IMPURE WATER IN STEAM GENERATORS

AND ISOLATION GENERATORS

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TABLE OF CONTENTS

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SUMMARY

1. Stress corrosion cracking (SCC) can occur in stainless steel (SS) and Inconel 600, but they do not behave in the same way.

2. SS is prone to SCC in Cl^- as well as NaOH. Inconel 600 is less prone to SCC in NaOH, and normally resists SCC in Cl^-.

3. Impure water ingress into PWR steam generators or BWR isolation condensers is discussed in terms of Cl^- - cracking and NaOH cracking, taking into account the kinetics of chemical changes, concentration changes and SCC. Changes in chemistry are relatively rapid.

4. Cl^- cracking of SS can occur at low pH or if O_2 is present. The pH drop in the use of sea water is believed to be less important than the presence of O_2.

5. NaOH cracking is a greater likelihood in SS than in Inconel, although both materials are susceptible.

6. Operation at temperature for up to a week with impure water may lead to SCC of the tubes by Cl^- or NaOH.

7. Elimination of O_2 will reduce the chances of Cl^- SCC of SS, NaOH cracking of Inconel, or pure water cracking of sensitized SS.

8. Silica may hold potential as an ingredient to suppress caustic formation due to concentration effects in alkaline impure waters.

9. Lowering the temperature as quickly as possible would also be beneficial in a steam generator with Inconel 600 tubes and a caustic-forming environment.

STATEMENT OF PROBLEM

A meeting was held in late June 1979 in Bethesda to discuss the matter of impure water that may be introduced into PWR steam generators or BWR isolation condensers. J. R. Weeks and D. van Rooyen represented BNL. It was said that new plants are or will be required to have a 36-hour supply of feedwater available in case of emergency. Also, such new plants are being designed to be capable of reaching cold shutdown within a period of 36 hours. In older plants, there are no such rules for supplies of feedwater to be available, and if it becomes exhausted for some reason then the plant would have to use an impure source for emergency cooling under cold shutdown is reached. Some of these plants may only have a 30 minute supply of pure water on hand.

Of major concern to the NRC is the possibility that stress corrosion cracking (SCC) will occur. Tube materials are typically stainless steel (SS) or Inconel 600, and both of these materials under certain conditions are subject to SCC. The most likely impure water that would find entry in steam generators or isolation condensers would be sea water, lake water, river water or water from a municipal supply. In the case of sea water, the pH of the resulting solution will drop and chloride can concentrate in crevices or at areas of local boiling.

Essentially, three problems are associated with chloride entry, i.e., those of SCC, accelerated corrosion of carbon steel and pitting. Of these, only the cracking of SS in chlorides is addressed in the section on sea water because pitting and denting are not forms of corrosion associated with safety questions in the time period of about one week.

Fresh water, from which carbon dioxide could be expelled, if introduced into a steam generator or isolation condenser, is usually expected to show a pH rise, so that caustic cracking may become a problem. The pH can also rise as a result of the reaction of Na salts in the impure water with existing oxides or hydroxides in the system, giving free NaOH. In this case, both Inconel 600 and SS are known to undergo SCC. River water or other sources of fresh water are known to contain sodium salts, and therefore, the matter of caustic cracking will be discussed in this section, including both of these alloys.

-2-

The questions that were raised by NRC for Brookhaven to look into concern mainly the matter of time. In other words, how long can a certain impure water be tolerated in the components that have been mentioned above? An additional question concerns the possibility of additions or other steps that could be taken to reduce or mitigate the effects of the impure water on tube integrity. It was agreed that the Brookhaven review would consider a period of approximately one week which would cover temperatures from operating temperature down to cold shutdown. In practice, a substantial portion of this time period would involve boiling and steaming while orderly emergency procedures and repairs are carried out. NRC felt that one week would be a reasonable basis for the present analysis.

CHLORIDE STRESS CORROSION CRACKING

Chloride cracking is considered a potential problem for SS but not for Inconel 600 tubing, which has a high nickel content. The cracking of SS in chlorides depends both on the chloride concentration, the pH of the solution, and the electrochemical potential. The higher the potential* the less chloride is usually required for cracking to start, and the opposite is also true. When Cl^- is introduced, the pH can be lowered in local regions such as crevices. For this to happen, local corrosion is needed. The latter is stimulated by oxidizing species. The pH drop will affect SCC, but since the oxidizing species will do the same, we emphasize the oxidizing aspect in this discussion. A curve showing the relationship between chloride concentration and oxygen concentration was developed many years ago[1] and is included in Fig. 1 with other data taken from a recent paper by Gordon.[11] Subsequent work by R. L. Jones[2] has extended the knowledge about the effect of electrochemical potential, using solutions with .1 N NaCl (which is equivalent to about 0.6% NaCl or 0.36% Cl^-) and tests which were made at $290^\circ C$. No SCC was found in 30-hour tests without

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*High oxygen concentrations give rise to high electrochemical potentials, so that the plot of chloride versus oxygen concentration is the same in principle as chloride versus electrochemical potential. The effects of O_2 per se can differ from that of controlling the potential at the same value by electronic apparatus, as shown by Rosborg and Rosengren[3] for sensitized SS in pure water.

-3-

any applied electrochemical potential, in tests done in an atmosphere of helium, i.e., no oxygen present. As the potential was increased, using electrochemical instruments, SCC was observed to take place in about +1000 mV on the hydrogen scale. This is quite a high potential, corresponding to an oxygen concentration well in excess of that in feedwater in contact with air. Cracks start from pits under these conditions and some additional work showed that when the instruments were switched off after pitting had started, in order to lower the potential, then no cracks penetrated the material. This suggests that even if chloride and oxygen are present for a time long enough to start pitting, SCC may still not be serious if the oxygen is removed soon enough. Time is obviously critical in this regard, but at any stage the removal of O_2 will reduce the chances of SCC. A point of uncertainty remains, since it is not established whether an existing crack will grow or would be arrested in the absence of O_2.

Recent data also indicate that there is an absence of cracking in C-rings stressed above the yield point exposed to solutions at 600°F with low O_2 and high chloride. These tests indicated only an extremely slight amount of intergranular penetration, which was not typical of SCC in sensitized SS. The oxygen was somewhere below 200 ppb, which was the maximum level in the starting solution; unfortunately the effluent frequently contained zero or much less oxygen than was introduced. Consequently, the tests can only be considered to have been oxygenated to the maximum of 200 ppb, and under various (most?) time periods probably contained no oxygen at all. The test does reinforce the conclusion though that removal of oxygen or keeping the oxygen very low will eliminate the risk of early SCC in SS.

The use of sea water in an emergency situation for cooling the steam generator would necessarily introduce an air-saturated aqueous electrolyte with high chloride. This, when in contact with SS at operating temperature in the vicinity of 290°C, would definitely pose a threat of early SCC, certainly well within a one week period unless the oxygen is removed from the solution. Therefore, if sea water is used as standby coolant, it should be deaerated or its use should be discontinued within a matter of hours in order to reduce the hazard of SCC in SS. The points of particular vulnerability here would be those sites where chlorides concentrate as a result of boiling or as a result

-4-

of corrosion taking place inside the crevices or inside pits that would form as a result of the intrusion of sea water.

The relationship between cracking and chloride concentration (as well as electrochemical potential), correlates well with the work by Jones, who found no cracking in his tests in a 30 hour test period when O_2 was absent, and potential not controlled. Also, he observed no pits in his tests. It seems reasonable to assume that the test by Jones could have run considerably beyond 30 hours with the same result, since the electrochemical potential was not suitable for cracks or pits to develop. Consequently, under similar conditions a steam generator with SS tubes or an isolation condenser would be expected to operate without cracking for a period of several days. However, Jones' work does not cover the case where local boiling takes place and where chlorides could be concentrated by a large factor. As discussed in the next section (for caustic cracking), local changes in concentration due to heat flux can occur relatively rapidly, so that the kinetics of SCC are expected to be rate determining. Conditions of increased concentration and heat flux would have to be explored in greater detail before a final conclusion can be drawn regarding the low O_2 solutions.

Additional laboratory results by Rosborg in Sweden[3] and B. M. Gordon[..] do somewhat to clarify the quantitative aspects of the question of Cl^- and __ vels. Fig. 1 includes older data together with more recent relationships between chloride and oxygen, as summarized by Gordon.

A remark here is needed concerning crack propagation and crack initiation. In SS the crack velocity can be of the order of 0.005 - 0.01" per hour. Consequently, once cracks initiate, they could penetrate a thin-wall tube quite quickly. Many alloys with increased resistance to Cl^- SCC have longer survival times only because cracks do not initiate readily. In 'immune' alloys, both initiation and propagation are extremely slow or absent.

CAUSTIC CRACKING

Whereas the influx of sea water into a steam generator or an isolation condenser causes a drop in pH, other natural waters such as river water, lake water,

and perhaps municipal water supplies would lead to higher pH and introduce the danger of caustic cracking.

Since the SCC problem is affected by several variables in this case, it is necessary to consider the two pertinent factors separately, in order to determine their effects on the kinetics of caustic SCC:

1. The rate and degree of concentration of NaOH due to boiling, chemical reactions, and the effect on pH of solution chemistry.

2. The SCC of the metals involved.

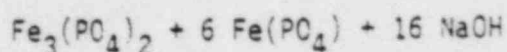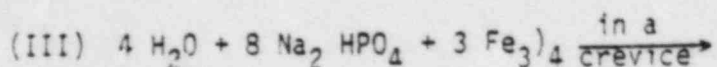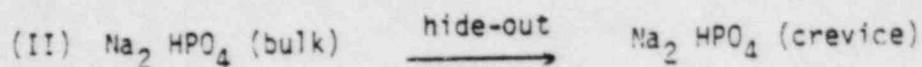## Local Boiling, Chemical Reactions, Species in Solution

It is important to establish some idea of the time needed to form a 1-10% localized solution of NaOH from the natural impure water and the environment within the condenser or steam generator. Concentration of alkali in waters can result from the high temperature shift of the equilibrium below to the right:

$$(I) \qquad NaHCO_3 \rightleftarrows NaOH + CO_2 \uparrow$$
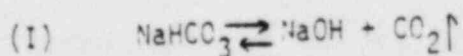
The chemical kinetics are rapid and the species always exist at equilibrium even at low temperatures. However, scale formation and crevices within the steam generator produce high heat flux crevices where the sodium hydroxide will concentrate. The chemical reaction will not determine the extent of high alkaline formation, but rather the thermal hydraulics will determine the concentration. Hence, if occluded high heat flux regions exist, NaOH will concentrate from an influx of alkaline waters such as those containing $NaHCO_3$. W. Pearl et al.[5] calculated a concentration of 0.1 molal NaOH within an isolated crevice with a heat flux giving a $10^\circ C$ temperature rise above bulk during a hypothetical influx of Mississippi waters. However, hydrolyzable species such as silicates which consume OH^- to form insoluble products will have a strong moderating influence on the rise in OH^- concentration (see Appendix A) The dynamics of the steam formation provide the rate determining step, not the chemical kinetics of reaction I. Specific rates will be qualitatively described later.

The case for the situation where a dissolved sodium salt reacts with corrosion products to form the alkaline crevice is different, as discussed next.

The anions of some heat-flux-concentrated dissolved sodium salts can react with metal oxide and hydroxides within occluded regions to produce free dissolved NaOH. For example, a possible scheme by which sodium phosphate will react with magnetite is as follows:[*]

(II) $Na_2 HPO_4$ (bulk) $\xrightarrow{\text{hide-out}}$ $Na_2 HPO_4$ (crevice)

(III) $4 H_2O + 8 Na_2 HPO_4 + 3 Fe_3)_4 \xrightarrow{\text{in a crevice}}$

$Fe_3(PO_4)_2 + 6 Fe(PO_4) + 16 NaOH$

(see Economy et al., ref. (4)

The steaming dynamics which cause local concentration as considered previously will determine the rate of (II). The chemical kinetics of (III), however, probably determine the rate of the overall process represented by the sequence of reactions. Times between 10-15 hours are required for III to equilibrate at $\sim 280^{\circ}C$ for .09 mole phosphate/kg H_2).[4]

There is more information suggesting that the hide-out process is more ____d than reaction (III). S. Yashima et al. reported the existence of a cor___e concentration of phosphate within a semi-isolated crevice to be independent of bulk phosphate concentration or Na/phosphate ratio as observed after the 400 hours of the test. Concentration of pyrophosphates produced the same rates as observed after 100 hours. The concentration process clearly is not the rate determining step for corrosion. In tests at BNL, using a

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[*]An example of cracking that occurred in the field is Benznau, where it was suspected that Na phosphate reacted with iron oxide formed earlier in the life of the steam generator and which was converted into NaOH and iron phosphate when dosing with phosphate was started. As will be examined later, it has been speculated and calculated by various scientists, that NaOH of a relatively high concentration can be generated especially in areas where it will not readily diffuse away such as crevices or underneath deposits. Other ingredients buffer these local electrolytes, so that the final pH depends on the overall electrolyte composition.

.01 M Fe_2SO_4 solution at $100^{\circ}C$, the concentration at a steam blanketed region via hide-out of $Fe(OH)_3$ through precipitation occurred within 1-2 hours, as shown by a rapid drop in local solution conductivity.

In summary then, concentration of species produced by heat flux proceeds quite rapidly and will be controlled by the relative rates of flow into and steaming from occluded regions. If concentration of NaOH proceeds merely by a heat flux concentrating mechanism of NaOH in the bulk solution, it will occur quite rapidly. Somewhat longer times will be required if chemical reactions between hide-out materials must occur to produce the alkalinity. For the purposes of SCC predictions, it has to be assumed that the time to form dangerous levels of NaOH, once impurities have been introduced, is short, i.e., one day or less.

An interesting possibility for mitigating the NaOH SCC problem is to add silicate to the impure water. As stated above, it is calculated to have strong suppressing effects on the level of caustic that is formed locally. (This is not standard practice, so that unidentified secondary pitfalls may exist, e.g., possible buildup of local acidity and scale formation.)

Rates of SCC of SS and Inconel 600 in Caustic

Laboratory tests with caustic have been done by various groups such as Westinghouse[6,7,8,9] and B&W[10] so that there is a good amount of data for predicting what would happen in NaOH solutions of various concentrations. Unfortunately, an unknown aspect in this correlation to be made with field conditions is that the influx of impurities will not give rise to a predetermined concentration of NaOH and a fixed electrochemical potential. Therefore, in different parts of the steam generator a whole series of caustic concentrations may arise depending on location, as stated before, and also on the concentration of other species such as silicates. Consequently, it is necessary to consider the effect of several levels of NaOH and O_2^- plus other ions in trying to determine how SS and Inconel alloy tubes will perform.

It is generally accepted that the use of slowly straining specimens gives most severe results, followed by U-bends, and that C-rings give the longest failure times. However, since stresses of unknown levels can exist under operating conditions, it is felt that sufficiently conservative conclusions can be

based on results with high stress, i.e., U-bends, for which the largest number of data are available.

Westinghouse data indicate that U-bends of Type 304 SS in deaerated 10% NaOH can crack in three days or less and similar results are obtained in higher concentrations. At 90% and 110% of the yield in 10% NaOH, 304 shows only minor surface penetrations in 220 days, and 25 mil cracks in 33 days, respectively. Obviously the stress level is proven to be quite significant. Compared to this, Alloy 600 cracks in a matter of several months and Alloy 800 (Inconel) behaves more like SS than the nickel base alloy. Since the earlier discussions showed that chemical changes can occur rapidly to raise the pH, it is evident that there should be concern about SCC in SS within a matter of a few days if impure (NaOH-forming) water is introduced. Mitigating factors would be (1) absence of high stress, and (2) species in solution that suppress NaOH level. For Inconel 600 in cases where O_2 is not present, less probability of SCC within one week exists, because laboratory data indicate relatively long failure times. This is believed to be a result of the higher Ni content of Inconel.

The performance of SS, and Alloys 600 and 300 in 50% caustic with and without additions is given in Table I, taken from reference (3). It is evident that Alloy 600 is much more resistant that 304SS. Also, some additions such as PbO or SiO_2 would be detrimental.

In practice, it must be considered that the introduction of river water or other relatively "high Na" impure water will be air-saturated, and the oxygen would be replenished as more and more of this solution is used, so that specific steps will be needed if O_2 is to be removed. Earlier International Nickel Co. results showed that Inconel 600 cracks in caustic soda at high concentration with an over-pressure of oxygen or air. While the level of oxygen in the Inco test was higher than the level of 6-8 ppm expected to be introduced by a solution in equilibrium with air, the field condition will nevertheless continue the supply of air (O_2), whereas in the closed system used by Inco the O_2 was gradually lowered by consumption during the test period. In this case, therefore, Inconel 600 is in an ill-defined grey area where it is not certain whether it possesses adequate resistance to SCC for one week if air is not removed. Another complication is that results obtained by Theus at 32¾[10] indicated that a small shift

in the anodic direction can introduce SCC in Inconel 600. This observation in-dicates that there are two bands of electrochemical potential in which there is a danger of SCC of Alloy 600 in caustic: the one lines at a high level, cor-responding to a considerable over-pressure of air in the International Nickel Co. tests, and the second one is lower and nearer the electrochemical potential of a deaerated solution and corresponds to the B&W and Westinghouse controlled potential data. A safe zone is believed to exist between these two, and there-fore there may well be cause for concern over a relatively low level of oxygen or other oxidizing species which could cause a sufficient snift of the corro-sion potential in the deaerated solution to move into the first band of caustic cracking, which could be as dangerous as much higher O_2 levels. The amount of oxygen required for this shift has not been determined accurately, and such tests are needed.

The bottom line for Inconel 600 is, therefore, that contact at operating temperatures with NaOH-forming impure water should be avoided or discontinued in less than two or three days, unless (a) O_2 can be removed, or (b) NaOH forma-tion suppressed in local regions. Further, lowering the temperature as quickly as possible would be beneficial, as caustic SCC of Inconel 600 is known to be strongly temperature-dependent. Also, it is evident that a better knowledge of what local conditions in terms of NaOH and stress may develop in service, would make predictions a great deal easier. The addition of SiO_2, which can buffer the buildup of NaOH, may also intensify the situation if large amounts of caustic are present, as can be seen in Table I.

CRACKING OF INCONEL AND SS IN RELATIVELY PURE WATER WITH A SMALL AMOUNT OF OXYGEN PRESENT

The cracking of SS in water with only a little oxygen present has occurred in sensitized SS even at low temperatures. Should such material be in service, then the simple introduction of a small amount of oxygen could pose a problem in highly stressed or actively straining regions. The cracking rates appear to be a maximum at $200^{\circ}C$. An analysis of the situation in a steam generator or isolation condenser indicates that the chances of such cracking are low, because the tubes are not usually installed in the sensitized condition, so that the time required for cracking can be expected to be longer than one week. This

would not be the conclusion for sensitized material; for this reason, it is also important to consider welds, the original material, and also the possible longer term sensitization that is known to occur at operating temperature. Experimental data along these lines are incomplete, and require emphasis if the SCC problem in impure water is to be addressed comprehensively. Reference to "original material" above concerns mill practice which may not be sufficiently controlled to ensure delivery of 100% unsensitized stainless steel tubing.

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11. B. M. Gordon, Materials Performance 19, #4 (April 29, 1980).

NOTE: Literature references to the subject of SCC are overwhelming, and several dozen, if not several hundred, could well be cited here but would not add to the basic arguments that were made above.
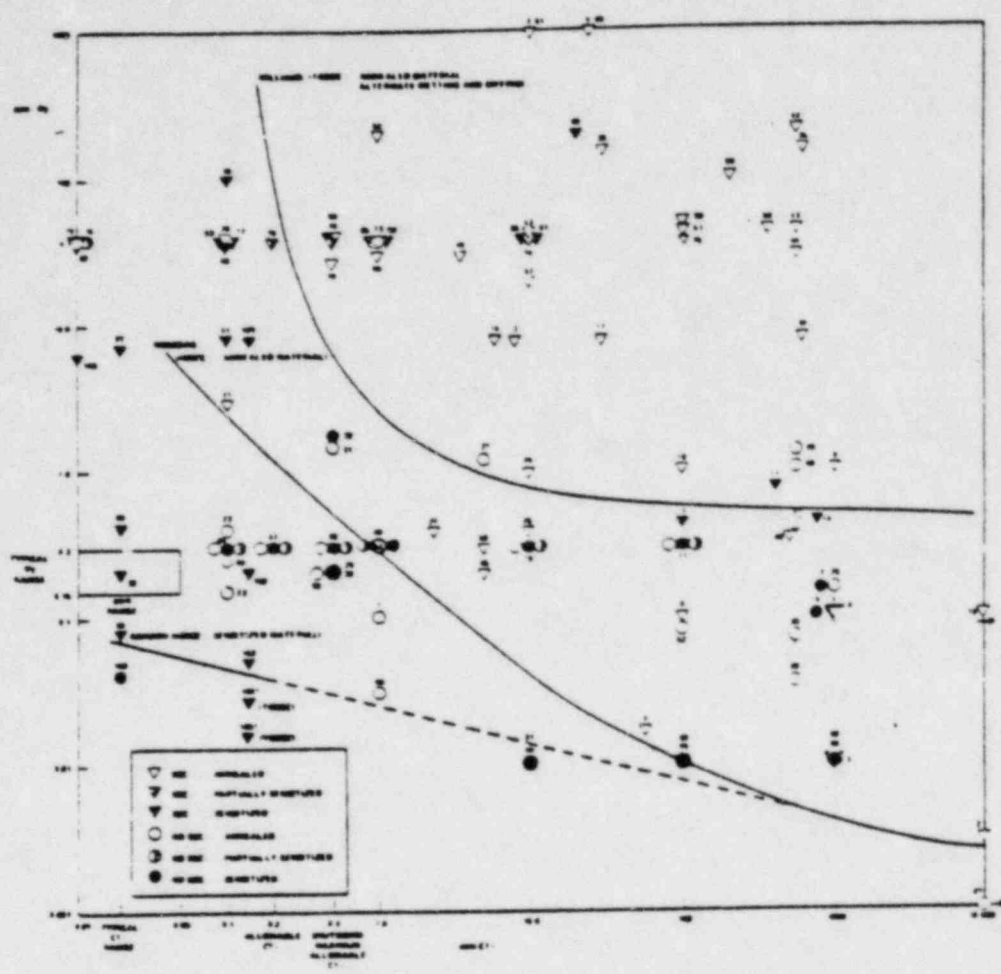
Figure 1. The Effects of Oxygen and Chloride on the
SCC of Austenitic Stainless Steels in High
Temperature Water

TABLE 1

(Ref. 8)

Stress Corrosion Test Incidence of Fe-Ni-Cr Alloys in Strong Caustic with Additives

[Mill-annealed C-rings in duplicate, at 110% of yield strength, exposed to equimolar 50% (KOH + NaOH) + additive; 620°F; 1-, 3-, or 6-month exposure. One sample/heat metallographically examined for cracking.]

Additive	Months	Type 304 Stainless Steel	Incoloy 800	Inconel 600[a]
None	1	Cracked	Not cracked	Not cracked
	3	Cracked	Not cracked	Not cracked
	6	Cracked	Cracked	Cracked
Secondary sludge[b]	3	Not cracked	Cracked	Not cracked
	6	Cracked	Cracked	Cracked
10% SiO_2	3	Cracked	Cracked	Cracked
	6	Cracked	Cracked	Cracked
$\frac{1}{4}$% Pb (as PbO)	3	Cracked	Cracked	Not cracked
	6	Cracked	Cracked	Cracked
1000-ppm Cl^- (as NaCl)	6	Cracked	Not cracked	Cracked
1000-ppm F^- (as F^-)	6	Cracked	Not cracked	Cracked
0.5% As (as As_2O_3)	6	Cracked	Cracked	Cracked
1% B (as H_3BO_3)	3	Cracked	Cracked	Cracked
10% sodalite[c]	6	Cracked	Cracked	Cracked
5% Zn	6	Cracked	Not cracked	Cracked
1% Cu (Cu_2O + Cu)	6	Cracked	Cracked	Cracked
5% Cr (as Cr_2O_3)	6	Cracked	Cracked	Cracked
10% $NaNO_3$	6	Cracked	Not cracked	Cracked

[a]Five heats of Inconel 600, 2 samples per heat.

[b]25 g of sludge in 500 ml of caustic solution. Sludge from plant with 2 yr of all-volatile treatment and 3 months phosphate.

[c]Sodalite approximated by a molar ratio of 8/8/12/8 of $Na_2SiO_3/Al_2O_3/NaCl/SiO_2$.

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APPENDIX A

o A. Paari and S. G. Sawochka[*] have made a calculation of the pH rise due to concentration of impurities introduced by a Mississippi River inleakage.

• Concentrating effect is limited by B.P. elevation which was taken to be $10^{o}C$

• $\left(\text{Define pH} = -\log\left[H^{+}\right]\right.$ $\left[H^{+}\right] = H^{+}$ concentration

  $\left(\text{neutral pH is that where}\right.$ $\left[H^{+}\right] = \left[OH^{-}\right]$

• For an isolated cavity with the $10^{o}C$ temperature rise and a fresh water ingress (Mississippi Water), the hydroxyl ion may reach a concentration of 0.1 <u>molal</u> in the absence of silica. This corresponds to a room temperature pH of 13.

  Silica can produce a suppressing (beneficial) effect.

  Through hydrolytic precipitation silica will buffer the solution to lower pH at high concentration factors. e.g., 100 ppb silica will reduce the level to ∿ 10^{-4} to 10^{-3} molal for the same conditions.

STAFF POSITIONS REGARDING
SEP SAFE SHUTDOWN SYSTEMS REVIEW
OYSTER CREEK NUCLEAR PLANT

1. The licensee must develop, by April 1981, plant operating/emergency procedures for conducting a plant shutdown and cooldown using only the systems and equipments identified in Section 4.0 of the SEP Safe Shutdown Systems report.

2. The licensee must propose a technical specification change to establish a minimum condensate storage tank inventory of 90,000 gallons to accomodate the safe shutdown water requirements identified in Appendix A to the SEP Safe Shutdown Systems report.