Chemical Effects/Head–Loss Testing

Quick Look Report, Tests 1 & 2

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Abstract

This report describes the results of preliminary tests to determine the potential for chemical products observed in the third Integrated Chemical Effects Test (ICET–3) to increase the head–loss associated with sump screen debris beds. The first test was intended to simulate the conditions in ICET–3. The second test was parametric and intended to determine the effect of a range of chemical product loadings on head–loss. With a pre-existing physical debris bed approximately 16 mm (5/8 in) thick consisting of equal weights of NUKON fiber and CalSil insulation, a large increase in head loss was observed for the chemical product loading intended to simulate ICET–3 conditions. In the parametric test with a similar physical debris bed, increases in head–loss were observed for a chemical product loading one-twentieth of the simulated ICET–3 conditions.

Background - Integrated Chemical Effects Tests (ICET)

The ICET project is a joint effort by the U.S. Nuclear Regulatory Commission (NRC) and the nuclear utility industry, undertaken through a memorandum of understanding between the NRC and the Electric Power Research Institute (EPRI).[1] The ICET tests simulate the chemical environment present inside a containment water pool after a loss-of-coolant accident. The chemical systems were monitored for an extended time to identify the presence, composition, and physical characteristics of any chemical products that form during the test. The ICET test series was conducted by Los Alamos National Laboratory (LANL) at the University of New Mexico (UNM).

The containment pool environments selected for study were based on input from the Westinghouse Electric Company, the NRC and EPRI. The specific conditions, material types, and parameters in the ICET test series are intended to be broadly representative of all domestic PWRs. The Westinghouse Owners Group and the Babcock & Wilcox Owners Group aided in soliciting information. To obtain the necessary details of plant-specific conditions within containment (materials present, containment pool conditions, etc.), Westinghouse reviewed plant-specific documents, (such as Post-LOCA Hydrogen Generation Evaluations), other available plant documents (e.g., updated final safety analysis reports), and submitted survey questions to plant personnel. The plant survey responses formed the primary source of data for determining the parameters used to define the ICET test conditions.[2]

The third ICET test, ICET–3, investigated the chemical behavior of boric acid/LiOH solutions containing 80% calcium silicate/20%fiberglass insulation with a trisodium phosphate (TSP) buffering agent to obtain a target pH of 7. The steam generator is the largest plant component that may have fiberglass or calcium silicate insulation and that might be affected by a postulated large break LOCA. Based on the dimensions of a representative steam generator and accounting for a conservatively–large zone–of–influence (ZOI) volume, Westinghouse estimated that the volume of fiberglass or calcium silicate insulation debris that could be generated is 141.6 m^3 (5,000 cubic feet). The smallest containment pool volume, based on the survey information, is about 36,500 ft^3 so a conservative estimate of the insulation debris per volume of containment pool fluid is 0.137 ft^3/ft^3. For insulation with 80% CalSil, this gives about 25 g/l of CalSil if all the CalSil debris is assumed to be immersed in the sump fluid.

The ICET–3 test was performed by first adding boric acid (2800 ppm) and LiOH (3 ppm) to water in the ICET tank. HCl was also added to simulate degradation of electrical insulation. The resultant pH of this solution was 4.2. CalSil corresponding to about 20 g/l was placed in the submerged portion of the ICET tank; the remainder of the CalSil was only wetted by the sprays during the initial 4 hours of testing. The circulation pump was then turned on and the solution was allowed to circulate for about 5 hours. At this time, a solution containing dissolved TSP was metered into the test chamber solution over the next four

hours. Within 20 minutes after the beginning of metering TSP into solution, a white flocculent precipitate was observed in the tank. The precipitate appeared to be neutrally buoyant. The precipitate was presumed to be calcium phosphate. Subsequent analysis showed that substantial amounts of calcium phosphate are present in the precipitates, although other products could also be present. It has also not yet been determined which specific varieties of calcium phosphates are present in the ICET-3 products. Hereafter in this report, this ICET-3 product is generically referred to as $Ca_3(PO_4)_2$, tricalcium phosphate, for convenience.

Small Scale Dissolution Test Results

No measurements were made of the dissolved calcium levels in ICET–3 at times prior to the addition of the TSP through the sprays. Therefore, small scale dissolution experiments were performed using additions of CalSil to solutions containing 2800 ppm boric acid and 3 ppm LiOH to estimate the dissolved Ca level initially present in ICET-3. In some cases, small amounts of HCl (to simulate breakdown of electrical cables) were added since these were included in the ICET–3.

Small scale dissolution tests were performed for a range of CalSil concentrations that encompassed the ICET–3 conditions for durations ranging from 35 minutes to 24 hours. The results of these tests are summarized in Table 1. The Ca concentration values in this table are the dissolved Ca levels at the end of the leaching period. The "initial pH" values given in the table are the initial starting pH of the solution before the CalSil addition while the "final pH" values represent the pH at test termination. The CalSil dissolution raises the pH of initially acidic solutions to near pH 7 due to the hydrolysis of potassium and sodium released from the CalSil. However, the pH of the solutions already buffered with either NaOH or LiOH did not vary much upon CalSil dissolution. The amount of dissolved Ca most strongly depends on the initial pH of the solution as seen in Fig. 1 while the initial CalSil loading has very little effect for the loadings examined in this study.

Dissolution of the CalSil is more rapid in initially acidic solutions, but will occur even in near neutral and buffered solutions as seen in Table 1. In ICET–3, in which the initial solution was acidic, the phosphate was exhausted by the end of the second day. Thus in ICET-3, the amount of calcium phosphate formed is ultimately limited by the amount of TSP available. Assuming the product is $Ca_3(PO_4)_2$, 1 mole of TSP can consume 1.5 moles of $CaSiO_3$. Because CalSil is mostly $CaSiO_3$, this implies that the formation of precipitate will be phosphate limited for CalSil loadings down to about 2 g/l (for TSP additions of 4 g/l), but this could vary somewhat depending on the actual calcium phosphate species that form.

Based on the small scale test results, the dissolved Ca level in the ICET–3 tests before the start of the TSP injection is estimated to be about 200 ppm. Because not all the phosphate is consumed by this amount of dissolved Ca, only the initial "burst" of $Ca_3(PO_4)_2$ formation (within the first four hours of the ICET simulated post-LOCA environment) is associated with this inventory of dissolved Ca. As noted previously, additional $Ca_3(PO_4)_2$ likely continued to form in the ICET-3 test until all the phosphate was depleted.

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Table 1.   Small Scale Dissolution Tests on CalSil

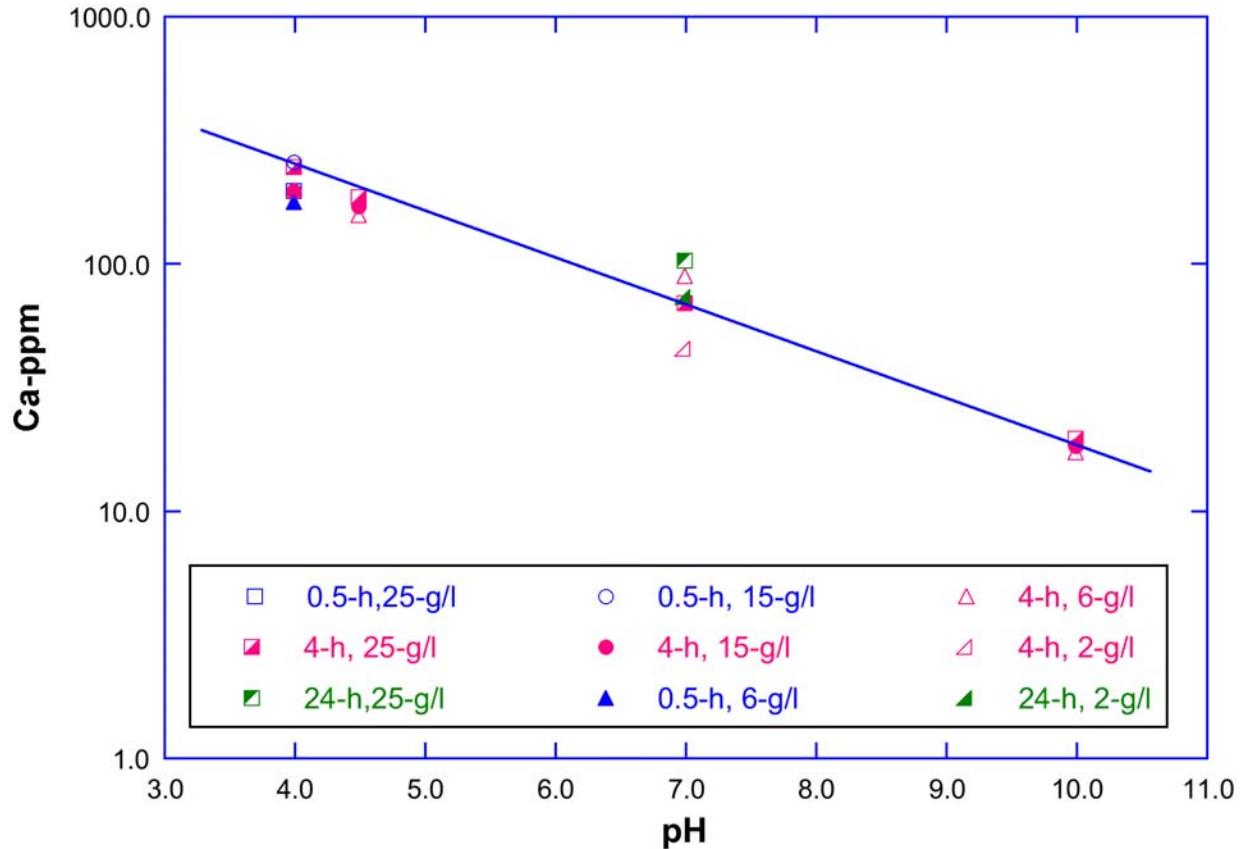| No.	Test Conditions					Dissolved Ca (ppm)	Notes
	Initial pH (RT)	T(C)	Time	CalSil g/l	Final pH (RT)		
1	4.0	60	35 min	6	7.5	176	Solution pH = 4.0 made from B(OH)3 + Li(OH) + HCl
2	4.0	60	35 min	15	6.9	256	
3	4.0	60	35-min	25	6.7	244	
4	4.0	60	35-min	166	6.5	228	
5	4.0	60	4-h	6	6.7	196	
6	4.0	60	4-h	15	6.9	195	
7	4.0	60	4-h	25	7.1	195	
8	4.0	60	4-h	166	7.7	168	
9	4.5	60	4-h	6	6.7	156	Solution pH = 4.5 made from B(OH)3 + Li(OH) + HCl
10	4.5	60	4-h	15	6.9	169	
11	4.5	60	4-h	25	7.1	184	
12	4.5	60	4-h	166	8.0	127	
13	7.0	62	4-h	2	7.1	45	Solution pH =7 made by B(OH)3 + Li(OH) + HCl + NaOH addition (No TSP added)
14	7.0	62	4-h	6	7.4	88	
15	7.0	62	4-h	25	7.2	69	
16	7.0	62	24-h	2	7.2	73	
17	7.0	62	24-h	6	7.3	108	
18	7.0	62	24-h	25	7.4	102	
19	10.1	60	3.5-h	6	10.0	17	Solution pH = 10.0 made by B(OH)3 + Li(OH) + HCl + LiOH excess addition (No TSP added)
20	10.1	60	3.5-h	15	10.0	18	
21	10.1	60	3.5-h	25	10.0	20	
22	10.1	60	3.5-h	166	9.7	23	

Figure 1.   Dependence of dissolved Ca level on initial solution pH

ANL Test Facility

A schematic of the ANL test loop is shown in Fig. 2. The test screen has an effective diameter of 6 in. The fluid volume in the loop is 4.2 ft^3. At 0.1 ft/s, the transit time around the loop is about 4 minutes. For these tests, a perforated plate with a 51% flow area and staggered 3/16 in. holes was installed in the test–section. The test screen is shown in Fig. 3. In scaling results from the ANL test facility, the mass of chemical product per unit area of screen must be considered. The amount of chemical product produced scales with fluid volume while the screen area per fluid volume determines the product mass per unit screen area.
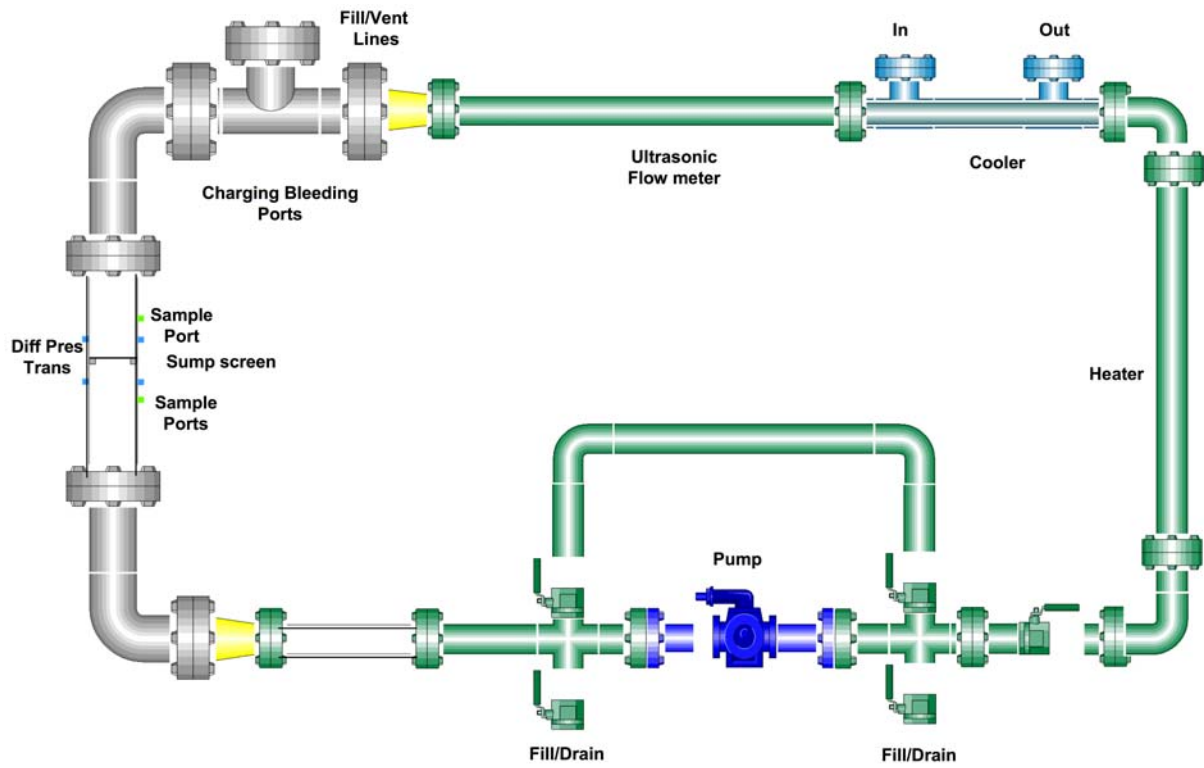
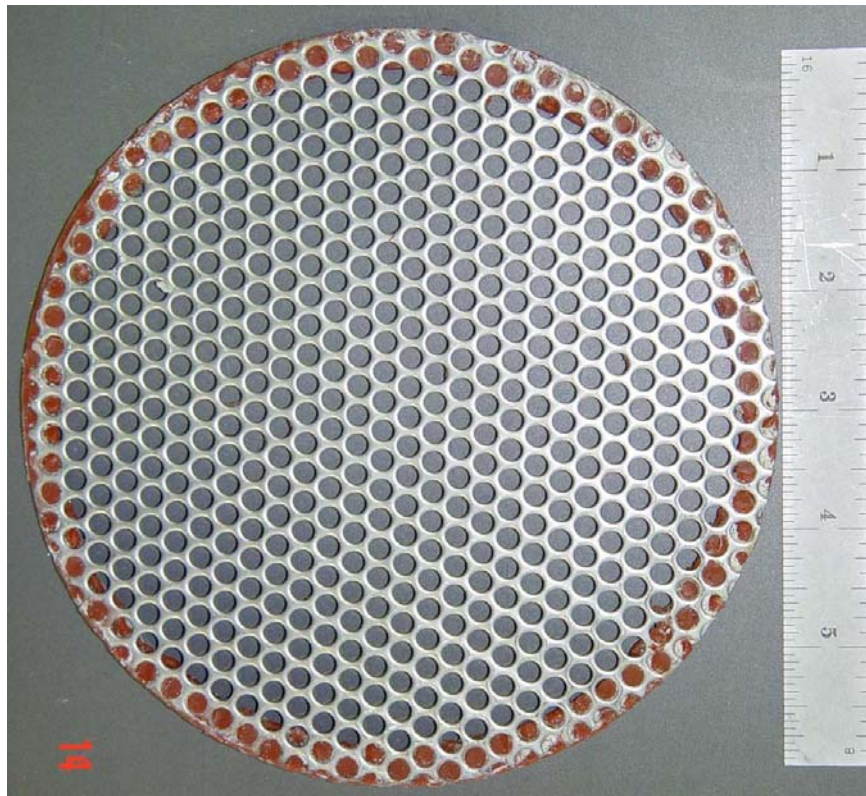Figure 2.   Schematic of the test loop

Figure 3.   Perforated plate test screen

Head Loss Test #1 Results

The initial tests in the Argonne National Laboratory (ANL) chemical effects/head–loss testing program were intended to investigate the potential head loss associated with the chemical products observed in the third Integrated Chemical Effects Test (ICET–3).

In the ICET–3 tests, the TSP was added to the CalSil solution through the sprays. In the ANL tests, the loop is filled with a solution containing boric acid, LiOH, and TSP. The concentration of TSP corresponds to that metered into the test solution over 4 hours in ICET–3 (about 4 g/l). Calcium chloride ($CaCl_2$) solution is then added to supply the desired inventory of dissolved Ca. In the first head loss test, the Ca inventory was taken to be that corresponding to the estimated Ca concentration in the ICET solution at the start of the TSP spray, which, as discussed previously, has been estimated to be about 200 ppm. As noted previously, this will result in the formation of an amount of $Ca_3(PO_4)_2$ per volume of solution comparable to that observed in the initial stages of ICET–3.

The loop was filled with deionized water and heated to 130°F. Boric acid in powder form was slowly added to the loop and circulated until it was dissolved. The LiOH and TSP were added as solutions. The concentrations of these chemicals in the loop were also chosen to match those in ICET–3. The test temperature was lower than that in ICET–3 (140°F), because the test loop was not fully insulated. Because of the retrograde solubility of $Ca_3(PO_4)_2$, the lower temperature results in the formation of slightly less precipitate.

After the chemical solution was prepared, the physical debris bed was built by adding a slurry containing 15 g NUKON/15 g CalSil to the loop with the loop flow at 0.1 ft/s. The bed was about 3/4 in thick. The NUKON bed formed essentially in the first pass of the debris past the test screen. The pressure drop across the bed slowly increased as the test loop solution recirculated, presumably due to increasingly effective filtration of fine CalSil particles. After recirculating for about 45 minutes, the flow rate was then increased to 0.2 ft/s. At this flow rate, the bed compressed to about 5/8 in thick. The flow rate was then reduced back to 0.1 ft/s. The pressure drop and flow velocity at each stage of the debris bed formation is shown in Fig. 4. The physical debris bed at this point in the test is shown in Fig. 5.
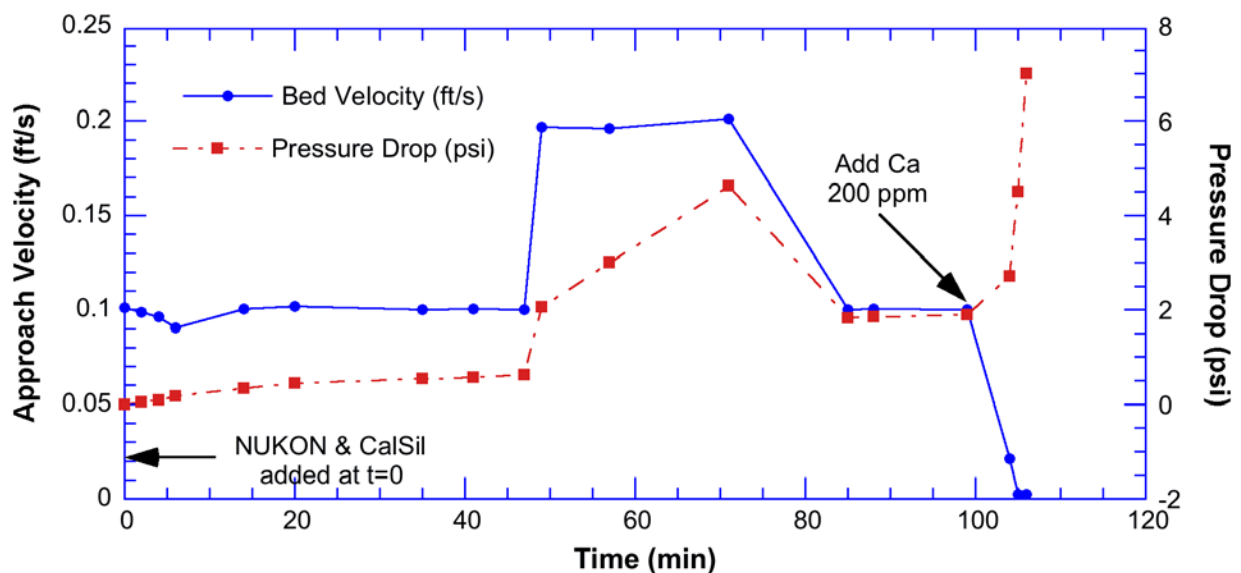

Figure 4.   Flow rate and pressure drop as a function of time in Test 1.
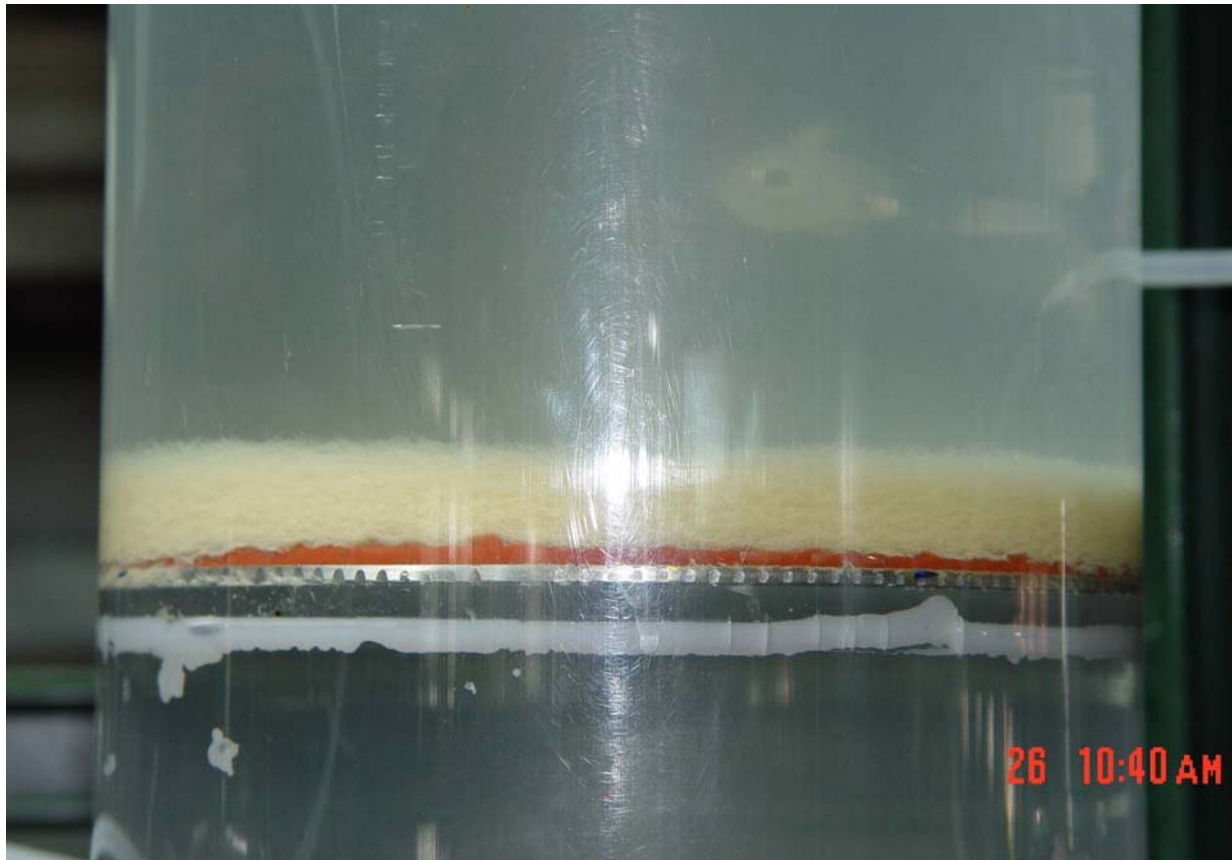
Figure 5.   NUKON/CalSil bed before formation of the $Ca_3(PO_4)_3$ precipitate

The $CaCl_2$ was then added to the vertical part of the test loop just above the clear test section. A total of 400 ml of $CaCl_2$ solution was added over a 4 minute period (the transit time around the loop at 0.1 ft/s) to obtain the 200 ppm dissolved Ca inventory. A fine, milky precipitate was observed as shown in Figure 6 just after the introduction of the $CaCl_2$. The pressure drop across the bed increased from 1.7 psi to greater than 7.0 psi within 10 minutes of introducing the $CaCl_2$. An accurate pressure drop measurement could not be obtained beyond this point, because the loop was running unpressurized, and the pump started to cavitate as the precipitate continued to accumulate on the bed. The flow rate and pressure drop as a function of time after $CaCl_2$ addition are also shown in Fig. 4. As discussed previously, the 200 ppm Ca inventory is likely not sufficient to produce the full amount of $Ca_3(PO_4)_2$ formed during ICET–3. However, no additional Ca was added to simulate the depletion of all the available phosphate as in ICET–3, since the pressure drop across the bed had already caused the pump to cavitate. Figure 7 shows the accumulation of the precipitate on the debris bed just before the pump was shut off.

Figure 6.
$Ca_3(PO_4)_2$ forming after addition of $CaCl_2$ and approaching the debris bed.

Figure 7.
Precipitate buildup on the fiber debris bed just after the pump was turned off.

Head Loss Test #2 Results

The initial procedure for the second test was similar to the first test. The loop was filled with deionized water and heated to 130°F. Boric acid in powder form was slowly added to the loop and circulated until it was dissolved. The LiOH and TSP were added as solutions.

The physical debris bed was again built from 15 g of NUKON and 15 g of CalSil. The bed was built at 0.1 ft/s and the flow rate was not increased above this value in contrast to the previous test. The debris bed was somewhat thinner than the initial debris bed for Test #1 at 0.1 ft/s (5/8 in for Test #2 and 3/4 in for Test #1). The pressure drop across the bed was also slightly smaller at this flow rate (0.4 psi in Test #2 and about 0.6 psi for Test #1).

For this test, the $CaCl_2$ additions were made in stepwise fashion starting with an initial addition equivalent to 10 ppm (one-twentieth of the simulated ICET-3 inventory) of dissolved Ca. Then amounts were added incrementally corresponding to total dissolved Ca inventories of 25 ppm, and 50 ppm. Each addition was metered in over a 4 minute period as in the first test.

When $CaCl_2$ equivalent to an inventory of 10 ppm dissolved Ca in the loop volume was added, the pressure drop at a flow rate of 0.1 ft/s increased from 0.4 psi to 1.4 psi. The $Ca_3(PO_4)_2$ precipitate was again visible, but the cloud was much fainter than the previous test which had a 200 ppm Ca inventory. Additional $CaCl_2$ was then added to simulate a 25 ppm inventory. The pressure drop increased from 1.4 psi to 6.4 psi and the pump again started to cavitate, since the test loop was unpressurized. The velocity was then decreased to 0.01 ft/s at which point the pressure drop decreased to 0.5 psi. A final increment of $CaCl_2$ was added to simulate a 50 ppm inventory of total dissolved Ca. At a flow rate of 0.01 ft/s, the pressure drop increased from 0.5 psi to 1.0 psi within 4 minutes. Under continuing operation for another 12 minutes, the pressure drop increased to 5.2 psi, but the velocity could not be maintained as the suction pressure on the pump dropped. The flow rate and pressure drop as a function of time in Test 2 are shown in Fig. 8.

An interesting qualitative difference was noted between the $CaCl_2$ additions at flow rates of 0.1 ft/s and those at 0.01 ft/s. At 0.1 ft/s, the precipitate was a finely dispersed milky cloud. At 0.01 ft/s, these particles seemed to agglomerate into light, flocculent assemblies up to perhaps 0.25 in. in diameter as shown in Fig. 9. These larger assemblies appear similar to the material observed in the ICET–3 tank where velocities are likely lower than 0.1 ft/s.
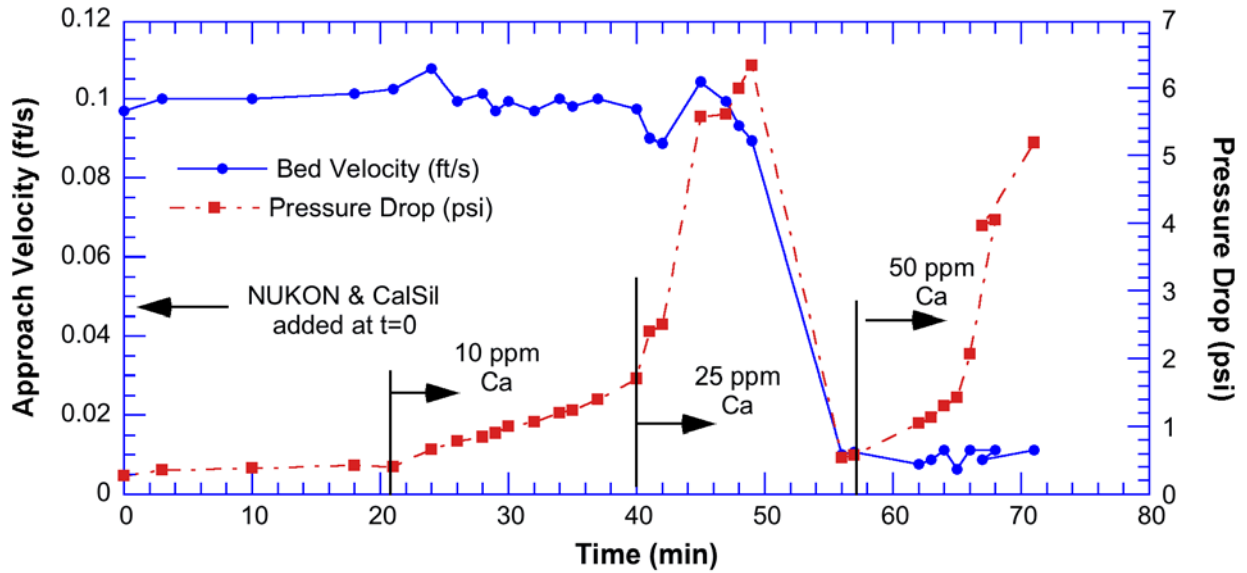
Figure 8. Flow rate and pressure drop as a function of time in Test 2.

Figure 9.
Flocculent precipitates observed at 0.01 ft/s in Test 2

References

1. For more information on the ICET program see:
   http://www.nrc.gov/reactors/operating/ops-experience/pwr-sump-performance/tech-references.html

2. *Test Plan: Characterization of Chemical and Corrosion Effects Potentially Occurring Inside a PWR Containment Following a LOCA*, Prepared by Timothy S. Andreychek, Westinghouse Electric Company (ADAMS ML052100426).