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《Original》

Analysis of Post-LOCA pH for Korea Nuclear Units

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국내 원자력발전소의 LOCA사고에 따른 pH 분석

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Abstract

The pH of containment spray and sump water following a LOCA for KNU 5&6 and KNU 1 was calculated to see if pH design criteria of containment spray system established by USNRC were met. The pH calculations have been made for the two cases; maximum pH and minimum pH. For KNU 5&6, results showed that long term sump pH values calculated for the maximum pH and minimum pH case well met the pH requirement of at least 8.5 and spray pH for the maximum case slightly exceeded the range of design criteria (8.5 to 11.0). For KNU 1, pH requirement of long term sump pH was also met, however, spray pH value for the maximum pH case was very largely greater than that of current pH requirement. (No pH requirement of containment spray water has been established at the time of designing KNU 1) In order to find the design parameters of containment spray system which are expected to meet the spray pH requirement, several calculations were made, by changing the input parameters to "LCCAPH". Finally, it was shown that the boric acid concentration in RWST (refueling water storage tank), which was the primary sources of containment spray water during injection mode, be maintained the range of 2750 ppm to 2850 ppm, or the flow rate of NaOH added to spray water be kept between 10 gpm to 24 gpm.

요 약

국내원자력 발전소중 고리 1호기 및 5,6호기의 LOCA 사고시 격납용기 살수용액과 썸프 용액의 pH값이 US NRC에서 요구하는 설계기준치를 만족하는가를 알아보기 위해 전산프로그램 "LOCAPH"를 개발하여 최대 pH경우와 최소 pH경우로 나누어 분석하였다. 고리 5,6호기의 경우, 썸프 용액의 pH는 설계기준(최소 8.5 이상)을 잘 만족하고 있으며, 살수 용액의 pH는 설계기준(8.5에서 11.0 사이)을 약간 벗어나고 있음을 볼 수 있었다. 그러나 고리 1호기의 경우를 보면 썸프 용액의 pH는 역시 설계기준을 잘 만족하고 있으나 살수 용액의 pH는 최대 pH 경우에 있어서 현재 설계에 반영되고 있는 설계기준을 상당히 벗어나고 있음을 알 수 있었다. (고리 1호기 설계시 살수 용액의 pH에 대한

설계 기준치는 없었음) 설계 기준을 만족시키기 위해 고리 1호기의 설계변수를 바꾸어가며 계산해 본 결과 격납용기 살수 용액의 공급원인 핵연료 재장전수 저장탱크(RWST)의 붕소 농도를 2750ppm에서 2850ppm 사이로 유지하거나, 격납용기 살수 용액에 첨가되는 NaOH의 유량을 10gpm에서 24gpm 사이로 유지해야 함을 알 수 있었다.

1. Introduction

The principal purposes of controlling the post-LOCA (Loss of Coolant Accident) pH are;

a) to minimize the probability of stress corrosion cracking leading to equipment failure or loss of containment integrity,

b) to reduce the iodine inventories in the containment atmosphere by iodine absorption and retention under post-LOCA conditions[1]

These purposes are met by maintaining the highest possible pH, within materials compatibility constraints, but not high enough to cause any substantial attack on aluminum fittings and to generate the excessive hydrogen.

This requirement is satisfied by a spray pH in the range of 8.5 to 11.0 and a long term sump pH of at least 8.5[2]

The alkalinity of the solution is obtained by adding solutions with a sodium hydroxide concentration of 30 w/o or higher from NaOH tank to the borated containment spray solution during containment spray system operation.

In this paper, it is attempted to develop computer program (defined "LOCAPH") which calculates pH values for the containment spray and sump water as a function of time following a LOCA.

In addition, pH values for KNU (Korea Nuclear Unit) 5&6 and KNU 1 are calculated by running "LOCAPH" to examine whether pH requirements are met for each unit.

2. Theoretical Consideration

The followings delineate the theoretical background of developing the computer program "LOCAPH".

2.1. Systematic Theory

The parameters for pH calculation include volume capacities, flow rates, temperatures, and chemical concentrations of Engineered Safety Features (ESF) systems, volume and boric acid concentration of Reactor Coolant System, and area & weight of metals for the consumption of NaOH by metal corrosion.

Postulating single failures of any active component in Containment Spray System, system operating modes are divided into three.

The three operating modes are as follows.

a) two spray pumps operating and addition of NaOH via two valves.

b) two spray pumps operating and addition of NaOH via one valve

c) one spray pump operating and addition of NaOH via one valve

The Emergency Core Cooling (ECC) following a LOCA is largely divided into two phases (short term injection phase & long term recirculation phase) by the time Refueling Water Storage Tank (RWST) is emptied.

Flow diagram of Engineered Safety Features systems considering these two phases is shown in Figure 2.1.

2.2. Chemical Theory

2.2.1. Boric Acid Chemistry[3]

Boric acid is a weak tribasic acid which is only slightly ionized following the relationship given by eq. (1) and eq. (2)

$$H_3BO_3 + H_2O \overset{K_{11}}{\rightleftharpoons} H^+ + B(OH)_4^- \quad (1)$$

$$3H_3BO_3 \overset{K_{13}}{\rightleftharpoons} H^+ + B_3O_3(OH)_4^- + 2H_2O \quad (2)$$

The ionization constants (K_{11}, K_{13}) as a

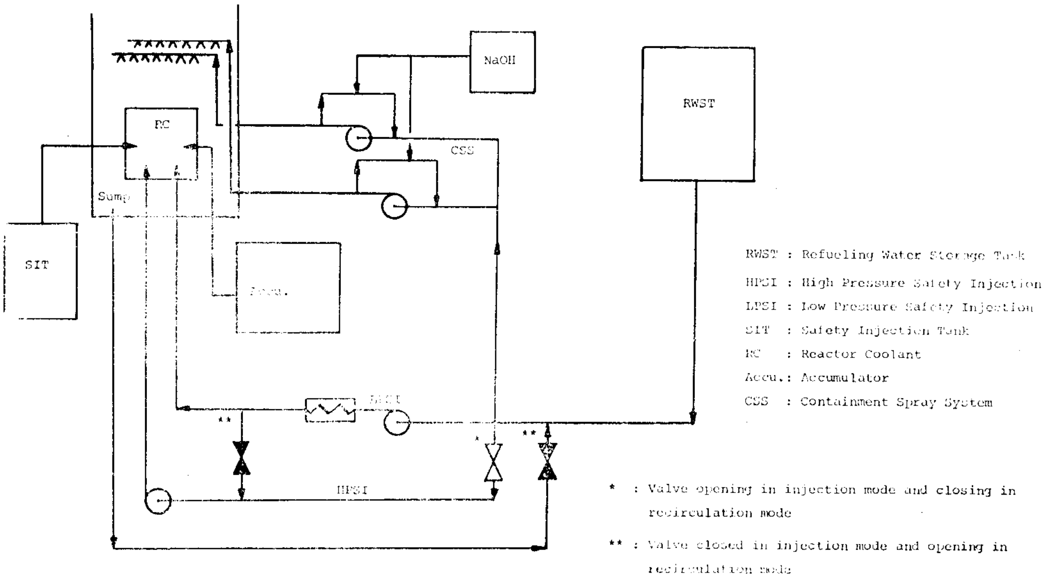

Fig. 2. 1. Typical ESF System Flow Diagram

function of temperature are shown in Figure 2. 2.

As shown in Figure 2. 2, the ionization constant for the first equation is several orders of magnitude lower than the second.

However, both equations are considered to preserve accuracy.

Since boric acid is a weak acid, the pH at operating temperatures is only slightly acidic and is greatly influenced by the pressure or addition of very small amounts of weak base.

2. 2. 2. Boric Acid Solution with Sodium Hydroxide Additive

Sodium hydroxide is added and mixed to the boric acid solution to partially neutralize the boric acid and to increase the solution pH.

Since NaOH is a strong base, it is considered completely dissociated in the solution.

In order to determine pH for the solution, the water dissociation equation must be considered.

$$H_2O \overset{K_w}{\rightleftharpoons} H^+ + OH^- \quad (3)$$

The temperature dependence of K_w is also shown in Figure 2. 2.

The dissociation constants of eq. (1), (2) and

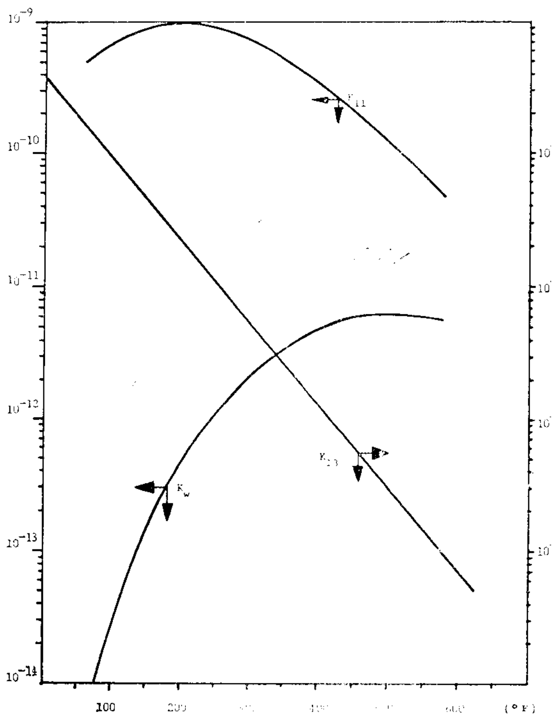

Fig. 2. 2. Ionization Constants (K_w, K_{11}, and K_{13}) as a Function of Temperature

(3) can be expressed as follows.

$$[H^+][OH^-]=K_w \quad (4)$$

$$\frac{[H^+][B(OH)_4^-]}{[H_3BO_3]}=K_{11} \quad (5)$$

$$\frac{[H^+][B_3O_3(OH)_4^-]}{[H_3BO_3]^3}=K_{13} \quad (6)$$

where, $[A]$=molar concentration of ion A By conservation of boron, eq. (7) is derived from eq. (1) & (2)

$$[H_3BO_3]_0=[H_3BO_3]+[B(OH)_4^-]+3[B_3O_3(OH)_4^-] \quad (7)$$

where, $[H_3BO_3]_0$=initial boric acid concentration Ionic balance results in eq. (8)

$$[Na^+]+[H^+]=[B(OH)_4^-]+[B_3O_3(OH)_4^-]+[OH^-] \quad (8)$$

where, $[Na^+]$=initial concentration of NaOH since it is a strong base.

Substitution of eq. (4), (5) and (6) into eq. (7) and (8) results in two non-linear eq. (9), (10) with two unknowns, e.g. $[H_3BO_3]$ and $[H^+]$

$$[H_3BO_3]_0=[H_3BO_3]+\frac{K_{11}[H_3BO_3]}{[H^+]}+\frac{3K_{13}[H_3BO_3]^3}{[H^+]} \quad (9)$$

$$[Na^+]=\frac{K_{11}[H_3BO_3]}{[H^+]}+\frac{K_{13}[H_3BO_3]^3}{[H^+]}+\frac{K_w}{[H^+]}-[H^+] \quad (10)$$

The simultaneous equations can be solved by Newton's method of tangents.[4]

Simultaneous convergence of non-linear equations using Newton's method of tangents requires that initial values for $[H^+]$ and $[H_3BO_3]$ be specified which are sufficiently close to the roots of the equation.

For the first iteration, the following values are assumed.

1) if $[H_3BO_3]_0 \leq [Na^+]$, then $[H^+]=\frac{K_w}{[Na^+]}$

2) If $[H_3BO_3]_0 > [Na^+]$,

i) $\frac{[Na^+]}{[H_3BO_3]_0} > 0.005$,

$[H_3BO_3]=0.5\times[H_3BO_3]_0$

ii) $\frac{[Na^+]}{[H_3BO_3]_0} \leq 0.005$,

$[H_3BO_3]=0.99\times[H_3BO_3]$

then, eq. (10) is put into the form of the quadratic equation and solved for $[H^+]$

Multiplying both sides of eq. (10) by $[H^+]$ gives:

$$[H^+]^2+[Na^+][H^+]-(K_{11}[H_3BO_3]+K_{13}[H_3BO_3]^3+K_w)=0 \quad (11)$$

Solving eq. (11), $[H^+]$ gives

$$[H^+]=\frac{-[Na^+]+\sqrt{[Na^+]^2+4(K_{11}[H_3BO_3]+K_{13}[H_3BO_3]^3+K_w)}}{2}$$

Since satisfactory $[H^+]$ is calculated with given initial values by iteration, pH is determined from $pH=-\log[H^+]$

2.2.3. Metal Corrosion

The presence of NaOH in the containment spray and sump solution will result in greater corrosion rates for metals in the containment.

As sodium hydroxide reacts with the metal, it will be consumed from the solution causing a decrease in the sump pH.

The basic corrosion reactions are given by eq. (12), and (13)

$$M+2NaOH \longrightarrow Na_2MO_2+H_2\uparrow \quad (12)$$

where, M stands for zinc and copper.

$$2Al+6NaOH \longleftarrow 2Na_3AlO_3+3H_2\uparrow \quad (13)$$

where, Al stands for aluminum.

It is obvious that for 1 lb-mole/ft²-hr of hydrogen generated due to metal corrosion, 2

Table 2.1. Hydrogen Generation Rate for Metals (lb-moles/ft²-hr)

Time (hr)	Zinc	Zinc-Based Paint	Time (hr)	Aluminum	Copper
0~24	1×10^{-5}	3.43×10^{-6}	0~167	5.8×10^{-4}	6.05×10^{-7}
24~48	3.83×10^{-7}	2.67×10^{-6}	167~on	9.8×10^{-6}	1.25×10^{-7}
48~72	1.52×10^{-7}	2.67×10^{-6}			
72~on	3.98×10^{-8}	4.08×10^{-7}			

lb-mole/ft^2-hr of NaOH are consumed.

Table 2.1 gives conservative hydrogen generation rates as a function of time for various metal corrosions.[5,6]

3. pH Calculation for Korea Nuclear Units

The pH calculation for containment spray

Table 3.1. Parameter Data for pH Calculation of KNU's

Parameter \ Case \ Unit	KNU 5&6		KNU 1	
	minimum	maximum	minimum	maximum
1. NaOH tank				
◦ volume (gal)	3600	4400	3000	4000
◦ concentration (w/o)	30	30	30	30
◦ flow rate (gpm)	30	40	35	35
2. CSS				
◦ flow rate (gpm)	3605	2945	1590	1440
◦ motive flow rate (gpm)	15	15	25	25
3. SIS				
◦ HPSI flow rate (gpm)	1300	300	1670	1400
◦ LPSI flow rate (gpm)	9000	6000	5840	4000
4. RWST				
◦ volume (gal)	530000	433000	340000	320000
◦ boric acid concentration (ppm)	2100	2000	2450	2000
◦ Temperature (F)	92	65	120	80
5. Accumulators				
◦ volume (gal)	23340	22665	20018	19030
◦ boric acid concentration (ppm)	2100	1900	2000	1900
◦ Temperature (F)	175	100	120	120
6. SIT				
◦ volume (gal)	900	900	8000	8000
◦ flow rate (gpm)	650	150	1670	1400
◦ boric acid concentration (ppm)	22500	20000	21000	20100
◦ Temperature (F)	175	155	175	155
7. RCS				
◦ volume (gal)	66650	66650	49215	49215
◦ boric acid concentration (ppm)	1100	100	1100	100
◦ LiOH concentration (ppm)	0.7	2.2	0	0
◦ Temperature (F)	550	590	550	590
8. metal area & weight				
◦ Zn area (ft^2)	70800	0	0	0
weight (lb)	8840	0	0	0
◦ Al area (ft^2)	38	0	317	0
weight (lb)	218	0	903	0
◦ Zn paint area (ft^2)	261620	0	0	0
weight (lb)	8500	0	0	0
◦ Al paint area (ft^2)	0	0	10000	0
weight (lb)	0	0	110	0

and sump water following a LOCA for KNU 1 and KNU 5&6 has been made for the following two cases.

3.1. Parameter data for pH calculation for KNU's

3.1.1. minimum pH case

In calculating the minimum pH, the following assumptions are made:

a) maximum boron concentration and volume of Refueling Water Storage Tank (RWST), Safety Injection Tank (SIT) and accumulators

b) maximum flow rates of Safety Injection System (SIS) and Containment Spray System (CSS)

c) boron concentration in BOL (Begin of Life) of Reactor Coolant System (RCS)

d) minimum volume, concentration, and flow rate of sodium hydroxide

e) consideration of pH reduction due to corrosion Table 3.1 presents the design parameters used for minimum pH calculation for each unit.[7,8,9]

3.1.2. maximum pH case

In calculating the maximum pH, the following assumptions are made:

a) minimum boron concentration and volume of RWST, SIT and accumulators

b) minimum flow rates of SIS and CSS

c) boron concentration in EOL (End of Life) of RCS

d) maximum volume, concentration, and flow rate of sodium hydroxide

e) no consideration of pH reduction due to corrosion. Similarly, design parameters for maximum pH calculation are given in Table 3.1.

3.2. Calculation results

Several computer runs are made by inputting the parameters given in Table 3.1 to "LOCA-PH".

The results of the calculation for KNU 5&6 are illustrated in Fig. 3.1.a for the maximum pH case and Fig. 3.1.b for the minimum pH case, comparing with the FSAR pH values.

Also, Fig. 3.2 shows the pH history as a function of time following a LOCA for KNU 1.

4. Discussion and Conclusion

For KNU 5 & 6, as shown in Fig. 3.1.a and Fig. 3.1.b, long term sump pH value calculated by "LOCAPH" is 8.62 for the minimum pH case and 9.10 for the maximum pH case.

Theses values are met with the pH requirements of at least 8.5.

The spray pH value varies in the range of 9.13 to 9.54 for the minimum pH case, and this is well within the pH limits of 8.5 to 11.0. For maximum pH case, the range of spray pH value (9.9 to 11.38) slightly exceeds that of design criteria.

Nevertheless, it is thought that the change of design parameters is not needed because of the high conservatism given in calculated reults.

For KNU 1, as shown in Fig. 3.2, long term sump pH value is 8.59 for the minimum pH case and 9.07 for the maximum pH case, which also meets the pH requirements.

The spray pH value is 10.9 for the minimum pH case and 12.4 for the maximum pH case.

Maximum spray pH of 12.4 for the maximum pH case exceeds considerably that of current pH requirements.

In order to satisfy this, it would be necessary to change the design parameters for KNU 1.

In fact, there are five parameters which influence the spray pH value such as boric acid concentration of RWST, flow rate and concentration of additive NaOH, and flow rate and temperature of containment spray system.

The change of NaOH concentration, which is definite parameter having an effect on the long term sump pH, is not considered, since long term sump pH value for the minimum pH

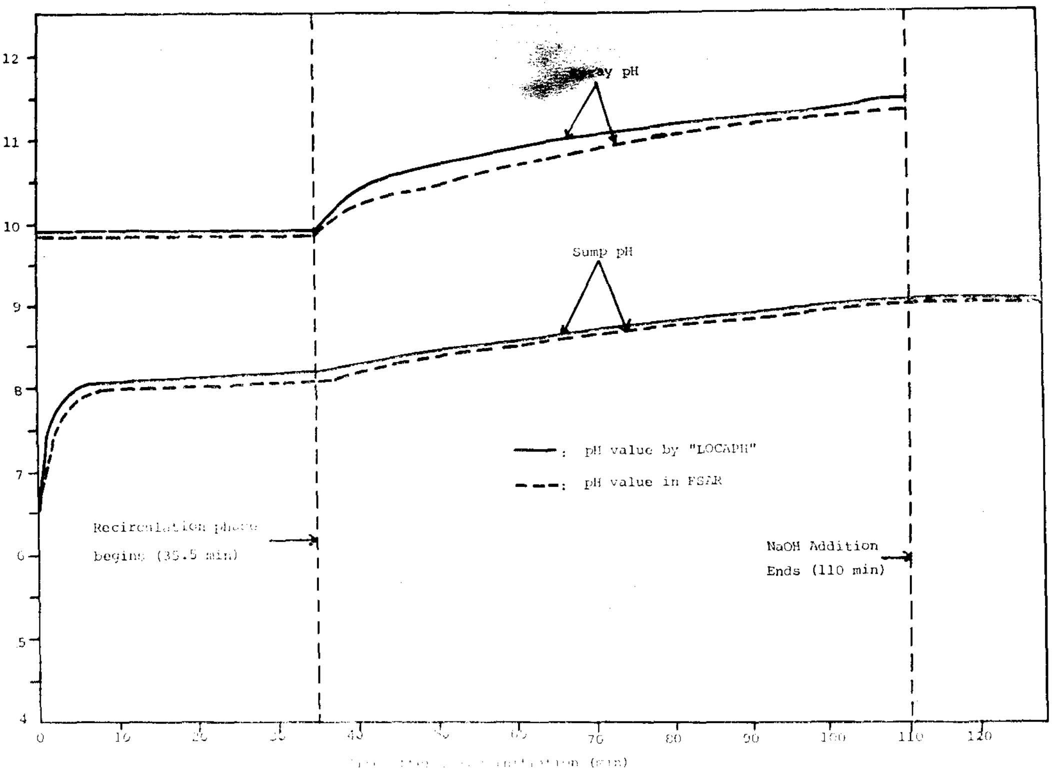

Fig. 3. 1. a. Maximum Spray and Sump pH versus Time (for KNU 5&6)

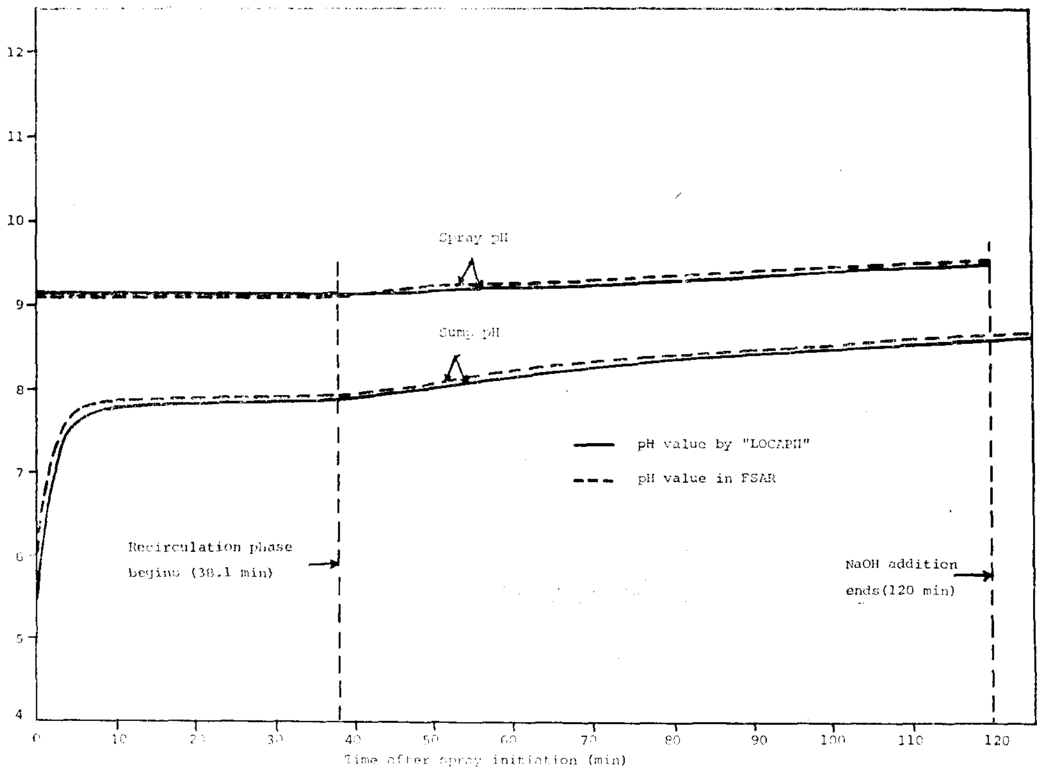

Fig. 3. 1. b. Minimum Spray and Sump pH versus Time (for KNU 5&6)

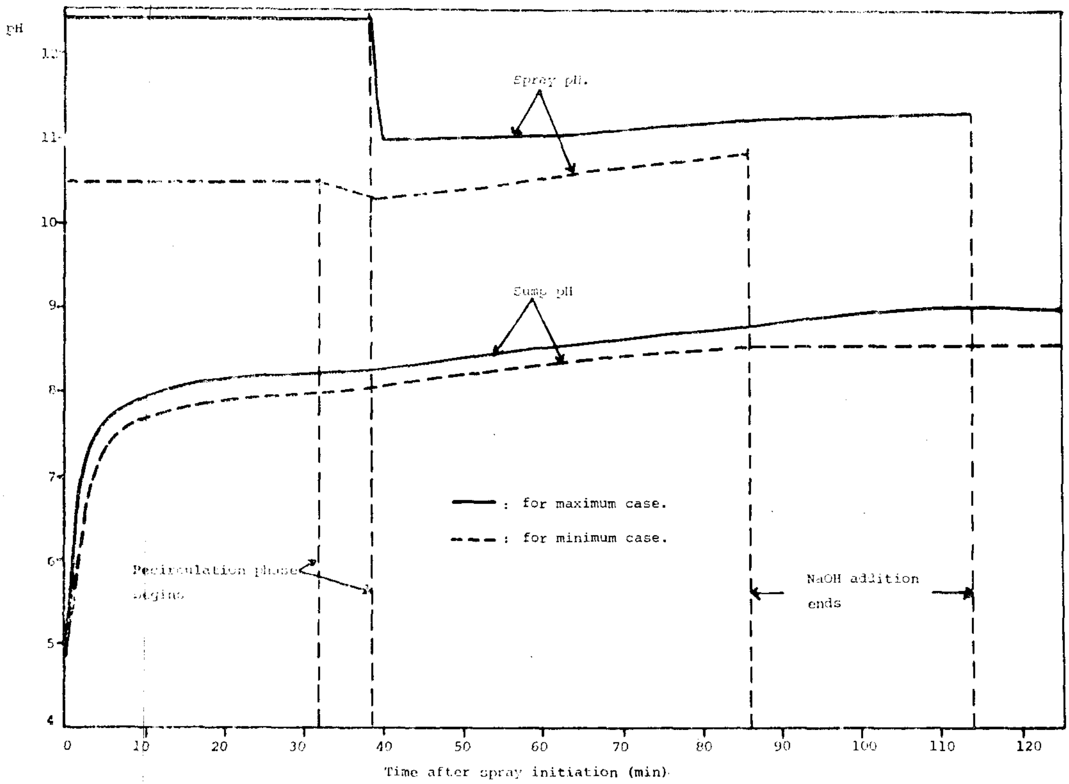

Fig. 3. 2. Spray and Sump pH versus Time (for KNU 1)

case nearly meets design criteria. And the change of CSS flow rate is also not considered, because it's not desirable to replace containment spray pump.

In this paper, the temperature of CSS is fixed at 80°F and 120°F for the maximum and minimum pH case, respectively. Two alternatives are suggested to implement the design change as follows.

1) Change of boric acid concentration in RWST

The first alternative is to change the boric acid concentration in RWST.

The change of the borc acid concentration in RWST influences not only spray pH value but long term sump pH value.

Therefore optimum value of boric acid concentration in RWST is searched for, considering maximum spray pH value for the maximum pH case and minimum spray and long term sump pH for the minimum pH case.

Table 4. 1. pH Values for Change of RWST Concentration

Case \ Concentration (ppm)		2700	2750	2800	2850
Spray	maximum	11. 05	11. 01	11. 0	*
	minimum	*	10. 60	9. 95	9. 91
Sump	maximum	8. 87	8. 86	8. 84	*
	minimum	*	8. 52	8. 51	8. 50

(*: Value to previously meet design criteria)

Table 4. 1 shows spray pH values and long term sump pH valuse for each case as a function of boric acid concentration.

It is shown that the pH requirement is satisfied with a boric acid concentration in RWST in the range of 2570ppm to 2850ppm.

2) Change of NaOH flow rate

As the second alternative, the change of NaOH flow rate is taken into account.

Since the long term sump pH is hardly

Table 4.2. Spray pH Values for Change of NaOH Flow Rate

Case \ flow rate (gpm)	9	10	…	23	24	25
maximum	*	*	…	10.9	11.0	11.6
minimum	8.48	8.59	…	*	*	*

(*: Value to previously meet design criteria)

influenced by the NaOH flow rate, spray pH values are only considered.

Spray pH values as a function of NaOH flow rate are given in Table 4.2.

This table indicates optimum pH control consists of maintaining NaOH flow rate between 10gpm and 24gpm.

References

1. "PWR and BWR containment spray system design criteria", ANSI/ANS 56.5 (1979)
2. "Containment Spray as a Fission Product Cleanup System" US NRC SRP section 6.5.2 (NUREG-75/087)
3. F.A. Cotton and Geoffrey Wilkinson, "Advanced Inorganic Chemistry", Interscience Publishers, New York (1972)
4. S.D. Conte and Carl de Boor, "Elementary Numerical Analysis", McGraw-Hill Book Company, New York (1972)
5. J.C. Griess and A.L. Bacarella, "Design Considerations of Reactor Containment Spray Systems-Part III. The Corrosion of Material in Spray Solutions", *ORNL-TM-2412*, Part III (1969)
6. G.P. Wachtell, "Test of Coatings in a Simulated Reactor Containment Post-Accident Steam Environment", *Final Report F-C 2697* (1970)
7. KNU 1-FSAR Chapter 6, 9, 15, 16. (1978)
8. KNU 5 & 6—Design Report, System 105, 106, 107 (1979)
9. KNU 5 & 6—FSAR Chapter 6, 9, 15, 16. (1983)