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NUCLEAR REGULATORY COMMISSION
OFFICE OF NUCLEAR REACTOR REGULATION
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January 20, 2006

NRC INFORMATION NOTICE 2005-26, SUPPLEMENT 1: ADDITIONAL RESULTS OF
CHEMICAL EFFECTS TESTS IN A
SIMULATED PWR SUMP POOL
ENVIRONMENT

ADDRESSEES

All holders of operating licenses for pressurized-water reactors (PWRs), except those who have permanently ceased operations and have certified that fuel has been permanently removed from the reactor.

PURPOSE

The U.S. Nuclear Regulatory Commission (NRC) is issuing this information notice (IN) to inform addressees about recent NRC-sponsored research results related to chemical effects in a simulated PWR sump pool environment. This supplement specifically provides additional information regarding test results related to chemical effects in environments containing dissolved phosphate, (e.g., from trisodium phosphate (TSP)), and dissolved calcium. NRC anticipates that recipients will review the information for applicability to their facilities and consider taking actions, as appropriate, to avoid similar issues. However, no specific action or written response is required.

DESCRIPTION OF CIRCUMSTANCES

NRC opened Generic Safety Issue 191 (GSI-191), "Assessment of Debris Accumulation on Pressurized-Water Reactor (PWR) Sump Performance," because debris accumulation on PWR sump screens may affect the emergency core cooling system pump net positive suction head margin. To address GSI-191, NRC issued Bulletin 2003-01, "Potential Impact of Debris Blockage on Emergency Sump Recirculation at Pressurized-Water Reactors," and Generic Letter (GL) 2004-02, "Potential Impact of Debris Blockage on Emergency Recirculation During Design Basis Accidents at Pressurized-Water Reactors." GL 2004-02 requests, in part, that licensees evaluate the maximum head loss postulated from debris accumulation (including chemical effects) on the submerged sump screen. Chemical effects are corrosion products, gelatinous material, or other chemical reaction products that form as a result of interaction between the PWR containment environment and containment materials after a loss-of-coolant accident (LOCA). NRC and the nuclear industry jointly developed an integrated chemical effects test (ICET) program to determine if chemical reaction products can form in representative PWR post-LOCA containment pool environments. These tests were conducted by Los Alamos National Laboratory at the University of New Mexico. The ICET series involved five tests, each representing a different post-LOCA environment, that are broadly representative of existing PWR plant conditions. Although chemical products were

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observed in all of the ICET environments, evaluating the head loss associated with these products was outside the scope of the ICET program. NRC initiated additional testing to obtain insights on the head loss associated with some chemical products that may form in PWR containment pools. Initial results from head loss testing performed at the Argonne National Laboratory (ANL) were provided in NRC IN 2005-26, dated September 16, 2005. ANL performed these tests in a simulated containment pool environment that was buffered with TSP and contained calcium silicate insulation (cal-sil). These tests were intended to recreate calcium phosphate precipitates observed in the ICET 3 environment and measure the head loss effect. Testing at ANL was conducted in a closed, unpressurized vertical test loop with NUKON fiberglass and cal-sil particulate first deposited on a test screen. Subsequently, dissolved calcium was introduced to react with the TSP buffer to create calcium phosphate. In these initial tests, calcium phosphate precipitate led to significant head loss for the conditions evaluated.

Subsequent to the issuance of IN 2005-26, three additional sets of tests were conducted at ANL: (1) head loss tests in a borated solution containing TSP, NUKON fiberglass, and varying concentrations of either dissolved calcium or cal-sil, (2) calcium phosphate settling tests performed in a static water column, and (3) dissolution tests to determine the dissolved calcium concentrations produced by various cal-sil amounts and the effect of TSP addition rate on cal-sil dissolution. Details from these tests are contained in an attachment, "Chemical Effects Head Loss Testing, Quick Look Report Tests ICET 3-4 to 3-11," (ML060190709) dated January 20, 2006.

DISCUSSION

As part of the mechanistic evaluation discussed in GL 2004-02, licensees are required to evaluate the sump screen head loss consequences of any chemical effects in an integrated manner with other postulated post-LOCA conditions. The most recent research results confirm that a simulated containment pool environment containing phosphate and dissolved calcium can rapidly produce calcium phosphate precipitate that can significantly increase head loss if transported to a fiber bed covered screen. Highlights from the attached report include the following:

- Initial testing with a debris bed of 0.33 kilograms per square meter (kg/m^2) NUKON fiberglass and 1.19 kg/m^2 cal-sil (0.2 grams per liter (g/L) cal-sil concentration) resulted in a significant pressure drop across the test screen in both a baseline test without chemical products and when TSP was present to form calcium phosphate precipitate. Therefore, subsequent head loss tests were performed with lower cal-sil concentrations to more clearly evaluate chemical effects related to calcium phosphate formation.
- Test results with a debris mixture consisting of 0.71 kg/m^2 of NUKON fiberglass and either 0.71 kg/m^2 of cal-sil (0.13 g/L cal-sil concentration) or an equivalent dissolved calcium concentration from calcium chloride showed a significant increase in pressure drop across the test screen attributed to the formation of calcium phosphate precipitate.
- Test parameters (e.g., amount of cal-sil dissolution prior to debris bed formation, TSP addition rates) were varied to investigate how the relative timing of calcium phosphate formation and the arrival sequence with respect to other debris affected head loss. Significant head loss occurred most quickly for tests that represented the maximum

cal-sil dissolution rates (i.e., instantaneous through calcium chloride addition) and had the greatest amount of calcium phosphate present initially. Although the head loss increased less rapidly in tests with less initial calcium phosphate precipitate, the head loss eventually approached the steady state values of the tests with maximum initial calcium phosphate.

- Tests performed with incremental calcium chloride addition suggest a strong nonlinear relationship between the amount of calcium phosphate precipitate and the pressure drop. For the ANL test loop configuration and test conditions (e.g., TSP concentration, debris loadings, etc.) dissolved calcium concentrations equal to or greater than 25 parts per million (ppm) caused a rapid and significant pressure drop increase.
- Settling tests were performed to assess the settling rate of calcium phosphate precipitate under conditions with no bulk directional flow. Precipitate agglomeration was observed at higher concentrations (300 ppm) of calcium phosphate and approximately 50 percent of the precipitate settled more rapidly (3.8 cm/min) at these concentrations. At lower concentrations (75 ppm) precipitate agglomeration was not observed and the settling velocity was estimated to be 0.8 cm/min.
- The dissolution of cal-sil was slowed by instantaneous TSP dissolution at higher (1.5 g/L) cal-sil concentrations. However, the cal-sil dissolution rate (for the concentrations evaluated) is not strongly dependent on the TSP dissolution rate within the range of complete TSP addition between one and four hours. Although complete dissolution of the cal-sil took up to 4 or more days under some test conditions, the equivalent dissolved calcium concentrations reached 75 ppm within a few hours for cal-sil concentrations down to 0.5 g/L.

The information provided in the attachments to IN 2005-26 and this supplement are relevant to plants containing phosphate (e.g., plants using TSP as a containment pool buffering agent) and calcium containing materials (e.g., insulations, concrete) that could dissolve within the post-LOCA containment pool to form calcium phosphate precipitate. These test results confirm that substantial head loss can occur if sufficient calcium phosphate is produced in a containment pool and is transported to a sump screen along with fibrous insulation debris.

Although NRC observed significant increases in head loss because of chemical effects, it is important to note that these head loss results were obtained in a recirculating test loop in which virtually all chemical products were transported to the test screen. These tests were not intended to be prototypical of a PWR plant containment. In similar plant containment pool environments, chemical product formation, transport, and subsequent head loss will be a function of several variables including: the cal-sil (or other calcium containing materials) debris concentration within the pool, the calcium dissolution rate, the TSP dissolution rate, the containment pool velocity profiles and fluid approach velocity at the sump screen, the LOCA break location, the containment fluid recirculation time, the containment pool temperature history, the containment floor layout and location of TSP baskets, the sump screen debris loading, and the sump screen design.

The NRC is continuing head loss testing in simulated PWR containment pool environments that use other chemicals to buffer pH.

CONTACTS

This information notice does not require any specific action or written response. Please direct any questions about this matter to the technical contacts listed below or the appropriate Office of Nuclear Reactor Regulation (NRR) project manager.

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Attachment:
Chemical Effects/Head-Loss Testing Quick Look
Report, Tests 1 and 2 (ML060190709)

Chemical Effects/Head-Loss Testing

Quick Look Report, Tests ICET-3-4 to 11

January 20, 2006

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Abstract

This summary report describes the continuation of studies conducted at Argonne National Laboratory on the potential contributions of chemical effects to head loss across sump screens in environments where trisodium phosphate (TSP) buffering is used to control pH and calcium silicate (CaSiO_3) insulation (cal-sil) debris may be present. Head loss testing, settling rate testing of calcium phosphate precipitates and cal-sil dissolution testing in TSP solutions are described. The objective of the head loss tests was to assess the pressure drop across debris beds created by various mixtures of cal-sil, fibrous insulation, and calcium phosphate precipitates. The effects of both the degree of cal-sil dissolution that will occur before the formation of the debris bed and the relative arrival time of the precipitates and insulation debris at the screen were specifically evaluated. The debris loadings and test temperature were chosen to be reasonably representative of those expected in limiting design basis analyses for plants with updated sump screen configurations. Other variables were then selected with the intent to encompass the variability in head loss due to the effect of TSP dissolution rates, debris residence time in the containment pool prior to accumulation at a sump screen, and other variables that could affect the amounts and homogeneity of calcium phosphate precipitates in the debris bed.

Settling tests were conducted to measure the settling rates of calcium phosphate precipitates (formed by adding dissolved Ca to boric acid and TSP solutions) in water columns having no bulk directional flow. The dissolution tests were intended to identify important environmental variables governing both calcium dissolution and subsequent calcium phosphate formation over a range of simulated containment pool conditions. The results from this testing were used to inform and interpret both the head loss and settling test series.

The results of the head loss tests demonstrate that chemical products (calcium phosphate precipitates) associated with TSP-buffered containment environments can contribute significantly to head loss across simulated sump screen debris beds. The head losses associated with pure physical debris beds of NUKON™ (a trademarked fiberglass blanket insulation, referred to hereafter as NUKON) and cal-sil can be much smaller than those that occur across debris beds in which some of the cal-sil has been replaced with a corresponding amount of calcium phosphate precipitates. The cal-sil dissolution rate for concentrations less than 1.5 g/L is not strongly dependent on the TSP dissolution rate over the range of TSP dissolution rates that are likely to be relevant. For cal-sil concentrations as low as 0.5 g/L, the equivalent dissolved Ca could be high enough after a few hours to potentially produce significant increases on head loss even for instantaneous TSP dissolution.

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 tests were 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

Post-LOCA Environment

After a loss-of-coolant accident (LOCA), physical debris will reside in the containment pool for some period of time before the initiation of emergency core cooling system recirculation. During this time, the sump pool environment will be changing as TSP dissolves. After recirculation starts, debris will begin arriving at the sump screen to form a debris bed. If both NUKON and cal-sil debris are present, the sump screen debris bed will consist of some mix of plant debris, including cal-sil, NUKON, and calcium phosphate precipitates. The relative amounts of cal-sil and calcium phosphate precipitates in the debris bed as it initially forms will vary depending on the residence time in the containment pool prior to the onset of recirculation, the transport time to the sump screen, the initial containment pool pH, the containment pool temperature, and the TSP dissolution rate.

For some conditions, e.g., long residence times, a large fraction of the cal-sil may have dissolved before the debris actually reaches the sump screen. In such cases, the debris bed will primarily contain a mix of NUKON fibers and calcium phosphate precipitates. In other cases, e.g., short residence times, little cal-sil dissolution may have occurred before the debris reaches the sump screen, and the bed that is initially formed will consist predominantly of a mix of NUKON fibers and cal-sil particulates. In this case, with time, the cal-sil within the bed can continue to dissolve, and any dissolved calcium (Ca) that is released will react with the available phosphate to form additional calcium phosphate precipitates.

Prior ANL Head Loss Testing

An initial Quick Look report by ANL³ 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 head loss test, identified as ICET-3-1, was intended to simulate the calcium phosphate precipitate concentration created by the initial burst of dissolved calcium that formed within the first 30 minutes of the ICET-3 test, prior to metering TSP into the test chamber. The initial dissolved calcium concentration in ICET-3-1 (200 ppm) was determined through dissolution testing of the corresponding ICET-3 cal-sil loading (19 g/L submerged cal-sil), but did not represent the total amount of calcium phosphate that could ultimately be created from the cal-sil and other calcium sources (e.g., concrete) within the ICET-3 test.⁴ The second test (ICET-3-2) was parametric and intended to determine the effect of a range of chemical product loadings on head loss.

In both tests, a pre-existing physical debris bed approximately 16 mm (5/8 in) thick consisting of equal amounts (15 g) of NUKON fiber and cal-sil insulation was formed. Then, dissolved calcium was added to the test loop, which contained TSP-buffered borated water, to form calcium phosphate precipitates. The added head loss due to the chemical product was then measured. A large increase in head loss was observed in ICET-3-1 with the chemical product loading (200 ppm of dissolved Ca)

intended to simulate initial calcium phosphate formation during ICET-3. In the parametric test (ICET-3-2), increases in head loss were observed when the chemical product loading was one-twentieth of that used in ICET-3-1 (10 ppm of dissolved Ca). A detailed description of the ICET-3-1 and ICET-3-2 results and a detailed description of the ANL test loop are given in the first ANL Quick Look Report Tests 1 & 2.³

Approach

ANL performed a series of follow-up tests (ICET-3-4 to ICET-3-11) that evaluated the potential for head loss due to chemical effects in a TSP-buffered environment. The tests were designed to explore conditions corresponding to a range of debris amounts, containment pool residence times, and TSP dissolution times. The two basic physical parameters that are affected by these variables are the degree of cal-sil dissolution that will occur before the formation of the debris bed and the interaction between the chemical products and the physical debris during bed formation. For instance, some fraction of chemical precipitates and the debris will arrive at the sump screen together and some fraction of precipitates will form due to cal-sil dissolution within the debris bed after the bed has initially formed.

The NUKON and cal-sil mass loading per unit screen area utilized in these tests are reasonably representative of those plants that currently have, or will have after sump modifications, relatively low debris mass loading (i.e., less than 2 kg/m^2). Because the Argonne test loop has a fixed ratio of screen area to fluid volume ratio, it is impossible in most cases to simultaneously match both the debris loading per unit screen area and the debris loading per unit volume of fluid that would be encountered in an actual sump configuration. In assessing the head loss, the screen loading per unit area is the critical scaling parameter. The cal-sil dissolution rate, however, can be a function of the debris loading per unit volume. The current plant estimates of the cal-sil loading per unit volume of the containment pool are less than 1.5 g/L. The small scale dissolution data presented later in this report show that the cal-sil dissolution rate at these low concentrations is not too strongly dependent on the concentration. Therefore, it is not too important to match the plant debris loading per unit volume within the test loop.

The NUKON fiberglass insulation and the cal-sil insulation used in the tests were prepared from materials obtained from Performance Contracting Inc. (PCI), Lenexa, Kansas. The NUKON was originally produced in the form of insulating blankets. The blankets were rough shredded to get a collection of loose fibers and clumps of fibers ranging in size from 1–2 cm in diameter. The shredded fiberglass is then mixed with water ($\approx 1 \text{ g}/65 \text{ mL}$ water) in a blender for a short time ($\approx 10 \text{ s}$) to produce a relatively smooth slurry. The cal-sil was originally produced in the form of molded blocks. The material is friable and was first broken up by hand-crushing with a mortar and pestle. The crushed material was mixed with water ($\approx 1 \text{ g}/65 \text{ mL}$ water) in a blender for about a minute to produce a smooth slurry. In the present tests, the two slurries were then mixed together. The preparation of the slurry is done just prior to the performance of the head loss tests.

To simulate the dissolution of the cal-sil that occurs during the residence time in the containment pool prior to the onset of recirculation, the cal-sil and NUKON slurry was presoaked at temperature (60°C) in the baseline boric acid, lithium hydroxide (LiOH) solution for 30 minutes, and then added as a slurry to the loop. Since only 2.5 liters of solution were used for the presoak, the cal-sil concentration is much higher than it would be in the loop or in an actual sump. At high cal-sil concentrations ($\geq 6 \text{ g/L}$), the total amount of cal-sil dissolution is limited by the solubility of calcium silicate (CaSiO_3).³ Regardless of the initial pH or the rate of addition of TSP, the pH of solution rises to about 7, primarily because cal-sil contains sodium silicate as an impurity. The sodium silicate is very soluble, and as it dissolves, the dissolved sodium (Na) causes the pH of the initial boric acid/LiOH solution to increase. At these high concentrations, the dissolved Ca level rises quickly to a saturation value of $\approx 200 \text{ ppm}$.³ In highly concentrated solutions, addition of TSP increases the amount of cal-sil that will eventually

dissolve, because the phosphate combines with the dissolved Ca and forms calcium phosphate precipitates, lowering the dissolved Ca level, and permitting further dissolution of the cal-sil. Thus, the highly concentrated presoak slurry is expected to form lower initial dissolved Ca concentrations than are realistically expected. In contrast, as subsequent dissolution data presented in this report show, at lower cal-sil concentrations, the increase in pH due to the dissolution of the sodium silicate impurity is much smaller, and rapid addition of TSP can decrease the cal-sil dissolution rate. Thus, because of the increase in pH, the highly concentrated presoak slurry, even with TSP additions, is expected to form lower initial dissolved Ca concentrations than would occur under prototypical conditions.

The tests were performed under isothermal conditions at 60°C (140°F). The debris in all the tests was introduced into the loop with the flow velocity in the loop at 0.1 ft/s. The intent in these tests was to maintain a constant velocity through the test until a stable bed configuration steady-state head loss was reached and then to cycle the velocity to examine the effect on head loss. However, in most the tests, the head losses were too large to maintain a constant flow of 0.1 ft/s. [The maximum head loss that currently can be maintained in the loop is about 6 psi (\approx 13.8 ft of water).] Because a flow velocity of 0.1 ft/s is higher than expected at the sump screen in most planned modified sump configuration, the head loss measurements are conservative with respect to this variable.

The test conditions used in this series of tests are summarized in Table 1. The judgments expressed in the Table 1 comment section that the test conditions represent “minimal”, “maximum”, or “typical” test values for the amount of cal-sil dissolution during the initial debris bed formation is based on the results of the cal-sil dissolution tests reported in the previous Quick Look Report³, the new dissolution tests described in this report, and expected plant TSP dissolution times.⁵

Each head loss test utilized a slightly different procedure for simulating specific chemical product formation rates and debris arrival sequences depending on the test objective. While the general test procedures are similar to those described in [3], the unique procedures associated with each test were varied to obtain the conditions described in Table 1. Descriptions of the unique procedures associated with each test are subsequently presented along with a summary of the results.

Table 1. ICET-3 Environment Head Loss Tests

Test No.	NUKON (g) ^a	cal-sil (g)	30 min Presoak	TSP ^b	Additional dissolved Ca (ppm)	Comment
ICET-3-1	15	15	No	Initially in loop	200	Simulates initial conditions in ICET-3; precipitates arrive after bed forms
ICET-3-2	15	15	No	Initially in loop	10, 25, 50 ppm Ca ^d	Parametric test starting with 1/20th dissolved Ca of ICET-3; precipitates arrive after bed forms
ICET-3-4	7	25	Yes	1/8th initially in loop; 7/8th metered in	None	Minimal cal-sil dissolution prior to initial bed formation; continued dissolution as test continues
ICET-3-5	7	25	Yes	None	None	Baseline physical debris only
ICET-3-6	15	15	Yes	1/8th initially in loop; 7/8th metered in	None	Minimal cal-sil dissolution prior to initial bed formation
ICET-3-7	15	15	Yes	None	None	Baseline physical debris only
ICET-3-8	15	0	No	Initially in loop	43.5 ^c	CaCl ₂ & NUKON added simultaneously; Maximum cal-sil dissolution prior to bed formation
ICET-3-9	15	0	No	Initially in loop	9, 18, 27 ppm Ca ^d	CaCl ₂ added after NUKON bed stabilizes maximizes arrival time of precipitates to bed; Maximum cal-sil dissolution prior to arrival at the bed
ICET-3-10	15	15	Yes	1/2 in metered during presoak; 1/2 metered in	None	Intended to represent a “typical” degree of cal-sil dissolution prior to bed formation
ICET-3-11	15	15	Yes	None	None	Baseline physical debris only (Replicates ICET-3-7)

^a1 g of debris corresponds to a screen loading of 47.6 g/m²

^bThe total amount of TSP in each test where TSP was added was always 3.4 g/L. Some fraction was either dissolved initially in the test loop or metered in during the presoak period. The remaining fraction was metered in during a 30-60 minute period after the debris was added to the loop.

^cCa equivalent to full dissolution of 15 g cal-sil.

^dCa additions added incrementally to sequentially reach values of dissolved Ca listed.

ICET-3-4 Test Procedure:

The physical debris in ICET-3-4 consisted of 25 g (1.19 kg/m²; 0.2 g/L) of cal-sil and 7 g of NUKON (0.33 kg/m²; 0.06 g/L). The amount of cal-sil per unit area of the screen in this test was intended to bound the values expected after plants have installed their modified screen designs.⁵ The cal-sil and NUKON were heated outside the test loop for 30 minutes at 140°F in borated water (2800 ppm B and 0.7 ppm Li) to simulate the cal-sil/NUKON dissolution that occurs in the period between the LOCA and the onset of recirculation. Because no TSP was added during the presoak phase, the dissolution testing results for high concentrations of cal-sil (> 6 g/L)³ show the concentration of dissolved Ca in the 2.5 L of presoak solution will saturate at ≈200 ppm. This gives an effective inventory of dissolved Ca in the loop of ≈ 4 ppm when the 2.5 L of presoak solution is added to the loop, which has a volume of ≈120 L. One eighth of the desired TSP concentration was premixed in the loop before the addition of the debris to simulate the TSP dissolution that occurs prior to the start for recirculation. The remaining TSP was to be metered into the loop over an hour to simulate the dissolution of the remaining TSP after the start of recirculation. Although there is uncertainty in how long it will take for the TSP to dissolve, even one eighth of the TSP inventory is sufficient, on a stoichiometric basis, to convert to calcium phosphates the dissolved Ca level equivalent to full dissolution of 0.2 g/L of cal-sil. Thus, the amount of precipitate that is formed as the debris slurry is added to the loop is limited by the dissolved Ca available.

This test was intended to be a lower bound (for this cal-sil loading) for the amount of calcium phosphate precipitate arriving at the screen as the initial debris bed is formed. However, additional cal-sil dissolution and calcium phosphate formation was expected to occur after the initial formation of the bed. Therefore, it was planned that the test would proceed until either all the calcium phosphate had formed (based on stabilized dissolved phosphorus levels in the loop mixture), or the head loss reached steady state. It was anticipated that the test could last up to three days.

ICET-3-4 Results:

The test started at 7:45 am and terminated at 12:07 pm on November 15, 2005. Figure 1 shows the bed approach velocity and differential pressure across the screen, as a function of time during the test. Figure 2 shows an expanded view of the velocity and pressure during the first 15 minutes of the test. After the introduction of the debris, the pressure drop across the bed increased very rapidly to 6.5 psi, before any additional TSP could be metered into the loop. The pump started to ingest air so the flow velocity was reduced to 0.03 ft/s. However, after operating for several minutes at that velocity it became apparent that large amounts of air had accumulated under the test screen and the test was terminated.

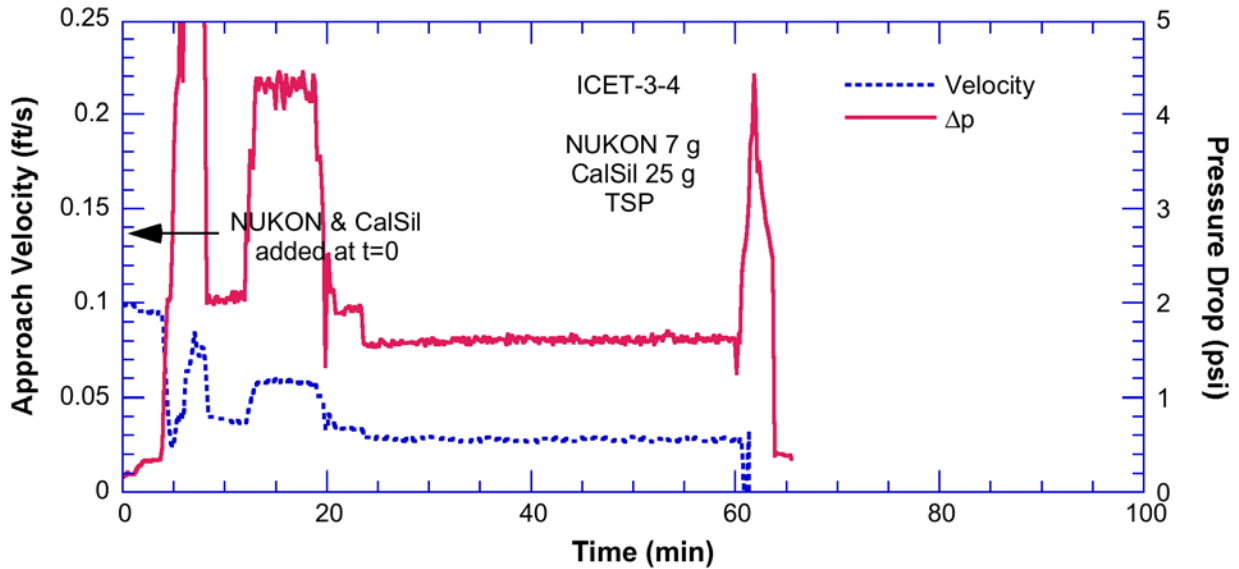


Figure 1. Bed approach velocity and differential pressure across the screen as a function of time for test ICET-3-4.

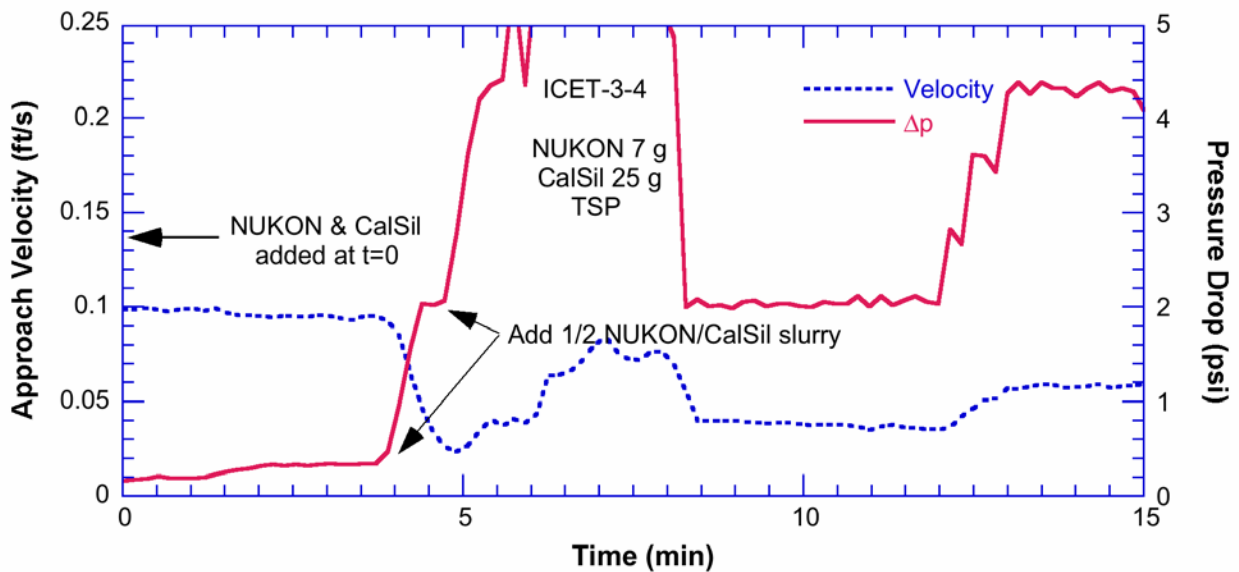


Figure 2. Expanded view of bed approach velocity and differential pressure across the screen during the initial 15 minutes of test ICET-3-4.

ICET-3-5 Test Procedure:

The type and amount of physical debris for this test was identical to that for test ICET-3-4. This was a baseline test to determine the effects of the debris alone with no calcium phosphate precipitates. The cal-sil and NUKON were again heated outside the test loop for 30 minutes at 140°F in borated water (2800 ppm B and 0.7 ppm Li), but no TSP was added either to the presoak or to the loop during this test.

ICET-3-5 Results:

This test again resulted in high head loss. Figure 3 shows the bed approach velocity and differential pressure across the screen, as a function of time during the test. After the debris was added to the loop,

the pressure drop increased very rapidly. When the pressure drop across the bed increased to about 3 psi, jetting through the debris bed was observed at 25 minutes and the test was terminated at 35 minutes. It is not clear whether the difference in the peak values of Δp attained between this test (3 psi) and ICET-3-4 (6 psi) reflects simple scatter in when jetting can occur or whether the presence of the chemical product helps prevent jetting by more effectively plugging weak spots in the bed. Figure 4 shows an expanded view of the velocity and pressure during the first 10 minutes of tests ICET-3-4 & 5. Head loss for the debris loading in these tests was substantial and occurred within the first six minutes (or after approximately one test loop recirculation) after introducing debris. Other than the maximum pressure reached during the test, the presence of calcium phosphate did not clearly alter the observed accumulation of head loss during these tests.

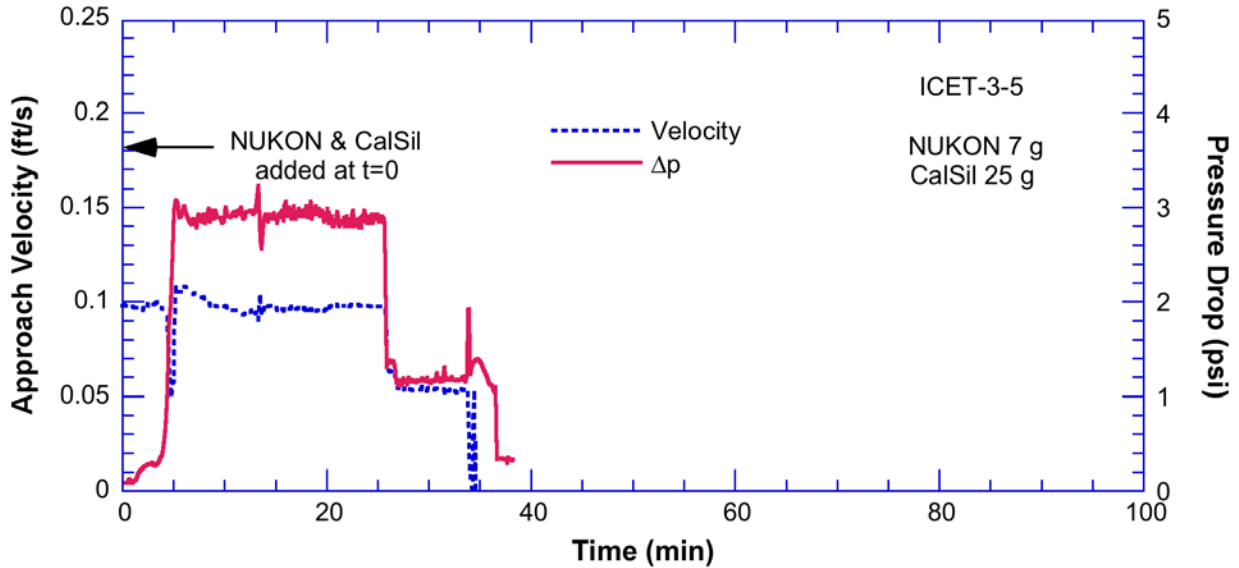


Figure 3. Bed approach velocity and differential pressure across the screen as a function of time for test ICET-3-5.

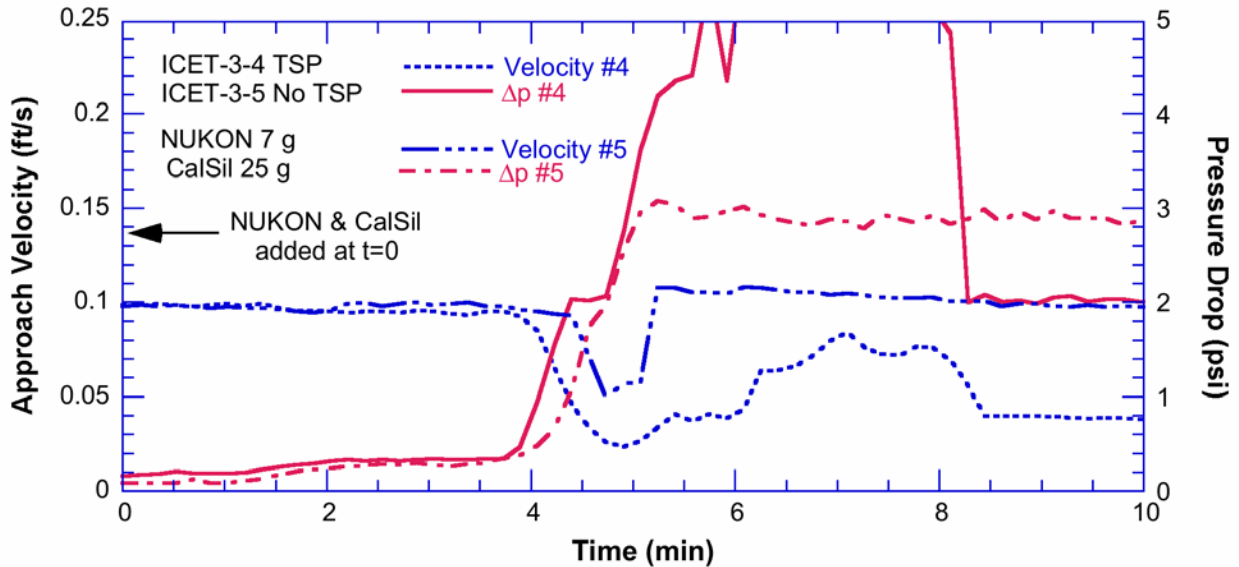


Figure 4. Expanded view of bed approach velocity and differential pressure across the screen during the initial 10 minutes of tests ICET-3-4 & 5.

ICET-3-6 Test Procedure:

Due to the high head losses observed with the debris bed loading used in the previous tests, the debris loading in ICET-3-6 was changed to 15 g of cal-sil and 15 g of NUKON. The intent of this test was identical to that of test ICET-3-4, i.e., to minimize the amount of initial calcium phosphate precipitate arriving at the screen as the debris bed is formed for a given cal-sil loading. The motivation for decreasing the loading was to attempt to more clearly understand the head loss contribution that could be attributed to calcium phosphate formation. This debris loading had been previously used in ICET-3-1 & 2 and exhibited only modest increases in head loss in the absence of chemical effects. The 15 g cal-sil loading (0.13 g/L) is also representative for some plants containing TSP and cal-sil.⁵

ICET-3-6 Results:

Figure 5 shows the bed approach velocity and differential pressure across the screen, as a function of time during the test. Figure 6 compares the head loss in this test during the first 45 minutes after introducing NUKON and cal-sil to the test loop with the earlier ICET 3-1 & 2 tests. Tests ICET-3-1 & 2 had similar amounts of debris loading as ICET-3-6, although the NUKON and cal-sil in ICET-3-6 came from different batches of materials. Additionally, the debris materials were not presoaked in ICET-3-1 & 2 to create an initial dissolved Ca inventory, thus less calcium phosphate would be expected initially in tests ICET-3-1 & 2. However, the initial amount of dissolved Ca in ICET-3-6 is minimized because no TSP was added during the 30 minute presoak. It is therefore not surprising that the difference in head loss between test ICET-3-6 and tests ICET-1 & 2 within the first 30 minutes is not too large. However, compared with ICET-1 & 2, the head loss in ICET-3-6 continues to increase as the test proceeds, more cal-sil dissolves, and more calcium phosphate is subsequently formed.

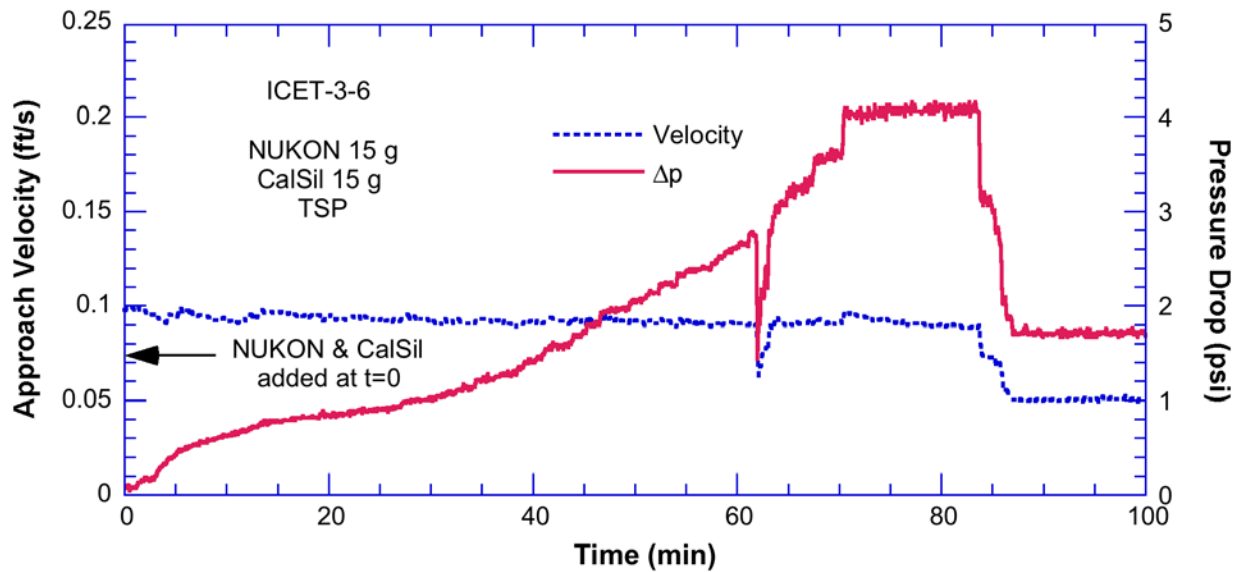


Figure 5. Bed approach velocity and differential pressure across the screen as a function of time for test ICET-3-6.

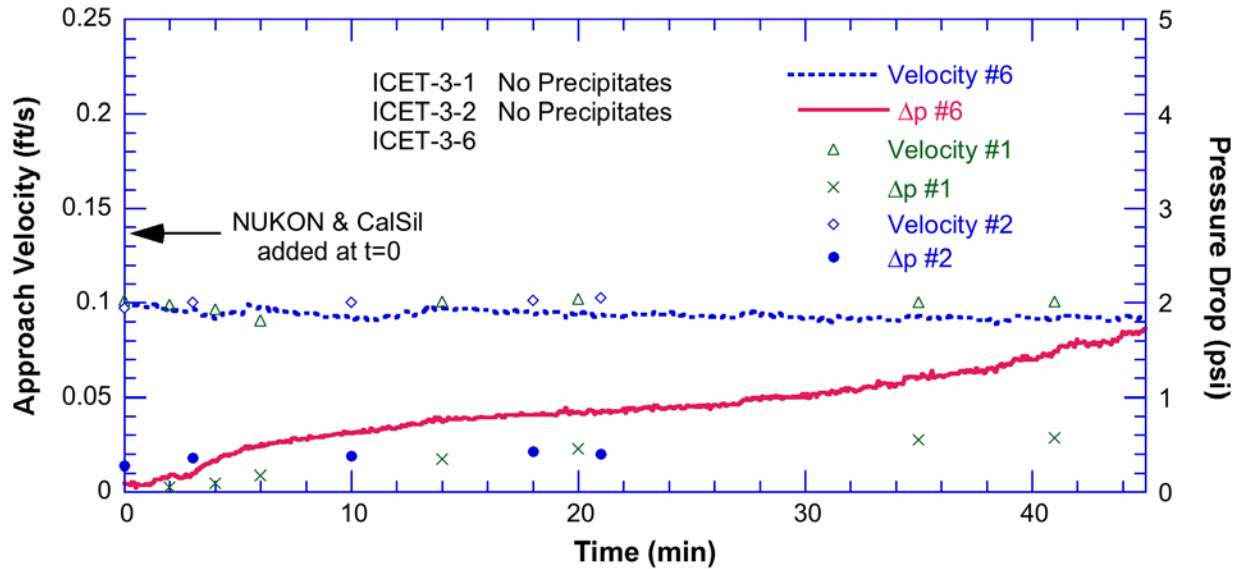


Figure 6. Expanded view of bed approach velocity and differential pressure across the screen during the initial 45 minutes of tests ICET-3-1, 2 & 6.

ICET-3-7 Test Procedure:

Test ICET-3-7 was a baseline test with a debris loading of 15 g of cal-sil and 15 g of NUKON and no TSP in the loop or in the presoak at any time. Therefore, no calcium phosphate precipitate is present to contribute to head loss. The cal-sil and NUKON were again heated outside the test loop for 30 minutes at 140°F in borated water (2800 ppm B and 0.7 ppm Li) and then added to the loop.

ICET-3-7 Results:

Figure 7 shows the bed approach velocity and differential pressure across the screen, as a function of time during the test. The pressure drop across the bed increased rapidly (within 25 minutes) to about 2.8 psi and then stabilized. It was suspected that, at this point, the bed had perforated and jetting was occurring even though the bed appeared smooth and uniform. However, a considerable layer of air had developed underneath the bed and this precluded the actual identification of any jet. To determine if jetting was occurring, the inlet tee, which is normally left open, was filled to the top with about one liter of demineralized water and sealed with a closure flange. The loop was then pressurized to 13 psi using demineralized water 46 minutes after the debris was added. Under pressure, the air layer under the bed was greatly reduced and it became possible to confirm that jetting was occurring and to identify jet locations in the bed, although the bed still exhibited no observable defects.

The pressure drop across the debris bed increased very rapidly compared to the corresponding pressure drops observed in ICET-3-1, 2, & 6 which had similar debris loadings. Because no TSP was introduced at any time during the test, no calcium phosphate precipitates were expected to form. Chemical analysis of grab samples taken periodically through the test confirmed that P levels were very low, as expected. Because the magnitude and rapidity of the pressure drop increase in this test are much greater than observed in both earlier tests with similar debris loading and in subsequent replicate tests under the same nominal conditions, the results of this test are believed to be anomalous.

During this test, some release of noncondensable gases was observed as the pressure drop across the bed increased to about 1.4 psi. This led to a re-evaluation of the procedure for deaerating the loop. In this test and in previous tests, the loop had been deaerated on the day prior to the test day by heating the water

to 71°C (160°F) and circulating the test loop fluid at fairly high speeds (2 ft/s) for several hours. The loop was then allowed to cool overnight. This procedure had been chosen to avoid running the pump overnight unattended. However, as the test loop fluid cooled, additional gases were re-entrained in the fluid and thus, were available to be released at relatively low pressures. Exploratory tests had shown that heating of the water induced sufficient natural circulation to maintain a uniform temperature in the loop without the pump. The deaeration procedure for subsequent tests was modified to never let the loop cool down after the initial heat-up in order to minimize the noncondensable gases in the fluid. Natural circulation was used to maintain a uniform temperature without the need to run the pump unattended overnight.

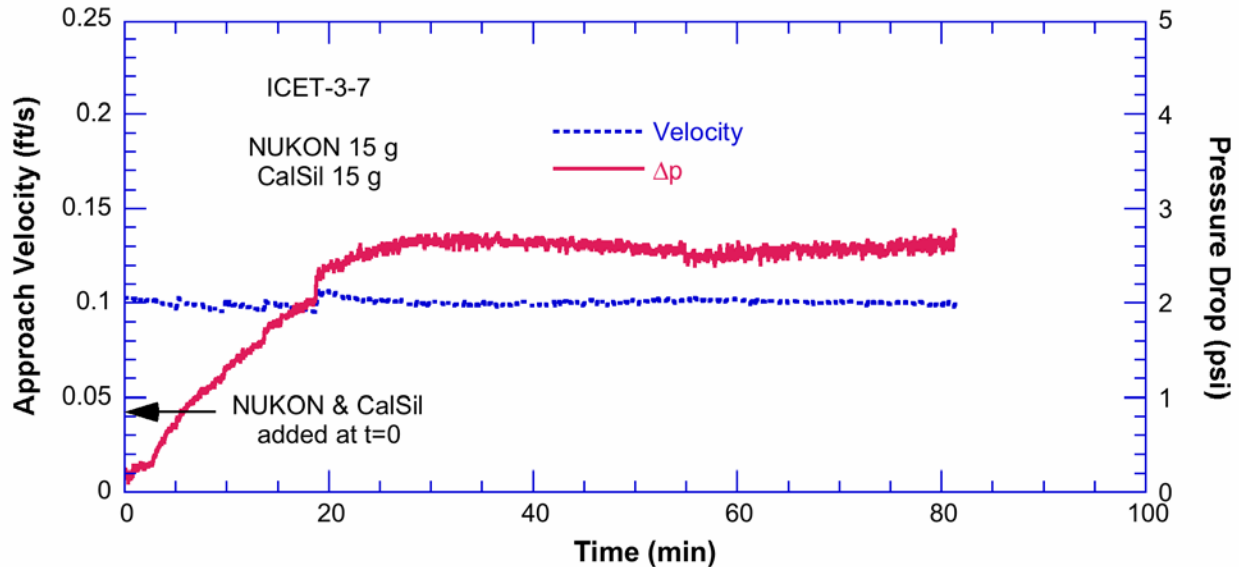


Figure 7. Bed approach velocity and differential pressure across the screen as a function of time for test ICET-3-7.

ICET-3-8 Test Procedure:

ICET-3-8 was intended to represent the limiting case when the cal-sil debris is largely dissolved prior to the formation of the debris bed. In this test, the boric acid, lithium hydroxide and all of the TSP were added to the loop water and heated to 60°C prior to adding the physical debris. The physical debris consisted of 15 g NUKON which has been presoaked for ½ hour at 60°C. The NUKON slurry was then combined with 14.3 g of CaCl₂, which gives an amount of dissolved Ca level equivalent to complete stoichiometric dissolution of 15 g cal-sil. The NUKON/CaCl₂ mixture (about 2.5 L) was then added to the loop. The addition was done in about 30 seconds. Because the reaction of the dissolved Ca with the phosphate is very rapid, the test screen debris bed was formed with a simultaneous mix of NUKON and calcium phosphate precipitates.

ICET-3-8 Results:

Figure 8 shows the bed approach velocity and differential pressure across the screen as a function of time. After adding the NUKON and CaCl₂ mixture, the pressure drop across the bed increased very rapidly and it was not possible to maintain the loop flow velocity at 0.1 ft/s through the pump. After ≈8 minutes, the flow rate was decreased to 0.03 ft/s, and the pressure drop stabilized at ≈5 psi. The debris bed appeared to be uniform with a thickness between 8 – 10 mm early in the test before the pressure drop got too large. The bed compressed to a thickness of approximately 6 mm at the end of the test. The loop water quickly cleared indicating rapid debris bed filtration. No jetting through the bed was observed.

Figure 9 shows the photographs of the debris bed from this test after removal from the loop and at the end of the test with the loop almost drained. The debris bed height (see Figure 9b) has increased slightly compared with thickness at the end of the test. Additionally, the debris bed is comprised of two distinct layers (Figure 9b). The bottom layer is mixed NUKON and calcium phosphate precipitate while the top layer is predominantly calcium phosphate precipitate.

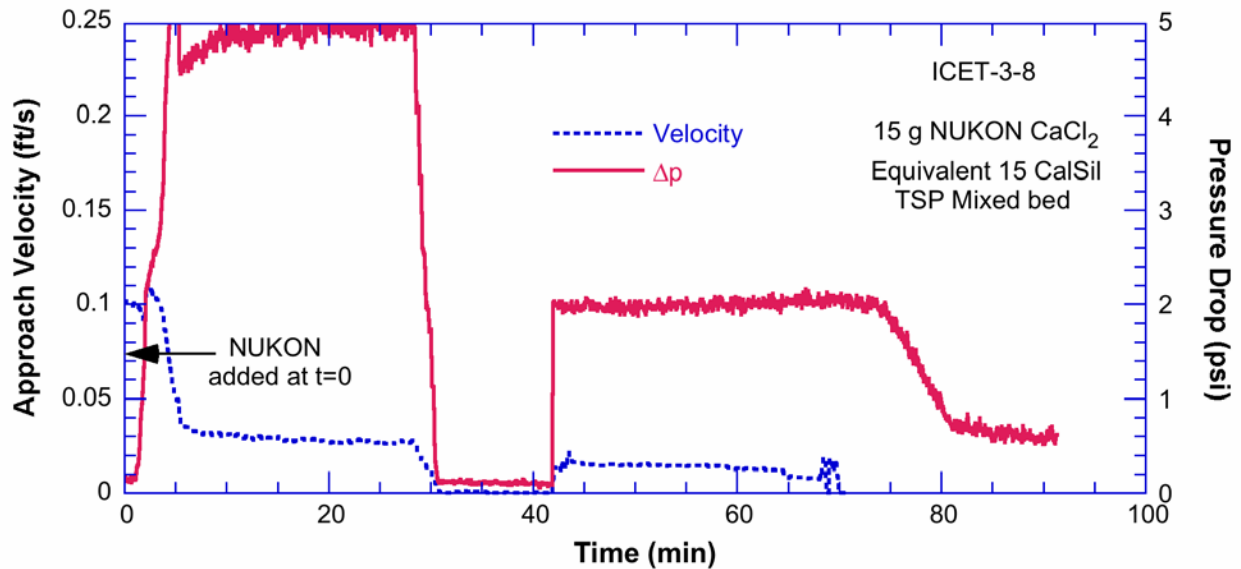


Figure 8. Bed approach velocity and differential pressure across the screen as a function of time for test ICET-3-8.

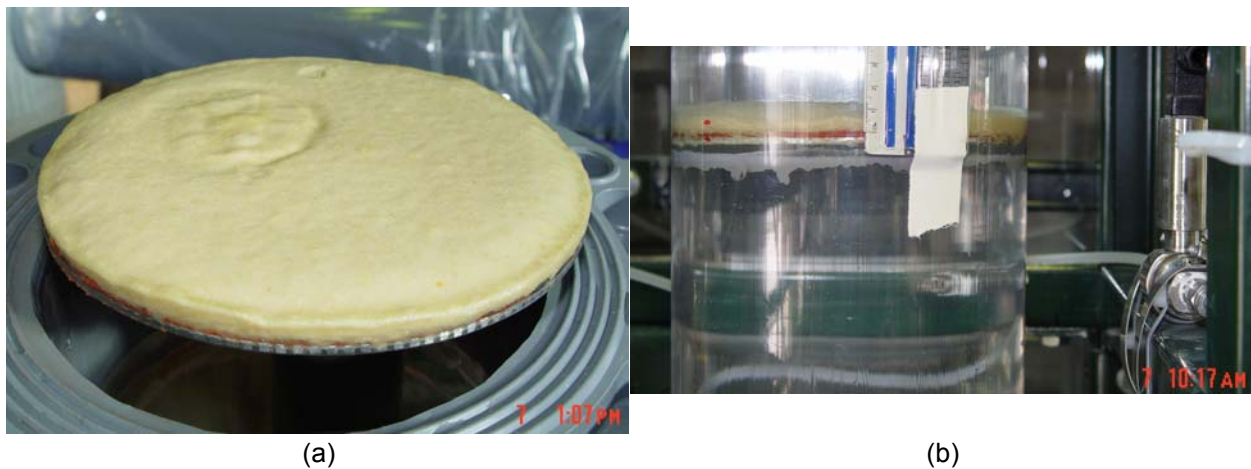


Figure 9. (a) Debris bed from ICET-3-8 after removal from the loop: (b) Debris bed in the loop at the end of the test with the loop almost drained. The bed has two distinct layers. (Readers of the electronic version may wish to zoom to 500% to see the layers more distinctly.)

ICET-3-9 Test Procedure:

ICET-3-9 was intended to evaluate the head loss from chemical phosphate precipitate arriving at the test screen after the NUKON bed had formed. This test objective and procedure is similar to previous ICET-3-1 & 2 tests. The physical debris bed consisted of 15 g of NUKON and was formed before the addition of any CaCl_2 , i.e., before the formation of any calcium phosphate precipitate. The loop initially contained a base solution with 2800 ppm B, 0.7 ppm Li, and TSP (3.4 g/L). A total of 14.3 g of CaCl_2

was chosen to give a dissolved Ca inventory equivalent to a complete stoichiometric dissolution of 15 g cal-sil. The CaCl_2 solution was planned to be added in 5 steps (1/5 of the total amount at each step) with the pressure drop allowed to reach steady state between each step. Only 3 of the 5 CaCl_2 additions were completed before the test was terminated.

ICET-3-9 Results:

The pressure drop across the screen prior to the addition of the NUKON was 0.07 ± 0.02 psi at an approach velocity of 0.1 ft/s. [The pressures are recorded approximately every 5 sec by the data acquisition system. When the pressure data are presented as a running average over a minute, the standard deviation of the running average is much smaller, ± 0.005 .] The pressure drop across the NUKON bed before the addition of any CaCl_2 is shown in Fig. 10. The steady state drop across the bed at this stage of the test was 0.14 ± 0.02 psi and the debris bed was about 14 mm thick. A relatively stable value of the pressure drop was reached after one pass around the loop (≈ 4 min).

Eighteen minutes after the NUKON was introduced, 200 ml of CaCl_2 solution was added. This addition represents the stoichiometric dissolved Ca equivalent (≈ 9 ppm) of 3 g of cal-sil. The pressure drop increased to 0.242 psi (Fig. 11) and the bed compressed to 12 mm. Twenty-eight minutes after the NUKON was introduced, a second 200 ml CaCl_2 addition was made. The pressure drop increased to 1.2 psi and the bed compressed to 9 mm. It appears from the data (Figure 11) that this value may not quite represent the steady state head loss for this condition. Forty-one minutes after the NUKON was introduced, the third 200 ml CaCl_2 addition was made. After this addition, the pressure drop increased dramatically and the approach velocity could not be maintained at 0.1 ft/s. The flow rate decreased to 0.02 ft/s 43 minutes after the initial NUKON addition, and could no longer be controlled because the pump inlet pressure was at 0 psi. The flow rate continued to slowly decrease slowly while the pressure drop continued to rise gradually during the remainder of the test. The pressure drop asymptotically increased to ≈ 5.2 psi, as the velocity decreased. The bed thickness decreased to 7 mm at the highest pressure. Figure 11 shows the bed approach velocity and differential pressure across the screen as a function of time for entire duration of the test.

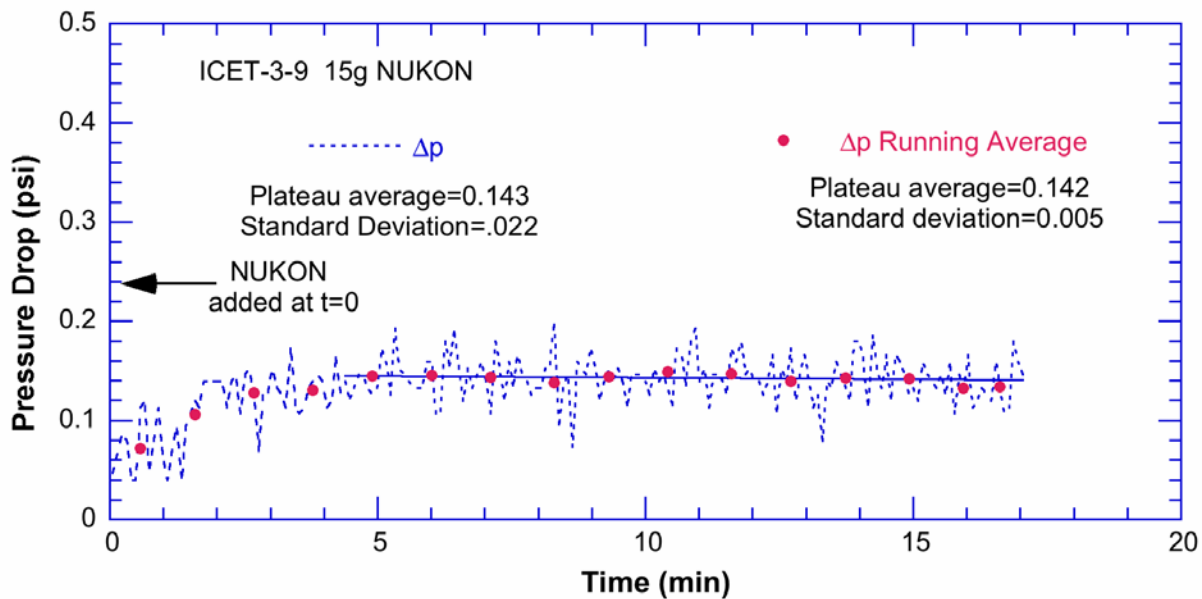


Figure 10. Pressure drop across the NUKON bed in test ICET-3-9 at an approach velocity of 0.1 ft/sec.

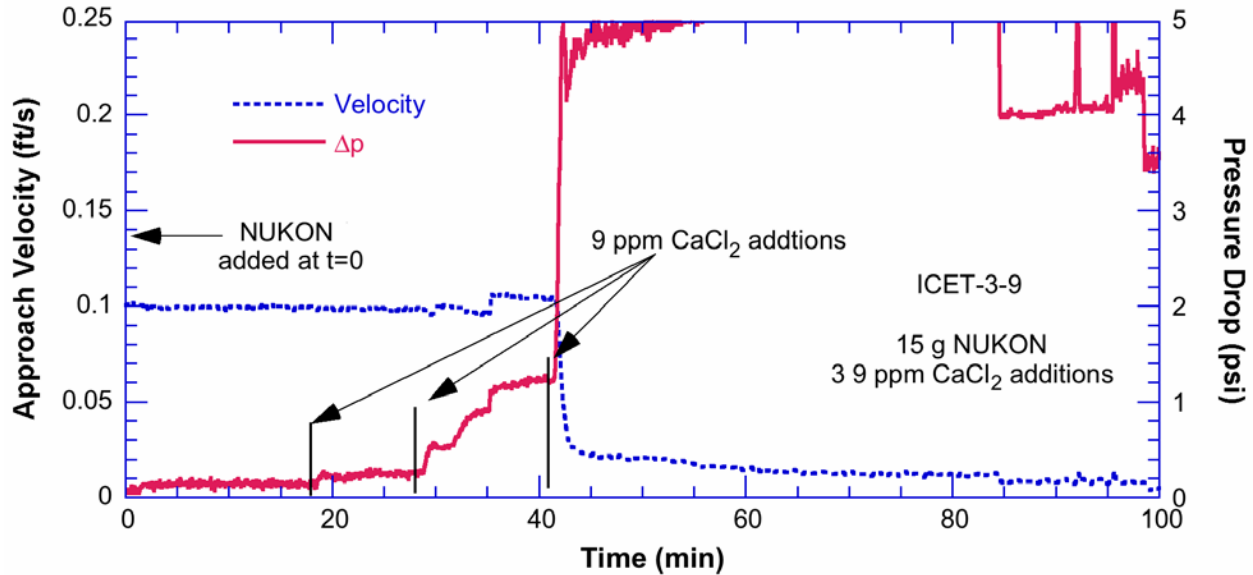


Figure 11. Bed approach velocity and differential pressure across the screen as a function of time for test ICET-3-9.

ICET-3-10 Test Procedure:

ICET-3-10 also used a debris loading of 15 g NUKON and 15 g cal-sil. The debris was presoaked for 30 minutes at 60°C, prior to introduction into the loop. One half of the total TSP addition was added to the debris slurry during the 30 minute presoak period, starting five minutes after the introduction of the debris and then continuing at a nominally uniform rate over the remaining 25 minutes. The remaining half of the TSP was metered directly into the loop over 30 minutes at a nominally uniform rate after the introduction of the debris. This TSP addition sequence was intended to represent a plant where TSP begins to dissolve 5 minutes after the start of a LOCA, and complete dissolution has occurred one hour after a LOCA. The conditions in this test were intended to represent a “typical” degree of dissolution of cal-sil prior to formation of the bed. However, because of the rapid rise in pH in the presoaking solution due to the high concentration of cal-sil, the presoaking probably leads to somewhat less cal-sil dissolution than would occur at more realistic concentrations for the same TSP history.

ICET-3-10 Results:

The bed approach velocity and differential pressure across the screen as a function of time for test ICET-3-10 is shown in Fig.12. This test resulted in a rapid buildup of head loss. After 10 minutes, the flow velocity could not be maintained at 0.1 ft/s and the flow velocity gradually decreased. At the end of test, the pressure drop across the bed was 4.7 psi ($\pm 0.9\%$) at a bed approach velocity of 0.06 ft/s ($\pm 0.8\%$).

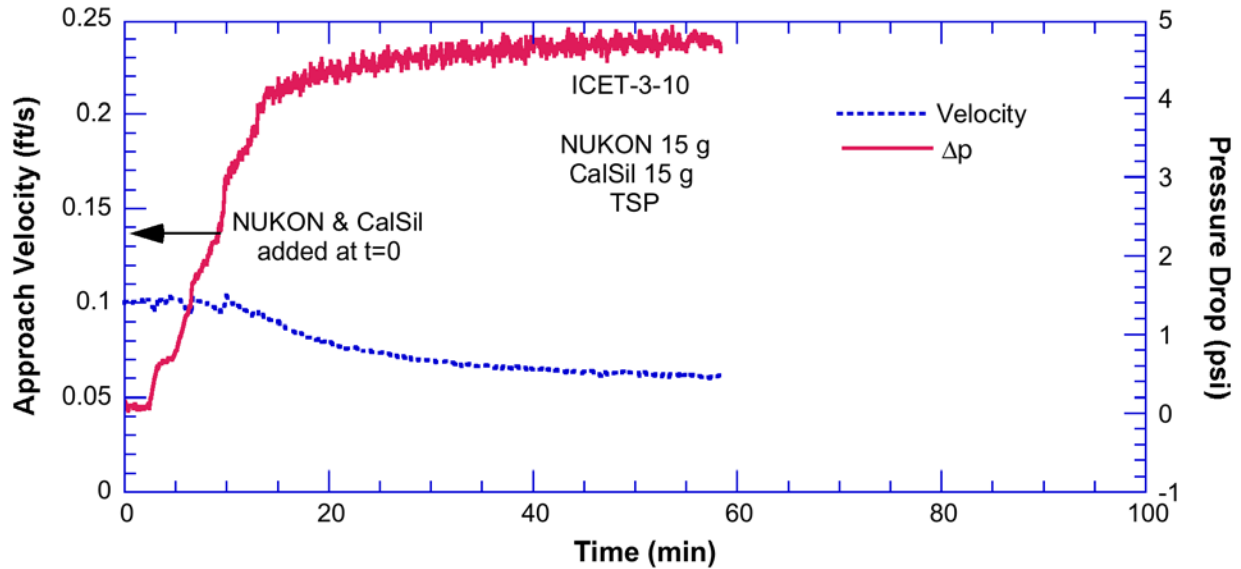


Figure 12. Bed approach velocity and differential pressure across the screen as a function of time for test ICET-3-10.

ICET-3-11 Test Procedure:

ICET-3-11 was a repeat of the baseline test, ICET-3-7, with a debris loading of 15 g NUKON and 15 g cal-sil. No TSP was introduced in the test during either the presoak or in the loop.

ICET-3-11 Results:

The bed approach velocity and differential pressure across the screen as a function of time for test ICET-3-11 is shown in Fig. 13. At 0.1 ft/s, the pressure drop stabilized at around 1.4 ± 0.03 psi. After 210 minutes (≈ 52 recirculations) at a loop velocity of 0.1 ft/s, the loop velocity was cycled from 0.1 ft/s to 0.01 ft/s to 0.14 ft/s and back to 0.1 ft/s. Figure 14 shows the variation of the pressure drop across the bed as the velocity is cycled. Comparison with Fig. 10 shows that it takes much longer for a NUKON/cal-sil bed to reach a stable pressure drop than it does for a pure NUKON bed.

Test ICET-3-11 was a repeat of ICET-3-7. However, the pressure drop across the bed is very different for the two tests as shown in Fig. 15. No reason for this difference in behavior has been determined. The behavior illustrated in ICET-3-11 is consistent with the behavior observed in other tests without TSP while the ICET-3-7 results are substantially different and appear to be anomalous. This point is illustrated in Fig. 16, which shows a comparison of bed approach velocities and differential pressures across the screen as a function of time for tests ICET-3-1, 2, & 11. Therefore, ICET-3-11 results have been used as the baseline for comparisons with tests in which precipitates are present.

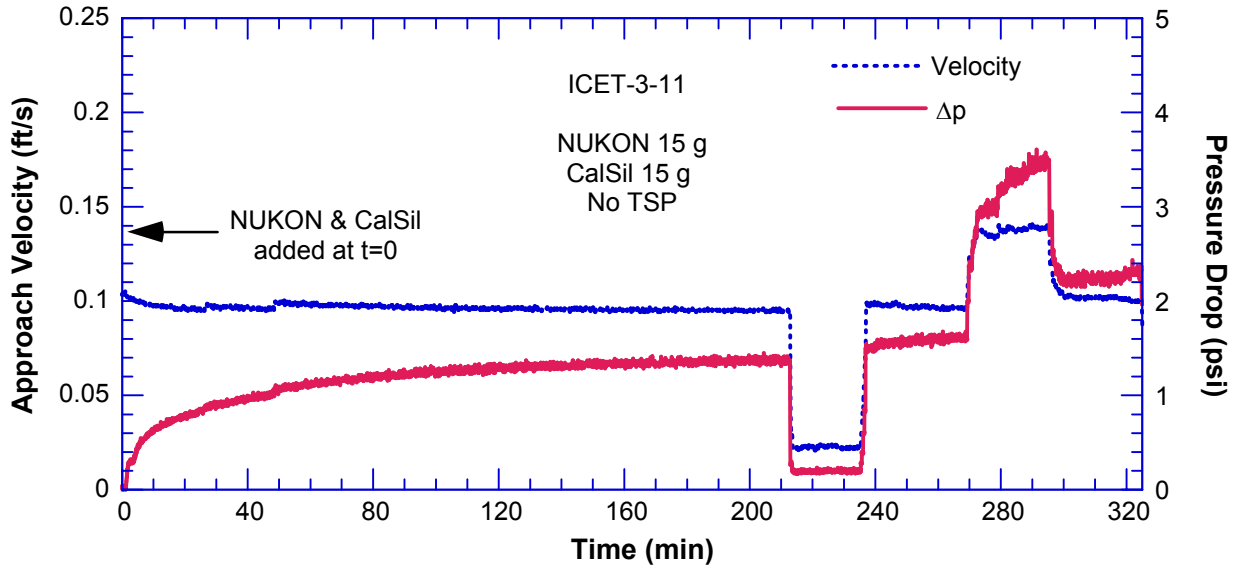


Figure 13. Bed approach velocity and differential pressure across the screen as a function of time for test ICET-3-11.

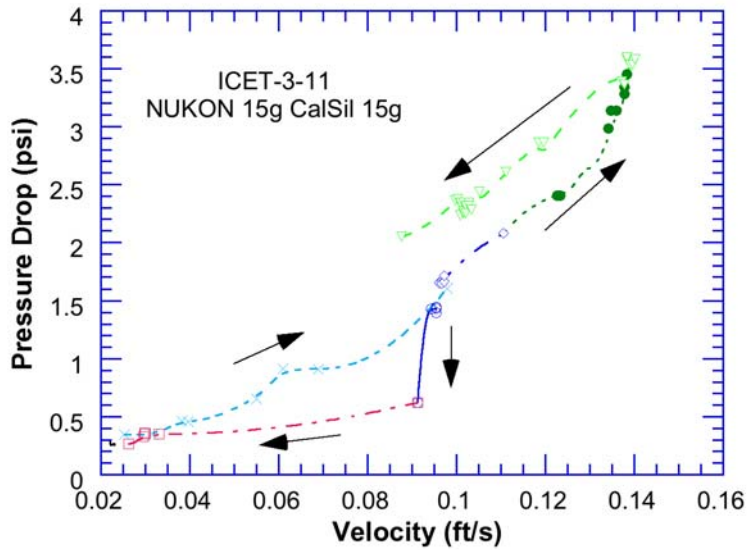


Figure 14. Change in pressure drop across the bed as the velocity is cycled from 0.1 ft/s to 0.01 ft/s to 0.14 ft/s and back to 0.1 ft/s.

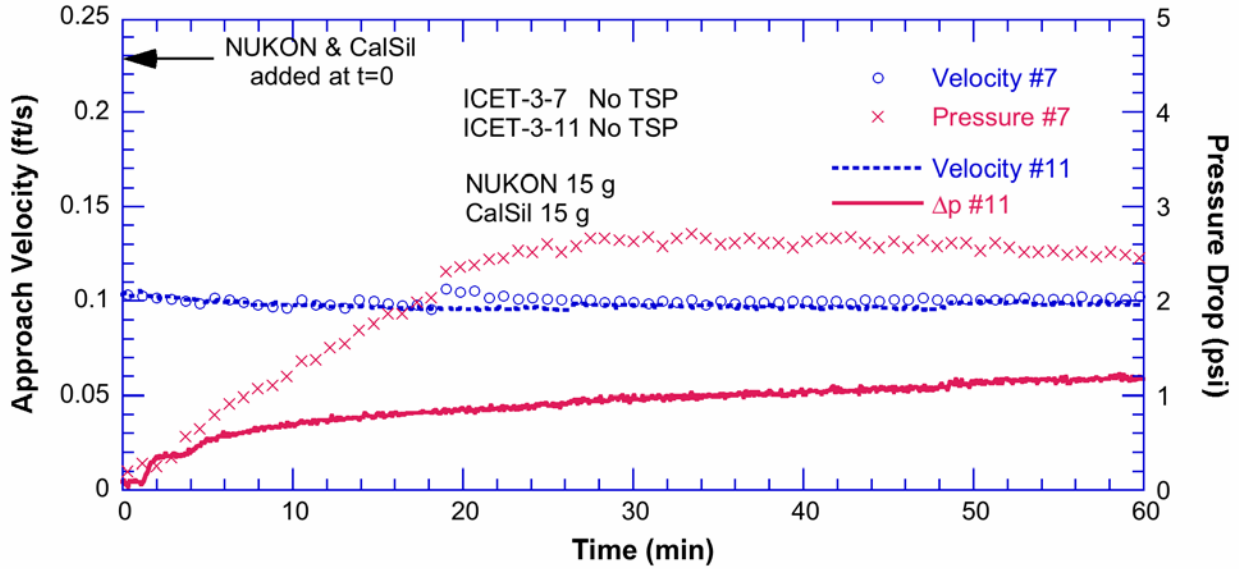


Figure 15. Bed approach velocities and differential pressures across the screen as a function of time for tests ICET-3-7 & 11.

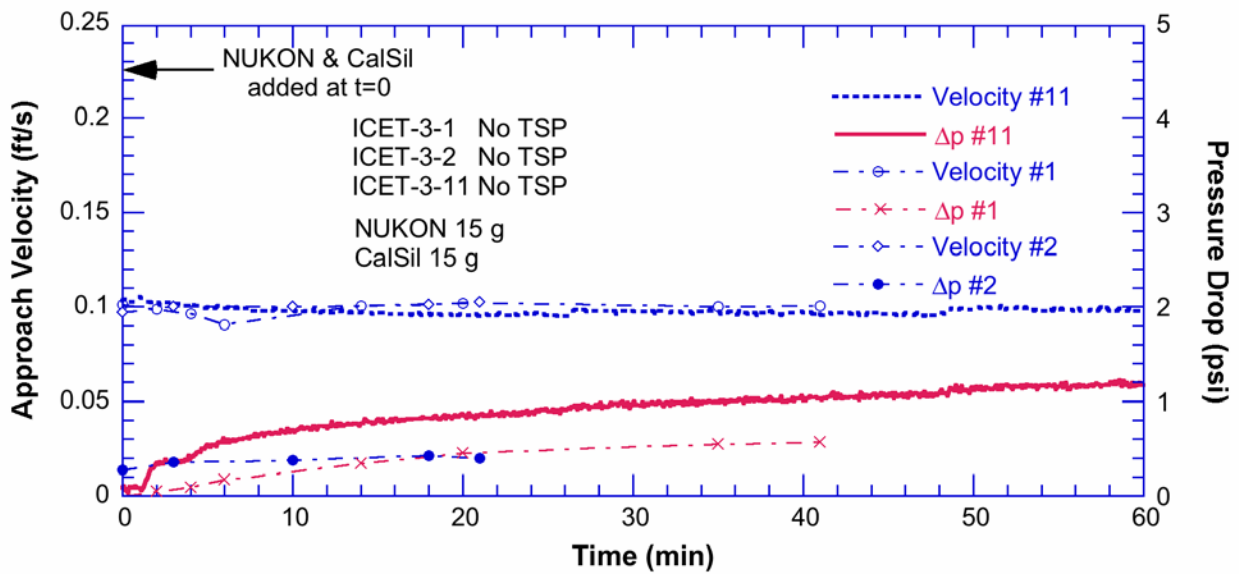


Figure 16. Bed approach velocities and differential pressures across the screen as a function of time for test ICET-3-1, 2, & 11.

Discussion of the loop test results

The pressure drops across the bed for tests with physical debris of 15 g NUKON/15 g cal-sil and TSP present (ICET-3-6 and ICET-3-10) are compared with the baseline test ICET-3-11, which had 15 g NUKON/15 g cal-sil but no TSP, in Figs. 17a and b, respectively. In ICET-3-6, no TSP was added to the presoak in order to limit the possible dissolution of the cal-sil. This scenario was intended to give a lower bound for the amount of calcium phosphate precipitate arriving as the debris bed is formed. As expected, the initial pressure drop behavior in ICET-3-6 is very similar to the baseline case ICET-3-11 in which no chemical precipitates are present (Figure 17a). However, a comparison of the maximum pressure drops reached in ICET-3-6 and -11 (Figs. 5 and 13) show that the difference in the pressure drop

increases with time. The increase of the pressure drop with time in ICET-3-6 is attributed to the continuing dissolution of cal-sil and additional formation of calcium phosphate precipitates.

Test ICET-3-10 was intended to give the “typical” amount of calcium phosphate precipitate arriving as the bed is formed in design basis analyses. As noted previously, at the end of the presoak period, a much larger amount of CaSiO_3 will have dissolved, and much larger amount of calcium phosphates precipitates will have formed compared to the ICET-3-6 case. This results in a much more rapid increase in head loss than in ICET-3-6 (Figure 17b), although the pressure drop in ICET-3-6 eventually approaches the steady state value obtained in ICET-3-10. Although this argument qualitatively explains the differences between ICET-3-6 and 10, the “lag” in the pressure drop is greater than the 30 minutes that would be expected due to differences in the amounts of cal-sil dissolved during the presoak.

A comparison of the pressure drops in ICET-3-8 and ICET-3-9, shown in Fig. 18, suggests a strongly nonlinear relationship between the amount of the calcium phosphate precipitate and the pressure drop. The first two additions of CaCl_2 in ICET-3-9 produced relatively small increases in pressure drop. The third addition resulted in a very rapid increase in pressure drop. The total inventory of dissolved Ca added in ICET-3-9 is equivalent to complete dissolution of 9 g of cal-sil. The pressure drop observed in ICET-3-8 after addition of 43.5 ppm of dissolved Ca as CaCl_2 is almost as the same as that observed in the ICET-3-2 test (see Reference 3) in which 50 ppm Ca as CaCl_2 was added to the loop. However, this comparison may be confounded by the difference in precipitate distribution through the bed. The bed in ICET-3-8 was formed from the simultaneous arrival of fiber and precipitate. In ICET-3-9, the precipitate was deposited on a preformed fibrous bed. Since precipitate can presumably move through and into the bed, the difference in the way the beds were formed may not completely define the actual structure. The beds from the two tests can be examined to compare the precipitate distribution, but this has not yet been done. An additional test would be required to directly compare the effects of either simultaneous or sequential arrival of the chemical precipitate associated with the complete dissolution of 9 g of cal-sil.

The pressure drop increases with time occur because more debris is trapped during each pass through the debris bed during recirculation and because of continued cal-sil dissolution and formation of additional precipitates. In ICET-3-10, which represents a “typical” amount of cal-sil dissolution before the formation of the bed, it takes about 3 recirculations (or approximately 12 minutes) of the test loop fluid to build to the maximum pressure drop. In ICET-3-8, which represents the maximum cal-sil dissolution before the formation of the bed, the maximum pressure drop is reached after 1 test loop recirculation. The head loss due to chemical products in both of these cases is dominated by the precipitates that formed due to dissolution prior to the initial bed formation, and the pressure drop increases as more of these precipitates are trapped during recirculation. The effect of continued dissolution could not be determined because the pressure drop quickly reached the capability of the loop. However, in ICET-3-6, which represents the minimum cal-sil dissolution that would occur before the formation of the bed, it takes about 15 passes test loop recirculations to approach the maximum pressure drop. In this case the pressure increase is probably dominated by the time needed for additional cal-sil dissolution.

The degree of dissolution that would occur before the debris reached the sump screen in a prototypical situation would presumably be bounded by the ICET-3-6 and ICET-3-8 limiting cases, and may be most similar to the ICET-3-10 case. The amount of head loss for a plant specific case is dependent on factors such as the sump screen debris loading, uniformity of the screen debris loading, propensity for flow bypass (i.e., jetting) through the debris bed, debris bed screen approach velocity, and transport of chemical precipitate. However, the ICET-3-6, 8, and 10 results indicate the variability of head loss behavior that could be encountered for a specific loading because of differences in the onset of recirculation, debris transport time, initial containment pool pH, and TSP dissolution rate.

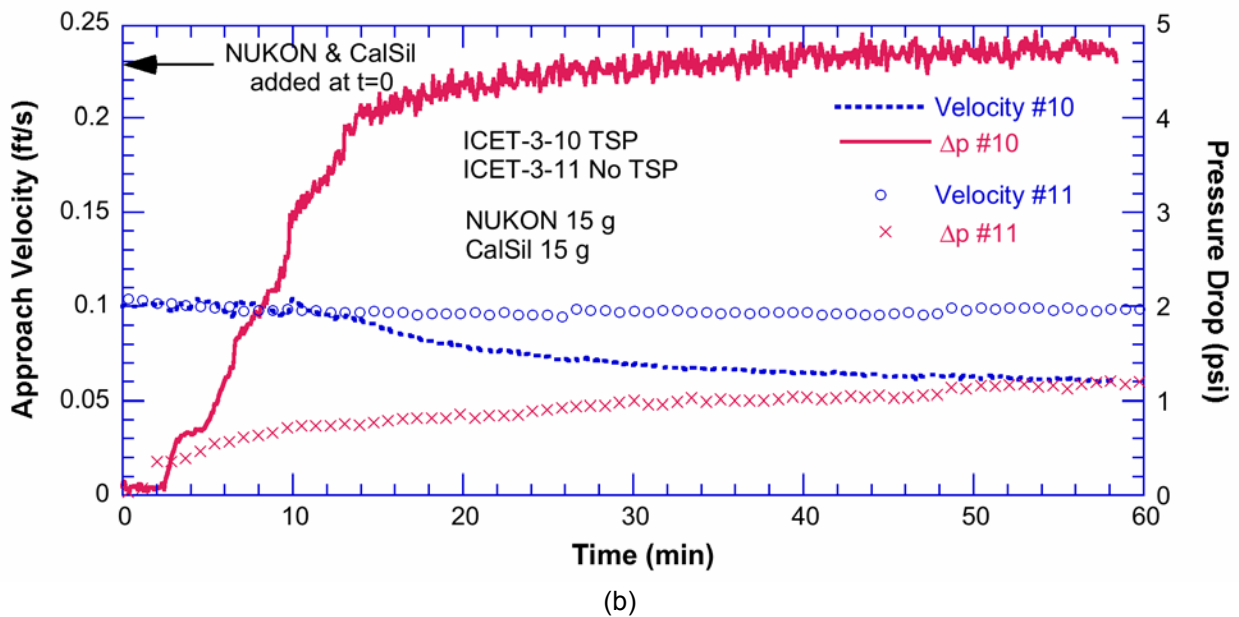
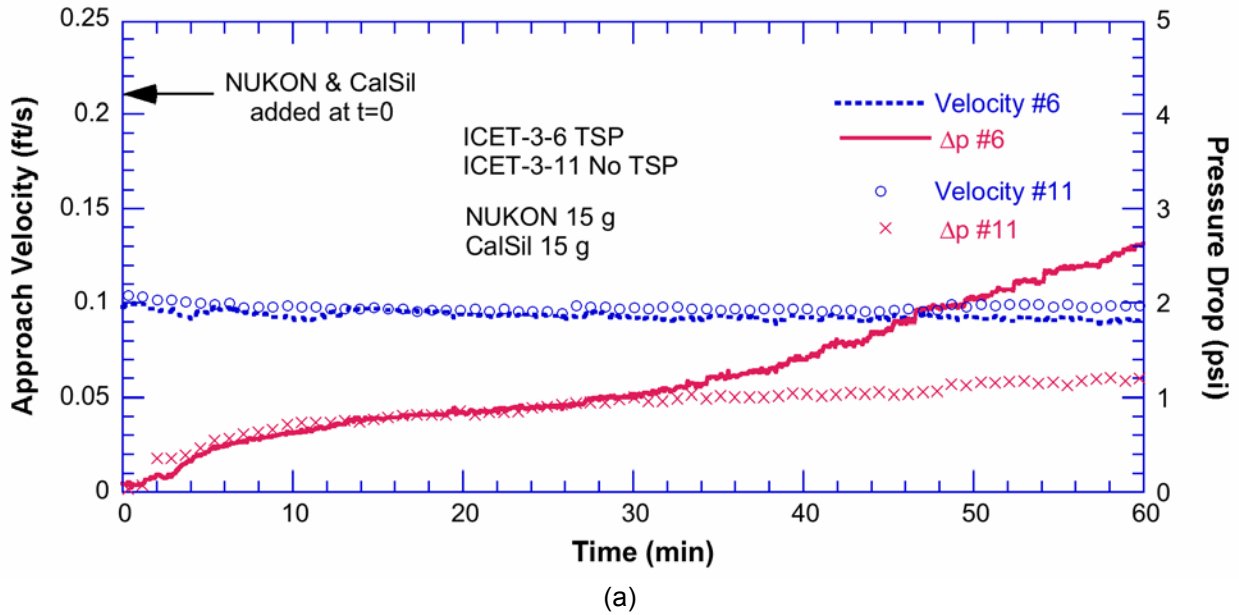


Figure 17. (a) Bed approach velocities and differential pressures across the screen as a function of time for test ICET-3-6 & 11; (b) Bed approach velocities and differential pressures across the screen as a function of time for test ICET-3-10 & 11.

In the tests with 15 g NUKON/15 g cal-sil, the strong effect of the chemical precipitates on pressure drop is readily evident. Such an effect is less evident in the comparison of the tests with 7 g NUKON/25 g cal-sil. The pressure drops in ICET-3-4, in which some precipitation of calcium phosphate would occur, and ICET-3-5, in which no precipitation would occur are compared in Fig. 19. Since no TSP was added to the presoak, the cal-sil dissolution in ICET-3-4 was limited similarly to ICET-3-6, so that a strong chemical effect would not be expected until there was time for additional dissolution in the loop. However, with this cal-sil loading, even without the effect of calcium phosphate precipitates, the head loss increases very rapidly to a high level.

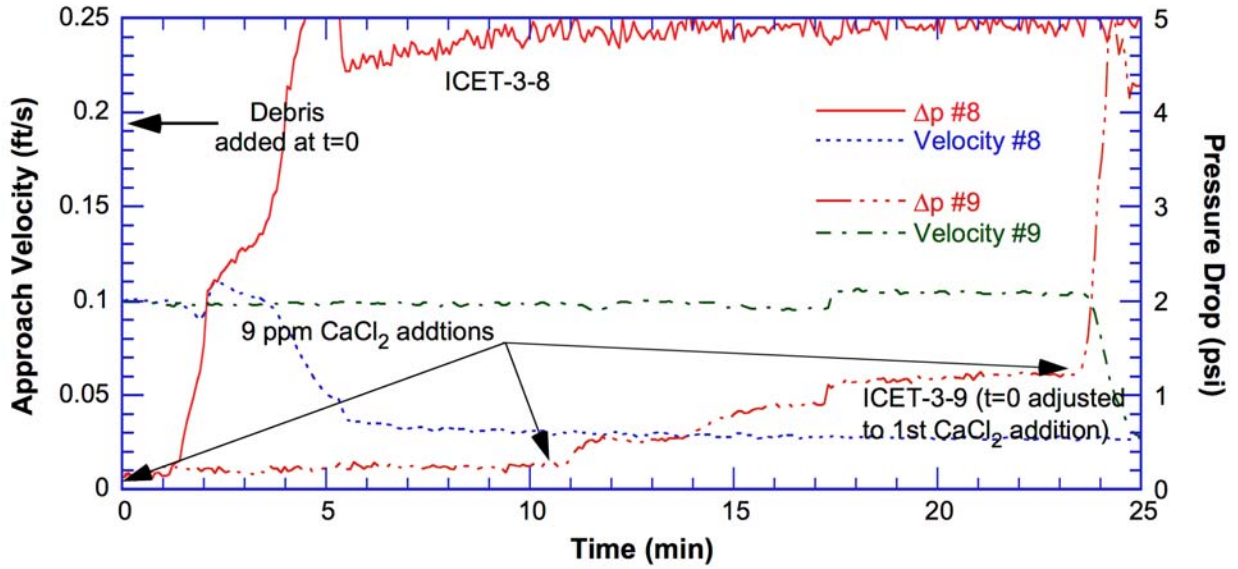


Figure 18. Bed approach velocities and differential pressures across the screen as a function of time for test ICET-3-8 & 9.

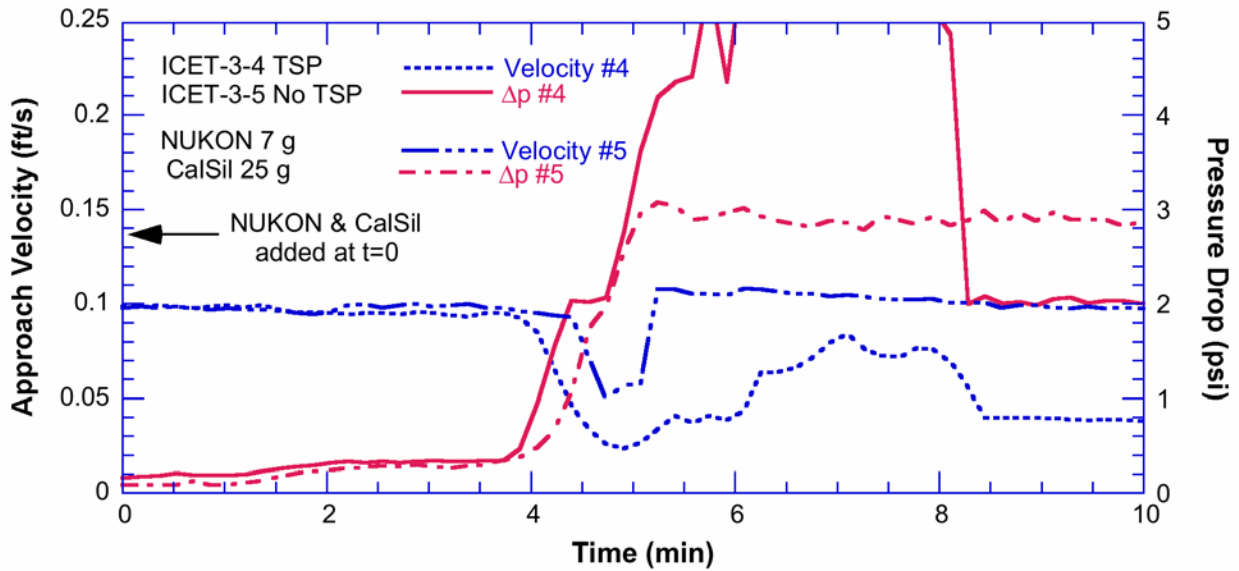


Figure 19. Bed approach velocities and differential pressures across the screen as a function of time for test ICET-3-4 & 5.

Calcium Phosphate Settling Tests

In the head loss loop tests, virtually all the calcium phosphate precipitates that form are transported to the bed. In an actual sump, there is a potential for the precipitates to settle before they reach the sump screen. Settling tests were performed to determine settling rates for calcium phosphate under conditions with no bulk directional flow. Tests were performed in a settling tower with an effective height of 71.5 cm. The tower was filled with a solution containing LiOH (0.7 ppm Li) and boric acid (2800 ppm B) and TSP (3.4 g/L). CaCl_2 solution was then added to the tower. The dissolved Ca reacts with the TSP in the solution to form calcium phosphate precipitate. The solution is stirred to get a uniform mixture and then the precipitates are allowed to settle. Two different CaCl_2 concentrations were tested. One produced a

dissolved Ca inventory equivalent to 300 ppm and the other an inventory equivalent to 75 ppm. The 300 ppm inventory is roughly equivalent to full stoichiometric dissolution of a 1 g/L concentration of cal-sil; the 75 ppm inventory is roughly equivalent to full stoichiometric dissolution of a 0.25 g/L concentration of cal-sil. In both cases, the solutions are phosphate-rich for a TSP concentration of 3.4 g/L, i.e., the formation of calcium phosphate precipitates is limited by the amount of Ca available. Replicate settling tests were conducted for each concentration.

In the 300 ppm tests, there was more of a tendency for precipitate particles to agglomerate and a visible settling front was observed, as shown in Fig. 20. Grab samples taken before and after the front passed suggest that about half the precipitate was removed as the front passed. The mixture behind the front looked relatively uniform and gradually became less cloudy. In the 75 ppm tests, a front was not visible. The mixture looked relatively uniform throughout most of the tower and gradually became less cloudy. There was a more noticeable mix of upward and downward moving individual particles.

The time histories of the settling front in the 300 ppm dissolved Ca tests were estimated by taking a sequence of pictures of the front at intervals and noting the location of the front relative to a scale mounted on the settling cylinder. As shown in Fig. 21, the front velocity is relatively constant until it approaches the bottom of the settling tower. The average velocity of the front in the 300 ppm tests is 3.8 cm/min. Settling of remaining particulate after the front passed occurred much more slowly and the settling velocities are likely more consistent with those measured in the 75 ppm tests.

In the 75 ppm dissolved Ca tests where no front was evident, the settling velocities were estimated by taking three grab samples at intervals from the top of the settling column and noting the relative decrease in the amount of precipitate in the samples with increasing time. The decay in the amount of precipitate in the samples can be modeled as exponential as shown in Fig. 22. The time constant for the decay is approximately 87.5 minutes. This corresponds to a settling velocity of 0.8 cm/min. This is more representative of the settling characteristics of the calcium phosphate precipitates at the concentrations of most interest.



Figure 20.
Settling front in test with 300 ppm Cl

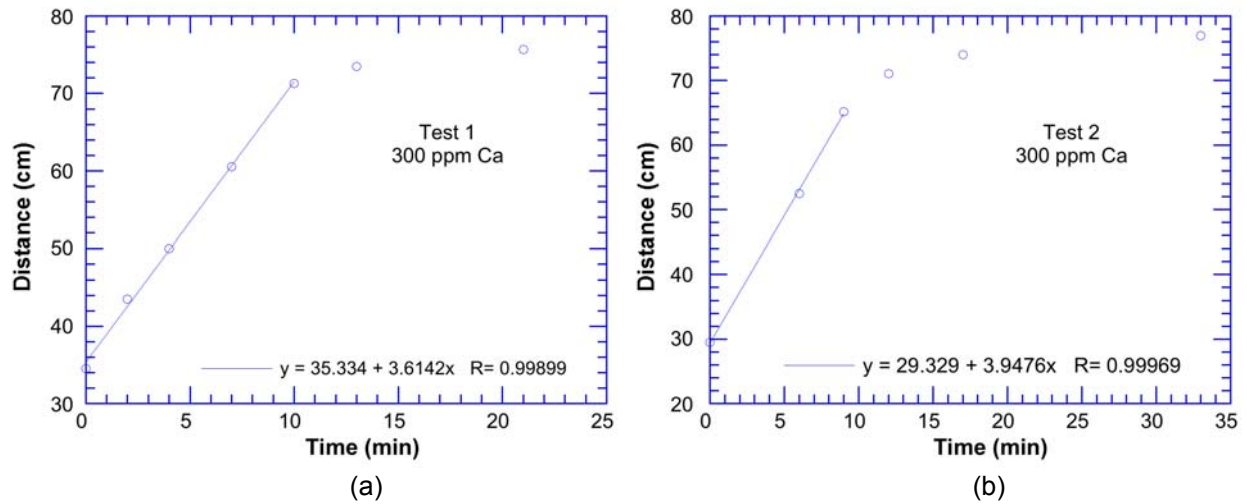


Figure 21. Time history of the motion of the settling front in the two 300 ppm dissolved Ca settling tests.

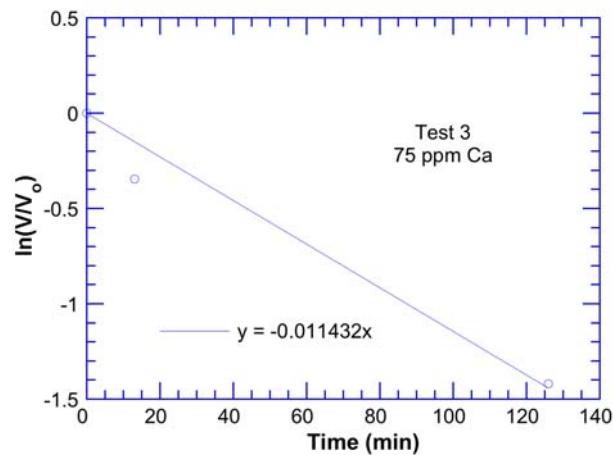


Figure 22.
Assumed exponential decay of volume of suspended precipitate in 75 ppm dissolved Ca test.

Small Scale Dissolution Testing

The objective of the small scale dissolution testing is to identify important environmental variables governing both dissolution of cal-sil and the subsequent formation of calcium phosphate precipitates over a range of simulated sump pool conditions. The variables considered in the results reported herein are the effect of the rate of TSP addition to the cal-sil solutions for various cal-sil concentrations.

Three different histories of TSP addition were studied. These histories are intended to encompass the range of histories of TSP dissolution expected within an actual containment pool:

1. Add TSP before cal-sil addition (instantaneous dissolution of TSP).
2. Titrate TSP over 1 hr period into solution after cal-sil addition (nominal case).
3. Titrate TSP over 4 hr period into solution after cal-sil addition (very slow addition of TSP).

The test temperature was 60°C. The base solution consisted of 2800-ppm-B and 0.7-ppm Li. The TSP concentration was 3.4 g/L which results in a nominal pH value of 7.1 in the buffered solution. The cal-sil concentrations for the tests were 0.5 and 1.5 g/L. The 0.5 g/L cal-sil concentration is generally representative of current plant design basis concentrations based on a survey of plants that utilize TSP buffering and expect cal-sil to be present in the containment pool.⁵ The 1.5 g/L concentration is greater than current plant concentrations. At these concentrations, the formation of calcium phosphate precipitates is expected to be Ca limited, since $\text{Ca}_3(\text{PO}_4)_2$ [tricalcium phosphate] or $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ [hydroxylapatite] are the two most likely forms for the calcium phosphate precipitates at this pH.⁶

The results from small scale dissolution tests performed at 60°C to date are summarized in Table 2. Time, in these tables, represents the elapsed time after the cal-sil was added to the base solution. However, grab samples were taken only after the TSP additions were completed in each test. The values for Ca, P, Si, and Na in the tables were determined by inductively coupled plasma (ICP) measurements on the grab samples. ICP measures the total amount of elements present in a sample whether they are present as solutes or solid species. However, the samples were filtered prior to ICP analysis and the ICP results are expected to represent only species in solution.

Since the Ca which is released (as the cal-sil dissolves) and quickly combines with the available dissolved phosphate to form a solid calcium phosphate precipitate, the ICP measurements of Ca in the filtered supernate are not representative of the amount of Ca that has actually dissolved. The measurements of dissolved P have been used to estimate the amount of Ca that has been precipitated. If all the P that was added as TSP remained in solution, the P concentration would be 277 mg/L. The measured P concentrations are always less than this concentration. It is assumed that the missing P has all combined with Ca to form solid calcium phosphate precipitates. There are a variety of calcium phosphate species having different stoichiometries. The least soluble species at the pH values of interest are $\text{Ca}_3(\text{PO}_4)_2$ [tricalcium phosphate] and $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ [hydroxylapatite].⁶ Values of the amount of Ca residing in calcium phosphate precipitate have been calculated for each of these assumed species based on the missing P in solution. This information is summarized in the last two columns of Table 2. The total dissolved Ca can be estimated by adding the measured Ca (column 4 in Table 2) with the Ca from either of the last two columns in Table 2.

The dissolved Ca that has combined to form calcium phosphate can be estimated based on the assumption that the precipitates are primarily hydroxylapatite. These values are shown in Figs. 23a and 23b. In these graphs, the time, once again, is measured from the time that the cal-sil is added to the solution. The data legend indicates if the TSP dissolution was instantaneous (“instant”), completed in 1 hour (“nominal”), or completed in 4 hours (“slow”). While there is variability in the data, it appears that

the TSP dissolution history has a larger effect at the higher cal–sil loading (1.5 g/L) than it does at 0.5 g/L. It appears from the data in Table 2, that it takes substantial time (approximately 4 days) to achieve full dissolution for the 1.5 g/L cal–sil concentration while the 0.5 g/L concentration appears to be completed within approximately 1 - 3 days. For both cal–sil concentrations, substantial Ca dissolution (> 75 mg/L) has occurred within a few hours regardless of the TSP addition rate.

These data are replotted in normalized form in Fig. 24. In this figure, the total dissolved Ca at each point in time is normalized by the Ca concentration corresponding to complete stoichiometric dissolution of the total amount of cal–sil present. The figure shows that for the case of instantaneous TSP dissolution, the fractional amounts of dissolved Ca are significantly different for the two different cal–sil loadings. For the more realistic 1 hour TSP dissolution history and the bounding 4 h TSP dissolution history, the normalized Ca values are close for the two loadings, i.e., the amount of dissolved Ca just scales with concentration. Even for the case of instantaneous TSP dissolution, the normalized dissolution rate of the 0.5 g/L cal–sil loading is similar to that observed for the 1 and 4h TSP addition rates for the 0.5 and 1.5 g/L loadings. This supports the assumption stated earlier that the cal–sil dissolution rate is not too strongly dependent on the concentration for these low cal–sil concentrations. Thus, the screen loading per unit area is the most important scaling parameter for head loss tests with calcium phosphate precipitates.

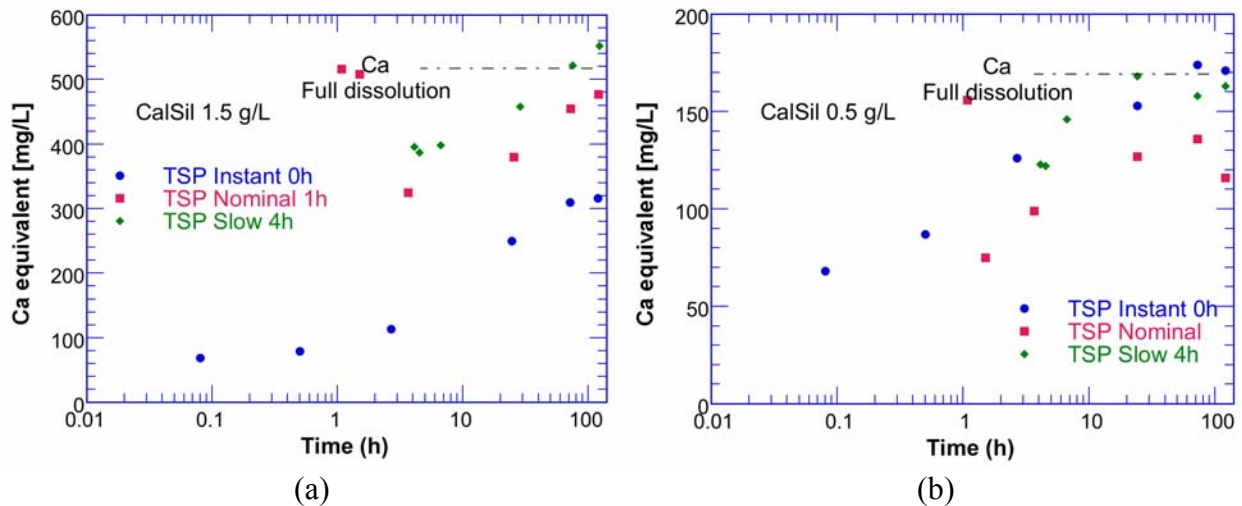


Figure 23. (a) Dissolution of cal–sil at a loading of 1.5 g/L for three different histories of TSP addition; (b) Dissolution of cal–sil at a loading of 0.5 g/L for three different histories of TSP addition.

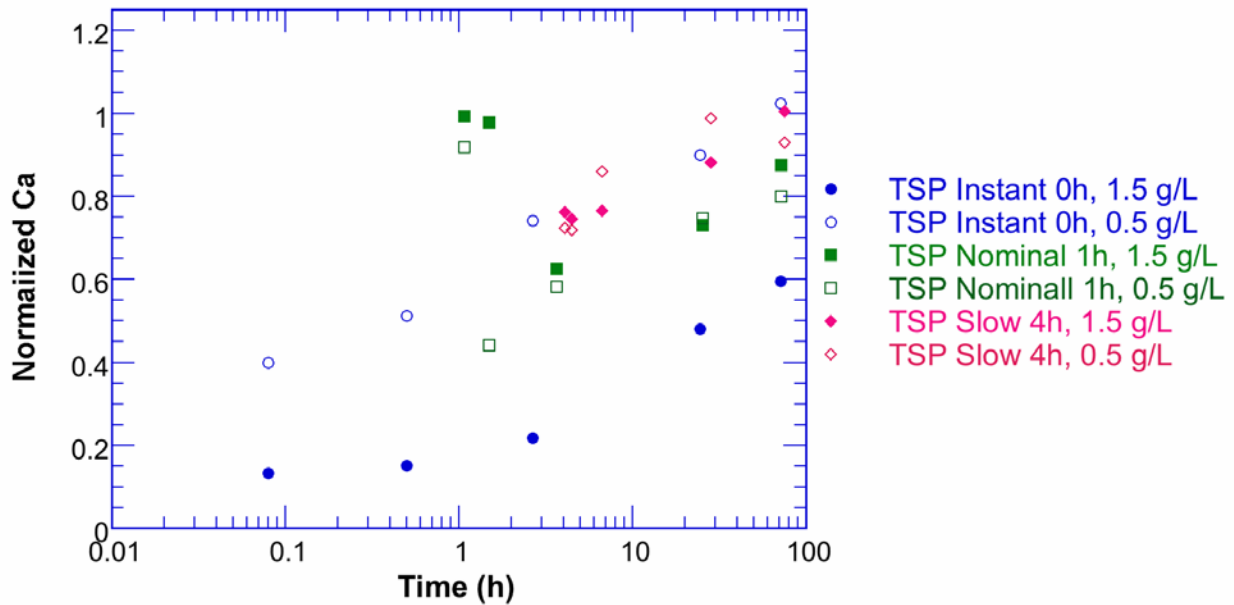


Figure 24. Normalized dissolution data, dissolved Ca/Ca for full dissolution for loadings of 1.5 g/L and 0.5 g/L for three different histories of TSP addition.

Summary of Important Findings

Chemical products (calcium precipitates) associated with the ICET-3 sump environment have a significant effect on head loss across simulated sump screen debris beds. The head losses associated with pure physical debris beds of NUKON and cal-sil are typically much smaller than those that occur across debris beds in which some of the cal-sil has been replaced with a corresponding amount of calcium phosphate precipitates.

The relative importance of chemical effects depends strongly on the debris loading at the screen. For a screen loading corresponding to 1.19 kg/m² of cal-sil and 0.33 kg/m² of NUKON (25 g and 7 g respectively in the ANL loop), the pressure drop associated with the physical debris bed is sufficiently large that the additional contributions related solely to chemical products could not be determined in the current test loop. Debris loadings of this magnitude produced significant pressure drop in the test loop even without consideration of chemical product effects. However, for a screen loading corresponding to 0.71 kg/m² (15 g each) of cal-sil and NUKON, the pressure drop across the physical debris bed in benchmark testing is approximately 1.4 psi at an approach velocity of 0.1 ft/s. With TSP, and thus calcium phosphate precipitates present, the same debris loading caused the pressure drop across the bed to be greater than 5 psi for the same approach velocity. Because the conversion of cal-sil into calcium phosphate significantly increased the head loss, the relative importance of chemical effects is greater for this NUKON and cal-sil debris mixture than for the higher cal-sil concentration.

Complete dissolution of the cal-sil could take one to four days or more depending on the TSP dissolution rate and the cal-sil concentration. Dissolution of 1.5 g/L cal-sil concentrations is retarded by instantaneous TSP dissolution. However, the cal-sil dissolution rate (for the concentrations studied) is not strongly dependent on the TSP dissolution rate over the range of slower, more realistic TSP dissolution rates studied. Regardless of TSP dissolution rate, the equivalent dissolved Ca exceeded 75 mg/L in a few hours for cal-sil concentrations as low as 0.5 g/L. Such an equivalent dissolved Ca concentration was shown to produce pressure drops on the order of 5 psi at an approach velocity of 0.1 ft/s across a 0.71 kg/cm² NUKON debris bed.

In the loop tests, all the calcium phosphate that is formed is transported to the screen. Settling tests were performed to determine settling rates for calcium phosphate under conditions with no bulk directional flow. At higher dissolved calcium concentrations (300 ppm), the precipitates can agglomerate. The agglomerated precipitates settle more quickly, but approximately one half of the total precipitate settles more slowly than the agglomerated precipitate. At a lower dissolved calcium concentration (75 ppm), which is expected to be more representative of plant conditions, the estimated settling velocity is 0.8 cm/min.

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).
3. ANL Quick Look Report Tests 1 & 2, September 16, 2005 (ADAMS ML052590238)
4. Integrated Chemical Effects Test Project: Test #3 Data Report (ADAMS ML053040479)
5. MEMORANDUM on "Summary of Meeting on September 30, 2005, to Discuss GSI-191 Chemical Effects Head Loss Information," dated November 2, 2005, ADAMS Accession Number ML053060359, <http://www.nrc.gov/reactors/operating/ops-experience/pwr-sump-performance/public-mtgs/2005/index.html>
6. Solubility of Calcium Phosphates, <http://www.azom.com/details.asp?ArticleID=2140>.

Table 2 Summary of Current Results for the Small Scale Dissolution Tests at T= 60°C.

Test Series	Time (h)	pH (RT)	Ca (mg/L)	P (mg/L)	Si (mg/L)	Na (mg/L)	cal-sil (g/L)	Ca equiv (mg/L) (Ca ₃ (PO ₄) ₂)	Ca equiv (mg/L) Ca ₁₀ (PO ₄) ₆ (OH) ₂
I TSP is added before the cal- sil is introduced	0.08	7.04	39	263	23	536	1.5	28	31
	0.50	7.17	25	252	24	554	1.5	49	55
	2.67	7.38	16	232	36	549	1.5	88	98
	24.50	7.24	8	165	60	534	1.5	217	242
	71.25	7.33	4	135	67	557	1.5	276	306
	119.00	7.48	3	132	68	567	1.5	281	313
II TSP metered over an hour after the cal-sil is added	1.08	6.83	58	65	21	159	1.5	412	458
	1.5	6.79	54	66	22	168	1.5	409	454
	3.67	7.1	11	131	25	357	1.5	283	315
	25.5	7.1	5	103	46	382	1.5	337	375
	72.25	7.15	3	67	62	405	1.5	407	452
III TSP metered over a 4 hour period.	120	7.26	3	57	65	395	1.5	427	474
	4.08	7.12	19	102	26	289	1.5	339	377
	4.5	6.85	14	104	28	295	1.5	336	373
	6.67	6.92	6	95	30	297	1.5	353	392
	28.5	6.99	5	67	42	292	1.5	408	453
IV TSP is added before the cal- sil is introduced	75.25	7.1	3	36	60	327	1.5	467	519
	123	7.25	3	22	65	331	1.5	494	549
	0.08	7.13	9	250	7	598	0.5	54	59
	0.50	7.29	9	241	9	585	0.5	70	78
	2.67	7.4	10	223	20	594	0.5	105	117
V TSP metered over an hour after the cal-sil is added	24.00	7.37	4	208	36	600	0.5	134	149
	72.00	7.26	3	198	42	579	0.5	154	171
	120.00	7.26	3	199	42	577	0.5	152	168
	1.08	7.2	14	211	9	512	0.5	128	142
	1.5	7.25	14	249	12	618	0.5	55	61
VI TSP metered over a 4 hour period.	3.67	7.26	13	237	20	620	0.5	78	87
	25.5	7.32	7	222	37	627	0.5	108	120
	72.25	7.23	4	216	45	631	0.5	118	131
	120	7.2	4	225	47	642	0.5	101	112
	4.08	7.24	21	230	22	585	0.5	91	102
VI TSP metered over a 4 hour period.	4.5	7.24	18	229	24	600	0.5	93	104
	6.67	7.26	7	212	28	582	0.5	126	140
	28.5	7.35	4	201	37	583	0.5	148	164
	75.25	7.24	3	206	44	600	0.5	139	154
	123	7.24	4	203	46	601	0.5	143	159