releasing trend of species through hideout return test.

Sodium, potassium and chloride are significantly released at 20 ~ 60 % power during power reduction phase. It is a typical behavior for these species to be released at Hot Zero Power (HZP) conditions while remained as soluble species at the crevice. Calcium, magnesium, phosphate and sulfate are released at cooldown phase while remained as adsorption on oxide surfaces or concentration in restricted geometries.

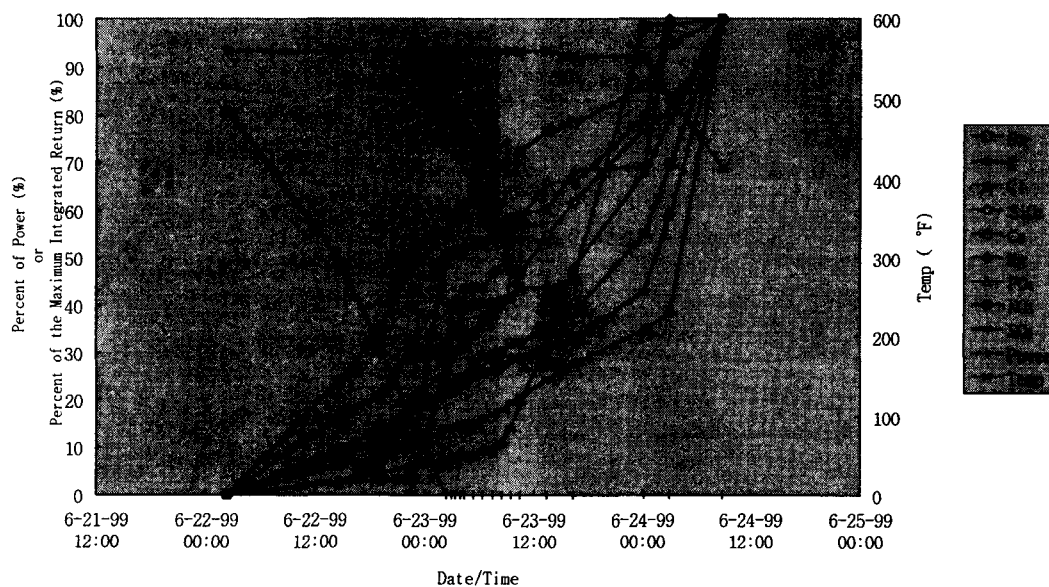


Fig.2. Total cumulative return of each species for UCN 3 SG A.

Nitrate is usually released at cooldown phase, but it was continuously released from power reduction phase to cooldown phase during UCN 3 HOR test.

Table 2 shows total cumulative return data for each species based on a hideout return data for UCN 3 SG A and SG B. The total amount of cumulative return for phosphate is higher than other species. The cumulative return and total amount of cumulative return for each species are almost same for SG A and SG B.

Table 2. Total cumulative return(g) of each species for UCN Unit 3.

	Na	K	Ca	Mg	Cl	PO ₄	NO ₃	SO ₄	SiO ₂
SG A	0.98	1.93	16.21	5.33	0.79	41.18	2.38	10.36	25.78
SG B	0.93	2.34	17.64	6.49	0.80	38.98	1.06	12.90	22.26

+ The cumulative return(g) is amount of accumulated return from 30% power to HZP condition^[2].

3-1-3 Molar Ratio Index (MRI)

MRI is an indicator of the relationship between soluble species in the crevice. The MRI is defined as follows:

$$\text{MRI} = \frac{[\text{Na}] + [\text{K}]}{[\text{Cl}] + [\text{excess SO}_4]} \quad (6)$$

To calculate the MRI and to evaluate hideout return data, the hideout return calculation spreadsheet, ChemTools #2 (EPRI chemWORKs) is used. Table 3 reveals MRIs for SG A and SG B using the values of Table 2. The MRI value of UCN 3 SG A is higher than that of SG B because potassium is released more at UCN 3 SG B during power reduction phase and less at HZP conditions than at UCN 3 SG A. The MRI for UCN 3 SG A and SG B indicates that the bulk conditions are alkaline.

Table 3. MRI for UCN 3 S/G.

	MRI	Crevice Condition
SG A	3.1	Alkaline
SG B	6.9	Alkaline

3-2. Crevice pH using MULTEQ

Based upon the hideout return test data, the crevice pHs is calculated with maximum concentration factor in the range of 10^8 under equilibrium conditions for removing or retaining precipitate using MULTEQ. Table 4 shows crevice pH variations to concentration factor calculated by MULTEQ. The crevice pH value is acidic using the values of Table 2 regardlessly whether precipitate is removed or retained.

Table 4. Crevice pH using MULTEQ for UCN 3 SG.

	Crevice pH		Crevice Condition
	Precipitate retained	Precipitate removed	
SG A	2.8	1.4	Acidic
SG B	3.0	1.6	Acidic

Table 5 reveals sensitivity analysis results of cumulative return for HPO_4 using MULTEQ. When 10 g of HPO_4 cumulative return is released, pH of crevice is alkaline condition at a value of 9.14. As 15 ~ 27.17 g of cumulative return is released, that of crevice pH is changed to acidic at a value of 1.73. A large amount of phosphate for UCN 3 SG A and SG B results mainly from the grease which is coated on turbine blade for the purpose of preventing corrosion. This trend shows similar to the case of YGN 3 &4 during initial core cycle.

Impurities having limited solubility at operating SG temperatures, such as calcium, magnesium, and silica have an effect on the pH. The quantity of these species returned from crevice regions cannot be distinguished from returns from other SG locations. Therefore, MULTEQ results are used only for the sensitivity analysis.

Table 5. Cumulative return of Phosphate vs Crevice pH for UCN 3 SG A

HPO_4 , g	0	5	10	15	20	27.17
Crevice pH	9.14	9.14	9.14	1.39	1.40	1.73

+ Based on precipitated removal.

3-3. Adjusting Methods & Recommendation

As shown in Table, 3 MRI values for UCN 3 SG A and SG B are 3.1 and 6.9, respectively, thus the crevice chemistry is not neutral but alkaline. The goal of MRC is to achieve a near neutral crevice pH by controlling the molar ratio of cations to anions.

There are three different methods to adjust MRI to a value of 1, i.e., a chloride injection, an ion exchange resin manipulation and a sodium source term reduction.

It is recommended the chloride injection be applied to UCN 3. The chloride injection method is most economical in achieving the desirable MRC as compared to other

methods and it also has an advantage of a simplicity of design and operation.

The ammonium chloride (NH_4Cl) is injected into the condensate line downstream of the condensate polishers. The devices such as an ammonium chloride storage tank, a chemical injection pump and the related connecting piping should be installed, if required.

4. Conclusion

The hideout return data from UCN 3 was evaluated to investigate the relationship between bulk water chemistry and crevice chemistry using the chemWORKs spread sheet and MULTEQ Code and to implement MRC scheme for the next fuel cycle.

Sodium, potassium and chloride were released at 20 ~ 60 % power during power reduction phase. Calcium, magnesium, phosphate and sulfate were significantly released at cooldown phase. Nitrate is usually released at cooldown phase, but it was continuously released from power reduction phase to cooldown phase during UCN 3 HOR test.

Based upon the hideout return test data, the crevice pHs is calculated with maximum concentration factor in the range of 10^8 under equilibrium conditions for removing or retaining precipitate using MULTEQ. The crevice pH value is acidic regardlessly whether precipitate is removed or retained.

There are three MRC methods available to be implemented such as a chloride injection, an ion exchange resin manipulation, and a sodium source term reduction. For UCN 3 SG A and SG B, the crevice chemistry condition is alkaline based on MRI value. Thus the chloride injection method is recommended to adjust MRI as close to a value of 1 as possible for the next fuel cycle. The chloride injection method is more economical as compared to other methods when implementing MRC and it also has an advantage of a simplicity of design and operation.

References

1. EPRI, "PWR Secondary Water Chemistry Guidelines : Revision 4," EPRI TR-102134-R4, November 1996.
2. EPRI, "PWR Molar Ratio Control Application Guidelines," EPRI TR-10481, 1995.
3. EPRI, "Equilibrium of an Electrolytic Solution With Vapor-Liquid Partitioning and Precipitation," EPRI NP-5561, (1992).
4. 한국전력공사, "제 12회 원전 화학분야 경험사례 발표집," 1999.8.