Technical Letter Report on WCAP-16530-NP, *Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191*

Summary and Conclusions

There are two major steps in the WCAP process for assessing chemical effects. One is the calculation of the amount of materials dissolved into the sump and the other is production of a realistic surrogate product. The WCAP makes the conservative assumption that the precipitation products are of low solubility and all the dissolve species that can form precipitates, do.

For the most part the calculation of releases seems appropriate. The model of Ca release includes a saturation term that is not relevant if phosphate is present, but this has little practical impact for the levels of Ca of interest in practice.

The recommended Al release model significantly underestimates releases in ICET–1 over the first 15 days of operation and underestimates the dissolution data in the WCAP. Unless passivation of the aluminum or saturation of the dissolved Al occurs, it may underestimate Al releases over the entire history in Al/NaOH environments. The release model is overly conservative in environments with significant Ca.

For Al/NaOH environments an alternate release model is given in the WCAP (Equation 6-1) that seems to better reflect the available data. It should be noted that the coefficients for this equation in Rev. 0 of the report are incorrect. This release model seems to overpredict releases in sodium tetraborate environments. However, in such environments the 50 ppm level observed in the ICET–5 tests may be considered bounding for virtually all plants.

The assumption that all dissolved Ca in TSP environments and all dissolved Al in other environments form precipitates is reasonable for the Ca/TSP case, but overly conservative in the Al/NaOH and Al/STB environments. Accurate prediction of solubility limits is difficult since they are sensitive to the choice of the solubility constant and pH.

The WCAP recognizes that the precipitation products developed by the proposed surrogate process are sensitive to the mixing conditions, especially the concentration, and imposes limits on the concentration. However, no good arguments are presented as to why these limitations are good enough. However, whatever differences there are between these products and the "real" products are, the surrogate products are so effective in producing head loss, that arguments over whether their capability to produce head loss is conservative or nonconservative seem moot.

Release Rates

Calcium

The release rates for the various species are computed on a "one species at a time" basis as though other species are not present. Probably in most cases this is conservative, in the sense that the total amount of dissolved material is overestimated. For example, the calculation of the Al release does not take into account the inhibiting effect of Cal–Sil seen in ICET–4 or the inhibiting effect of Al on the dissolution of NUKON seen in ICET–1. However, in some cases this assumption leads to nonconservative results.

The release rate for Ca is modeled in the WCAP using Equation 6-4:

$$RR = kA(1-C/K)$$ Equation 6-4

where:

   RR = release rate
   A = amount of material

k = a constant dependent on pH and temperature

C = the concentration of the released species

K = the saturation limit of the released specie (a quasi-equilibrium constant).

In the calculations in the WCAP spreadsheet, C is treated as the concentration arising from the integrated release of Ca. The spreadsheet does not take into account that in the presence of phosphate, Ca is largely removed from the system by precipitation of $Ca_2(PO_4)_3$. If excess phosphate is present, C is not given by the integrated release of Ca, but rather by the solubility of $Ca_2(PO_4)_3$ at the conditions of interest. Thus the WCAP model underestimates the release rate of Ca.

For the Cal–Sil levels of interest in an actual sump, the errors involved are small in most cases, because the concentrations are low compared the saturation level. For the sample calculation in the worksheet, the WCAP procedure gives 36.6 kg of Ca available after 72 hours, a calculation with C = 0 (i.e., all the Ca immediately precipitates out) gives 38.84 kg of Ca after 72 hours. By 96 hours both calculations predict the Cal–Sil is completely dissolved.

Aluminum

Two release rate equations are given for Al. The first is based a fit to the WCAP dissolution tests and is given as Equation 6-1:

$$RR=10[A + B(pHa) + C(1000/T) + D(pHa)2+E(pHa)(T)/1000] \qquad \text{Equation 6-1}$$

where:

RR = release rate in $mg/(m^2\ min)$

A = -4.049 [12.950, 13.035]

B = 0.4371 [0.540, 0.531]

C = 0.7172 [-4.467, -4.493]

D = -0.024398 [0.014, 0.014]

E = 3.065 [-1.413, -1.403]

pHa = initial pH corrected to 25°C

T = temperature (°K).

The first numbers given for A, B, ... are from the WCAP. Rev 0. They are clearly wrong and must be a typographical error. The first numbers in the brackets are obtained by fitting to the WCAP test and ICET-1. The second number in brackets is obtained by fitting just the WCAP dissolution tests.

A second is given as Equation 6-2:

$$RR=10[A + + B(pHa) + C(1000/T) + D(pHa)2+E(pHa)(T)/1000] \qquad \text{Equation 6-2}$$

where:

RR = release rate in mg/(m2 min)

A = 14.69039

C = -4.64537

D = 0.044554

E = -1.20131

pHa = initial pH corrected to 25°C

T = temperature (°K).

Equation 6-1 with the coefficients obtained by fitting by the ICET–1 and WCAP data fits the WCAP Al data very well with errors ≤ 19%. It also essentially matches the initial linear portion of the ICET–1 data (from day 1 to day 14). A best fit to the ICET–1 data over that time period gives a rate of 30.1 mg/(m^2 min). The model predicts 30.6 mg/(m^2 min) at 60°C and pH 9.6. The CNWRA estimate at 60°C is 20.3 mg/(m^2 min) about 50% lower than the model. The WCAP model predicts a stronger temperature dependence than observed in the CNWRA. The corrosion rate at 110°C was 5.8 greater than the corrosion rate at 60°C. The WCAP model predicts a 12.4 fold increase in corrosion rate for this increase in temperature. Since the CNWRA data are estimated from impedance spectra, greater weight should be given to the WCAP dissolution data.

The WCAP reports that the corrosion rate for ICET–1 is 12.2 mg/(m^2 min) at a pH of 10. This appears to be an average value of the rate over the full 30 days rather than over the initial 14 days when the dissolved Al level was increasing linearly. This is also a significant overestimate of the pH in ICET–1. The average value is about 9.43.

The WCAP recommends the use of Equation 6-2. It gives a poorer fit both to the WCAP data (underpredicts up to 133%) and to the linear portion of the ICET–1 data (underpredicts by factor of 3.3). It does give a reasonable fit to the ICET–1 data at 30 days (underpredicts by ≈ 50%), but underpredicts significantly for the first 15 days. Even the 30 day fit is contingent on the Al either passivating or the concentration reaching a solubility limit. If neither of these occur, the WCAP approach gives a poor, nonconservative estimate of Al dissolution in NaOH/NUKON environments even at 30 days.

On the other hand, based on ICET–4 results, both Eq. 6-1 and 6-2 will be very conservative for environments with significant amounts of Cal–Sil.

Solubility of Precipitation Products

The WCAP makes the assumption that all the dissolved species for which precipitation products have been identified will form precipitates. For the $Ca_2(PO_4)_3$ this is quite reasonable. The solubility of $Ca_2(PO_4)_3$ is quite low and with excess phosphate available virtually all the Ca that dissolves with form a precipitate.

For the precipitation of Aluminum oxyhyroxides in NaOH/NUKON systems, this assumption may be very conservative. Although the crystalline forms such as gibbsite have very low solubilities, experience with ICET–1 suggests that over the time frames of interest, the solubility is controlled by the formation of amorphous products.[1] This is also supported by studies in the literature. Van Straten et al.[2] showed that in precipitation of aluminum hydroxides from a basic supersaturated solution the first products to form are the less thermodynamically stable forms and then the product transforms through a series of forms to reach the thermodynamically stable form, gibbsite. The progression suggested by Van Straten et al[2] is amorphous, pseudo boehmite, bayerite, and then gibbsite.

For the pH range of interest the primary solubility product is aluminate, $Al(OH)_4^-$ and the equilibrium reaction with the solid phase is given by:

$$Al(OH)_3 \text{ (solid)} + H_2O = H^+ \text{ (aq)} + Al(OH)_4^- \text{ (aq)}$$
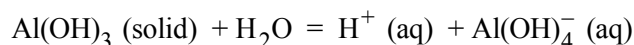
The $Al(OH)_4^-$ concentration at equilibrium is a function of pH:

$$\log Al(OH)_4^- = \log K - \log H^+ = \log K + pH$$

3

Values of the solubility constant log K are given by Van Straten et al.[2] and Langmuir[3] and can be inferred from experiments by Klasky[1] and Park at ANL and the ANL loop tests. The available data are summarized in Table 1.

Table 1   Measured values of the solubility constant K
at 25°C for amorphous $Al(OH)_3$

	log K 25°C
Van Straten	-12.1
	-12.0
	-12.7
	-12.8
Langmuir	-12.1
Klasky	-12.25
	-12.6
Park (bench)	-12.28
ANL loop tests	≈-12.2

The literature data cited in Van Straten and Langnuir is for simple Al/NaOH systems. The data from Klasky, Park, and the ANL loop tests are for systems with 2800 ppm B and LiOH. Data on the solubility as a function of temperature are given by Benezeth et al.[4]. These suggest that the variation of K with temperature can be expressed as

$$K = K_o \exp(-6969/T)$$

where T is in degrees Kelvin.

The uncertainties in the solubility constant can lead to substantial variability in the predicted solubility limits. Sample calculations for solubility as a function of temperature and pH are given in Table 2. The "best estimate" value for log K based on experiments in B containing environments is about -12.2. A log K of -12.4 would give more conservative values and a log K of -12.8 would give bounding results.

Nature of the precipitate

The WCAP states that the precipitates formed are amorphous and settle slowly. It recognizes that concentration during the precipitation process affects the size of the precipitate product and places limitations on the maximum concentrations in the reaction vessels. The effect that relatively small changes in the precipitation process can have is illustrated in Fig. 1. The precipitate in beaker 4 is much denser and more compacted than the other solutions.

The solutions in beakers 1–3, which meet the WCAP requirements for settling do appear to be more realistic. However, the concentrations in the mixing vessels are still very high compared to the concentrations expected in the sump, in the ANL 100 ppm loop tests, or ICET–1. The solutions in the 100 ppm loop test were very effective in causing head drop, but produced barely visible colloidal suspensions after being allowed to settle for a day. The WCAP provides limitations on the concentrations and the settling rates, and these do seem effective producing fine precipitates. However, no argument or data are available to show that they are in any physical sense equivalent to the suspensions that would be produced at concentrations more representative of those that might occur in a sump.

4

Table 2   Solubility of Al in ppm in equilibrium with amorphous $Al(OH)_3$ solid as a function of pH and temperature for different values of the solubility constant K.

log K = -12.2			
T°C	9.3	9.4	9.5
10	10	13	16
15	16	20	25
20	23	29	37
25	34	43	54
30	49	62	78
35	71	89	112
40	100	126	159
45	140	177	223
50	195	245	309
55	268	337	424
60	364	458	577
log K = -12.4			
T°C	9.3	9.4	9.5
10	6	8	10
15	10	12	16
20	15	18	23
25	21	27	34
30	31	39	49
35	45	56	71
40	63	80	100
45	89	112	140
50	123	155	195
55	169	213	268
60	230	289	364
log K = -12.8			
T°C	9.3	9.4	9.5
10	3	3	4
15	4	5	6
20	6	7	9
25	9	11	14
30	12	16	20
35	18	22	28
40	25	32	40
45	35	44	56
50	49	62	78
55	67	85	107
60	91	115	145

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Figure 2 shows x–ray spectra from surrogates similar to those developed by the WCAP process. The pH values for the "B" and "C" surrogates are outside the specifications and these surrogates would not pass the settling test. However, it might be argued that they are chemically and physically similar. The "B" and "C" surrogates are clearly crystalline (bayerite). Because of the small size of the "A" surrogate, no clear diffraction pattern can be obtained, but it appears likely that it too is crystalline. The WCAP does not provide other information such as solubility under changing pH or temperature conditions that might provide information on whether the products are crystalline or amorphous.

However, the loop test results at Alion and ANL appear to render further discussion of the products moot. Whatever differences there are between these products and the "real" products are, the surrogate products are so effective in producing head loss, that the only important question is whether or not the products will form. If they do form, very small amounts are sufficient to produce very large increases in head loss.

(a)

(b)

Figure 1.   (a) Solutions of Al(NO$_4$)$_3$ and NaOH after initial mixing; (b) Solutions after settling for 20 h.
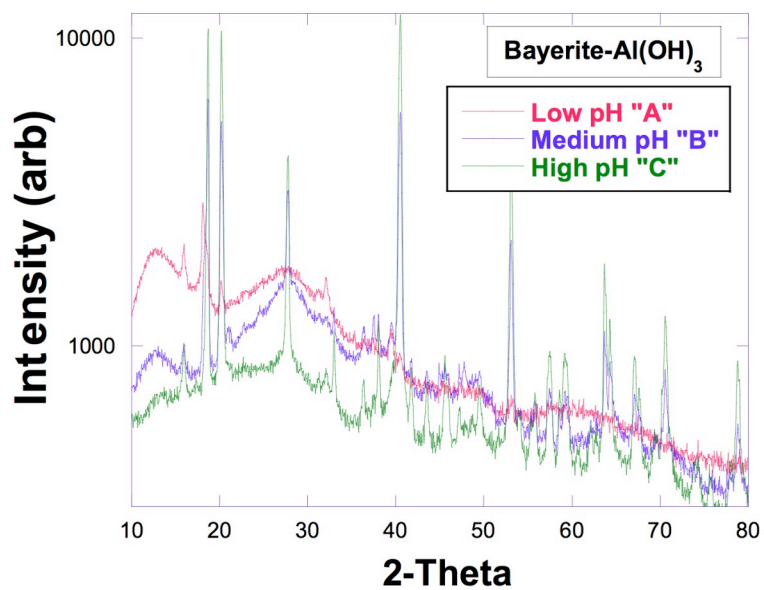

Figure 2.
X- ray diffraction spectra from WCAP like surrogates

References

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4. P. Benezeth, D.A. Palmer and D.J. Wesolowski (2001) Aqueous high-temperature solubility studies. II. The solubility of boehmite at 0.03m ionic strength as a function of temperature and pH as determined by in situ measurements, *Geochimica et Cosmochimica Acta*, v. 65, pp. 2097-2111.