

INTEGRATED CHEMICAL EFFECTS TEST PROJECT

Response to Industry Request for
Expedited Sample Characterization
Revision 0
April, 2005

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1 Introduction

This technical addendum has been prepared in response to a request for information submitted to the Nuclear Regulatory Commission (NRC) by the nuclear utility industry through the Electric Power Research Institute (EPRI) regarding specific physical and chemical attributes of the debris types observed in Integrated Chemical Effects Tests (ICET) 1 and 2 conducted by Los Alamos National Laboratory (LANL) in the civil engineering department at the University of New Mexico (UNM). The topics addressed here include: (a) characterization of Test 1 (T1) sediment recovered from the floor of the ICET test tank with respect to moist/dry mass ratio and qualitative resuspension and settling behavior; (b) scanning electron microscope (SEM) images of T1 and Test 2 (T2) sediment with qualitative assessment of the fiber to particulate volume ratios, energy dispersive spectroscopy (EDS) determination of elemental composition, and total hydrated masses recovered from T1 and T2, and (c) elemental composition of white chemical precipitant observed in T1 with SEM images. In addition to the above information requested by the industry, (d) SEM images of chemical deposits found in fiberglass samples have also been provided for consideration as a possible source of adverse head-loss phenomena.

2 Characterization of T1 Tank Sediment

This section documents the qualitative characterization of T1 tank sediment performed on April 13, 2005 at UNM. Recall that T1 was terminated on December 21, 2004. A draft procedure for this examination was provided by EPRI on March 4, 2005 to satisfy two objectives: (1) determine the moist to dry mass ratio so that moist-sediment inventories reported after the test was completed can be converted to dry quantities, and (2) qualitatively describe the propensity of sediment for resuspension and settling in the T1 tank solution.

2.1 *Recommended Procedure for Sediment Examination*

A recommended procedure was provided as follows. Italicized annotations have been added where needed for clarity.

A. Weighing

- 1) Obtain a small (~1/2 teaspoon) sample of sediment from one of the four containers. *Sediment from each quadrant of the tank was collected and stored separately.* The sample should be obtained by first removing some of the material on the surface of the sediment in the container. *This was proposed in order to avoid uneven moisture content in the event of surface drying.*
- 2) Weigh the sample without delay and record the weight.
- 3) Place the sample in an oven and allow to dry at ~220°F for 24 hours.
- 4) Weigh the dried sample and record the results. Label and save the sample.

B. Suspension

- 1) Obtain another small (~1 teaspoon or less) sediment sample from one of the containers *and weigh while still moist*.
- 2) Place sediment into a ~50-ml sample bottle.
- 3) Add some decanted fluid from one of the end-of-T1 1-L archival samples and fill the sample bottle containing sediment about half full. (Do not agitate the archival sample jar. The objective is to obtain decanted fluid without any of the precipitate/sludge that has settled in the archival solution).
- 4) Using a glass or stainless steel rod, agitate the sediment and fluid to break up the sediment material and attempt to resuspend it in the liquid. Make notes of how readily the sediment material breaks up and is or is not resuspended.
- 5) Add more decanted fluid to fill the 50-ml sample bottle to about 90% full and place the cap on the bottle.
- 6) Vigorously shake the bottle to resuspend as much of the sediment as possible.
- 7) Set the bottle down and observe how much sediment immediately settles to the bottom of the bottle (linear measurement in mm on the bottom of the bottle).
- 8) Record the approximate length of time it takes for most of the material to settle, and the fluid becomes visibly clear.
- 9) Measure how much sediment is in the bottom of the bottle (mm).
- 10) Report the results and label and retain the sample bottle with the sediment.

The intent of the draft procedure was followed as closely as possible and additional measurements were added to track the settling of the fine particulate. However, a check list was not prepared to ensure explicit execution of each step. Deviations from the procedure are noted in the following narrative account of the observations.

C. In addition to the requested procedures, time-dependent settling of very fine particulates was examined using a turbidity meter. A table of settling rate data is provided with an accompanying plot.

2.2 Part A: Wet/Dry Mass Comparison

All characterization of T1 sediment was performed using material from the south quadrant of the ICET tank (87.4 g moist); however, the mass and visual appearance of sediment in each quadrant is consistent. The sample has been stored in a plastic container with a threaded lid. The sediment is still visibly moist with uniform color and consistency. No free water is present and no moisture condensation was present on the interior of the container. The aggregate sample of moist sediment appears wrinkled (accordion folds) and grayish brown in color like wet cardboard that has been scraped from a surface. This appearance suggests that a relatively thin layer of material was removed from the bottom of the tank and that constituent fiber may be present to help hold together the structural mat. Some patches of the debris clearly contain more sand-like particles than others, and the location of particulates relative to the wrinkled surface suggest that larger amounts of particulate were located near the bottom of the bed.

A small, penny-sized sample of moist sediment was extracted from the interior of the debris using tweezers and placed on a tared filter paper and metal sample cup. The

sample was weighed on the Mettler AE 200 mass balance located in the Environmental Engineering Laboratory at UNM. The moist sample (measured to be 1.665 g) was placed in an air convection drying oven at 100°F. After 10 min. in the oven, the surface color changed to ash gray indicating rapid drying. (See Figure 1 and Figure 2). After drying overnight for approximately 29 hrs, the sample had a dry weight of 0.6395 g indicating a loss of approximately 62% of the original moist mass. Earlier repetitions of this measurement using larger quantities of sediment indicated losses of 51%. Thus, the ratio between dry sediment mass and moist sediment mass (M_{dry}/M_{wet}) is between 0.4 and 0.5. Similar measurements of T2 sediment exhibited a 48% mass reduction, which is again consistent with a dry to moist mass ratio of 0.5.

A larger sediment sample was similarly removed from the interior of the aggregate debris for use in the settling tests. Some effort was taken to obtain a representative fraction of both the particulate “mud” and the wrinkled surface layer. The sample was placed directly into a pretared, clean glass vial for testing to avoid any sample losses that might occur during transfer between containers. The sediment material dropped cleanly to the bottom with very little deposit on the side of the glass vial. The measured moist mass was 4.203 g. (See Figure 3).



Figure 1. T1 sediment container from south quadrant (right) and a 1.67-g sample for drying (left).



Figure 2. T1 sediment container from south quadrant of tank (close up).



Figure 3. Sediment sample (4.2 g) extracted for settling tests.

2.3 Part B: Qualitative Resuspension and Settling Characteristics

The information reported in this section is largely qualitative, but the basic attributes of container volume, sample mass, and sediment layer thickness may be useful for inferring particle-size information. Some additional desired information will need to be extracted from the photometric evidence that is supplied here. For physical reference, vials of two sizes with similar cylindrical shapes were employed. The volumes of each vial were determined using a calibrated syringe to fill them up to the beginning of the glass neck with distilled water. The small vials have a volume of 32 ml and the large vial has a volume of 65 ml. The large vial has an inside diameter of approximately 1 inch (2.54 cm) and an outside diameter of approximately 1 1/8 inch (2.86 cm) as measured across the bottom using a steel rule with 1/32-inch (0.79 mm) graduations (shown in later photos). Thicknesses of the glass walls were estimated visually. The small vials have an inside diameter of approximately 7/8 inch (2.22 cm) and an outside diameter of approximately 15/16 inch (2.38 cm).

The recommended procedure requested that settling behavior be observed in supernatant liquid archived from the end of T1. At this time, there are approximately 10 to 12 one-liter bottles of test solution remaining. One partially empty bottle (labeled #18 12-21-04) was selected for use. There is visible precipitate present in the bottom of each bottle, so care was taken not to disturb the settled material. Archival solutions are stored at room temperature and all resuspension/settling tests were conducted at room temperature.

Approximately 30 ml of supernate was removed from the top of bottle #18 using a syringe to avoid disturbing the precipitant at the bottom. This test solution was added to the sediment by tipping the large vial nearly horizontal and slowly injecting the liquid to avoid disturbing the sediment. Little to no evidence of disruption was observed in either the reservoir or the test sample as indicated by the uniform color (pale yellow) and no visible suspended or swirling matter. The large test vial was approximately half full with T1 solution and immersed debris. (See Figure 4).

A separate sample of test solution was extracted by syringe to fill a small test vial. The baseline turbidity of this sample was measured to be 2.2 NTU (nephelometric turbidity units) using the Hach ratio turbidimeter present in the ICET lab (UNM Civil Engineering hydraulics lab). After shaking the vial, turbidity increased to 2.4 NTU.

The potential for resuspension of the immersed sediment material was investigated by sequentially sweeping or picking at the surface of the debris with a glass stirring rod and noting the results. Each interrogation became increasingly invasive until finally the vial was swirled and then eventually shaken. Observations for each level of disturbance are described below.



Figure 4. T1 archive solution and large vial used for resuspension/settling tests.

A gentle sweep over the surface of the immersed debris released significant quantities of fine particulate that swirled like “wisps of smoke” in the liquid. This verbal description was applied by two independent observers upon seeing the sample for the first time. A typical eddy generated using very little energy released a component of larger particles that fell back to the bed within 15 seconds and a portion of very fine visibly indistinguishable particles that remained suspended for the duration of these examinations.

After 2 or 3 stronger sweeps through the surface layers of the sediment, a uniform brown haze was visible in the top 2 cm of solution above the sediment, but because the vial had not yet been uniformly mixed, the dirty layer sat beneath the “clean” solution with a well defined interface at the mixing boundary. Gently rocking the vial side to side like a pendulum tended to settle the debris pile more uniformly and to separate some of the larger particles to the bottom. These exams leave the impression that the sediment present in T1 was very loosely aggregated. It may be that the constituent soil and concrete dust added to the test as latent debris simulant would behave in much the same manner. Extremely fine particulates are easily released from the sediment sample with almost any degree of small agitation, so the fiber fraction, confirmed to be present by SEM examination, and any chemical constituents (if present) do not appear to enhance the cohesiveness of the sediment layer collected from T1. (See Figure 5 and Figure 6).



Figure 5. T1 sediment in T1D30 T1 test solution after gently probing surface layers of debris. Note the brown haze of suspended particulate below the relatively clean solution.

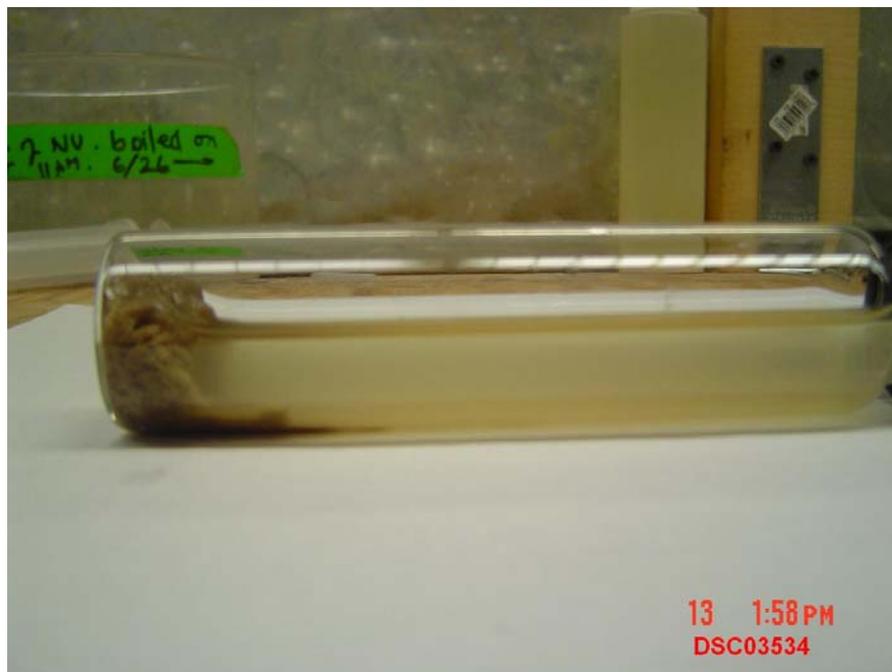


Figure 6. Horizontal sediment vial showing mechanical behavior of a slumping bed prior to shaking.

When swirling the vial to the point of uniformly mixing the brown color, the solids behave like a suspension of river-bed silt. After significant agitation is stopped, the solids immediately stratify into well defined layers by size and color. At the bottom of the vial were found (a) the larger visible grains followed by (b) a layer of dark brown “mud.” The largest portion of the vial in the middle, (c) was uniformly brown in color and appeared to be homogeneous in mixture. Near the top, was (d) a layer of relatively clean semitransparent solution with a well defined boundary separating it from the homogeneous mixture in the middle of the vial. The bottom sediment layer and the top clean layer grow with settling time as the middle layer shrinks through deposition and settling. Figure 7 shows the vial after vigorous swirling and approx. 5 minutes of settling.

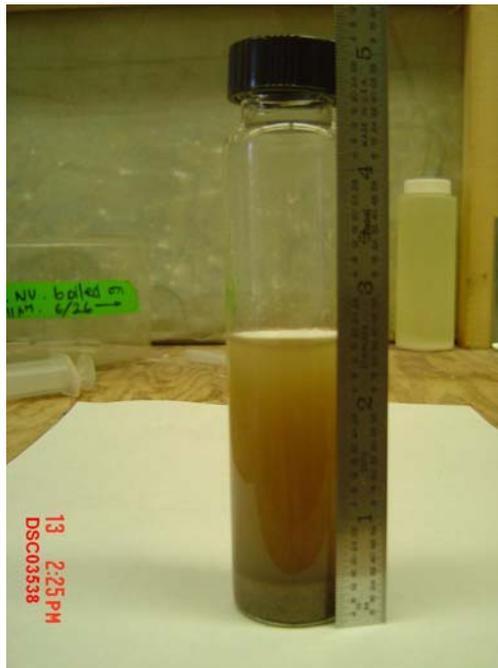


Figure 7. Large sediment vial after thorough mixing and 5 minutes of settling.

Manually shaking the vial to the point of air entrainment and bubble formation had the somewhat surprising effect of floating fibrous material to the top of the column. Small clumps, networks, and strands of very fine fibers were visible in the foam residue on the glass around the top of the mixture.

Next, the large test vial was filled to the neck with additional T1 archival solution and the agitation tests were repeated. Additional liquid diluted the stratified layers to make the internal structures more visible, but the qualitative separation described above was the same. At the deposition interface between layers (b) and (c) the material appeared to collect in a loosely aggregated bed that was almost “fluffy” in appearance. The grayish color of this material is suggestive of the original description of sediment in the storage container as wet shredded fiber board. Figure 8 shows the full vial after approximately 5 minutes of settling.



Figure 8. Large sediment vial after filling, thorough mixing, and 5 minutes of settling.

2.4 Part C: Time-Dependent Turbidity Measurements

Steps 7-9 of the recommended settling procedure do not provide specific criteria for desired settling times or fluid clarity. Furthermore, while an apparently large portion of the sediment mass was observed to settle on the time scale of minutes, a significant portion appeared to be settling on a time scale of hours. Given the limited time available for this examination, an alternative method was applied using time-dependent turbidity measurements to characterize settling rates.

The large vial filled with solution and sediment was shaken and allowed to settle for 11 minutes as described above. A syringe was used to extract ~32 ml of solution (about half) from the homogeneous middle layer of the vial without disturbing the aggregate layers near the bottom. This volume was sufficient to fill a single small test vial for direct turbidity measurement. Upon thoroughly shaking the small vial, the measured turbidity exceeded the 200 NTU range of the instrument.

Approximately one half of the shaken contents of the small vial was poured into a second small vial and diluted with tap water. It was noted before shaking that the clean tap water

remained stratified above the suspension of sediment. Figure 9 shows the first dilution vial before and after shaking. The turbidity of clean tap water was measured to be 0.8 NTU. The turbidity of the diluted suspension still exceeded 200 NTU, so the dilution process was repeated a second time, and a third time before the turbidity could be successfully measured. At this point, suspended solids were only visible as a slight discoloration with an initial turbidity of 110 NTU as shown in Figure 10.

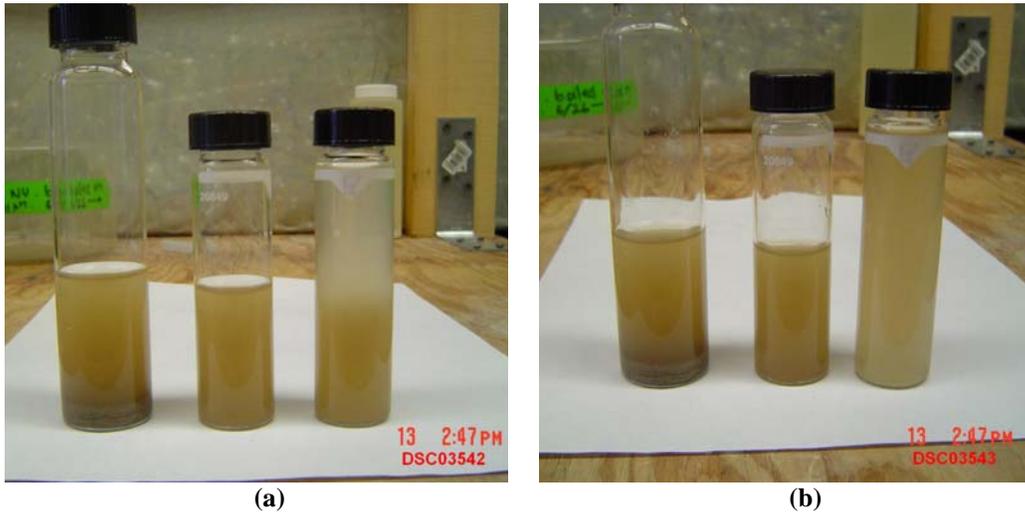


Figure 9. Dilution vial to the right before (a) and after (b) shaking.



Figure 10. Successive stages of dilution just prior to measuring turbidity. From left to right, the first two vials are original concentration followed by the first, second, and third dilution, respectively.

The time dependent turbidity of the successively diluted sample was monitored periodically for 60 minutes without removal from the turbidimeter, and again after 17 hours of settling. Figure 11 shows the test vials after approximately 40 minutes of settling time and Figure 12 shows the test vials again after approximately 17 hours. Material sufficient to cover the bottom of each vial was noted in every sample. The depth of debris in the original large vial after settling overnight was measured to be 7.94 mm in a water column of 8.10 cm in height. The turbidity of the last diluted sample had decreased to 17.6 NTU. Time dependent turbidity data are tabulated in Table 1 and illustrated in Figure 13.

At the conclusion of this examination, the contents of the first small turbidity vial (undiluted) was returned to the large sample vial and archived as requested. The mass fractions present in the remaining vials were not determined, but are judged to be small. This information could be recovered at any time by filtering, drying, and weighing the contents of the large vial to compare the initial mass introduced to the mass recovered after the tests.

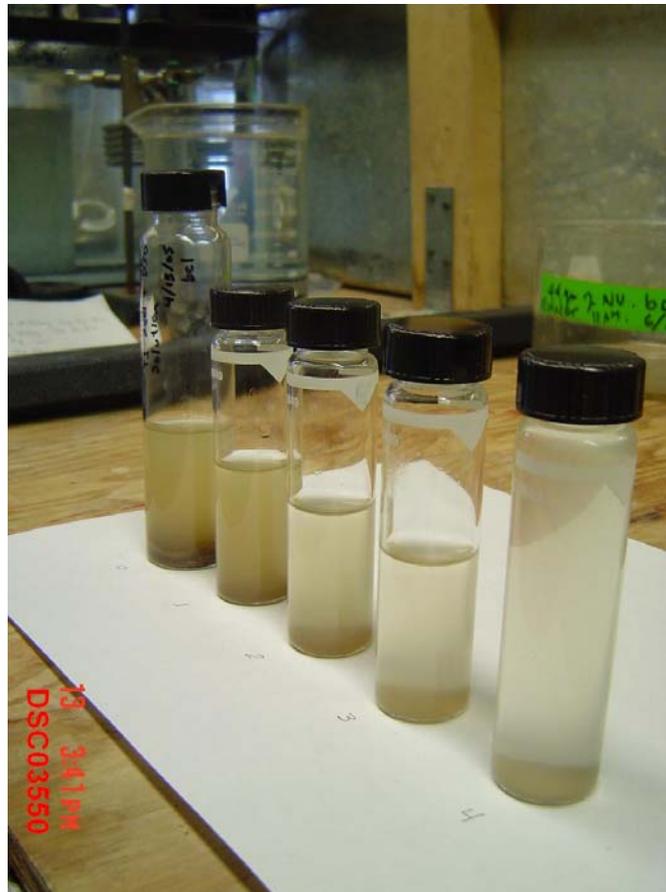


Figure 11. Sediment vials after successive dilution and 40 minutes of settling.



Figure 12. Sediment vials after successive dilution and approximately 17 hours of settling.

Table 1. Time-dependent turbidity data for settling of T1 sediment.

Time (minutes)	Turbidity (NTU)
0	110
2.5	105
5	103
11	100
17	95
35	79
40	77

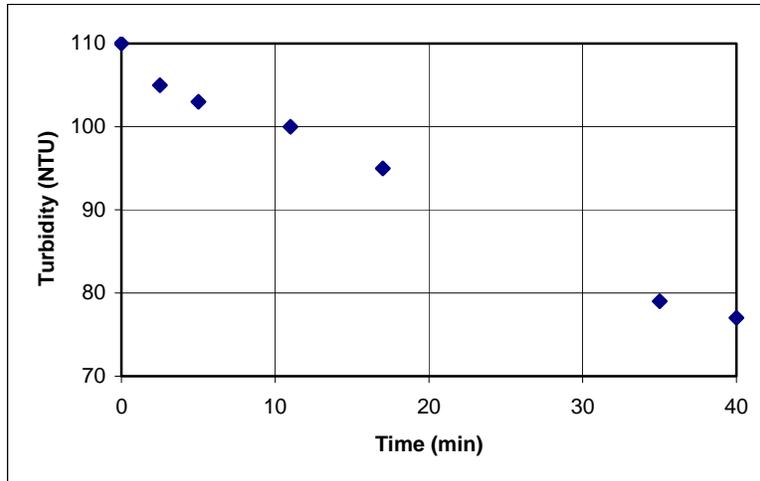


Figure 13. Time-dependent settling behavior of T1 sediment as indicated by turbidity measurements.

3 Sediment Images, EDS Composition, and Quantities

Each ICET test is initiated with a background loading of latent debris composed of crushed concrete and dirt. In both T1 and T2, this material was observed to settle completely on the floor of the tank over the course of several days. This particulate in combination with fugitive fiberglass strands form the basic substrate of the sediment layer recovered from the tank at the end of each test. In addition, this bed may serve as a repository for chemical products that are either formed in the bed or deposited on top via settling over the course of the tests. Among all the sample types collected during the ICET tests, tank sediment is the most heterogeneous in terms of both physical configuration and elemental composition. After draining the tank and manually recovering the sediment, 339 g were collected following T1 and 302 g were collected following T2. These are total masses as measured when thoroughly drained by gravity of free water, but while still moist.

Figure 14 illustrates the complexity of sediment collected from T1. This view suggests that a significant amount of fiberglass is present in the debris. Qualitative visual estimates of the fiber fraction might range from 60 to 75% fiber by volume. Note that visual assessments can only compare the volume ratios and not the mass ratios. The fiber present at the bottom of the ICET tank represents fiberglass that has escaped the stainless steel mesh bags that were constructed to hold the primary volume of this debris type. In the containment pool, the fiber to particulate ratios might vary greatly by location and may not resemble the ratios suggested by this image.

Figure 15 through Figure 17 present a set of increasing magnification images that successively focus on a clump of particulate material. This set of images highlights the wide range of particle sizes present in the ICET sediment layer ranging from 30 μm down to submicron particles attached to individual fibers. The close up provided in Figure 17 suggests that some of the larger observed particles may, in fact, be agglomerates of smaller constituents.

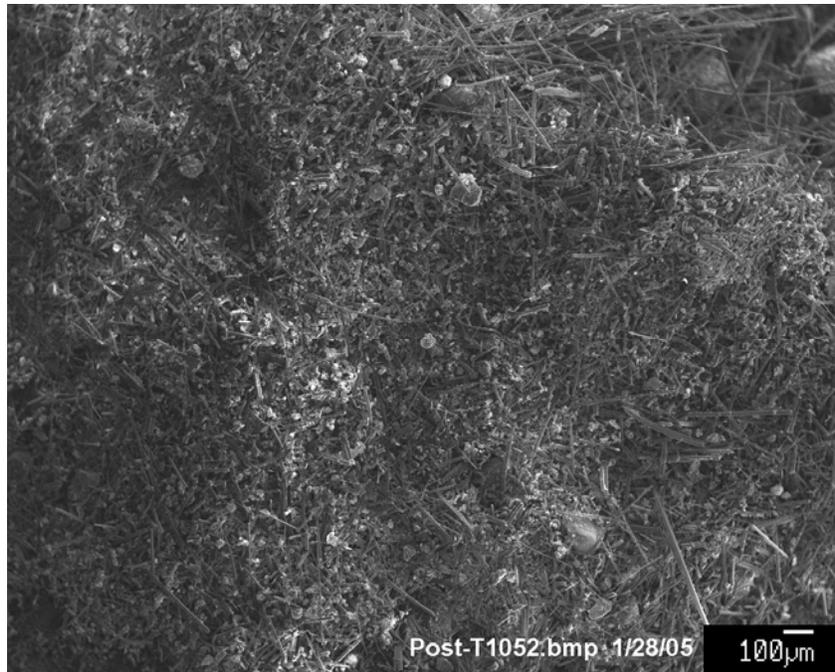


Figure 14. T1D30 tank sediment magnified 43 times showing combination of fiber and particulate.

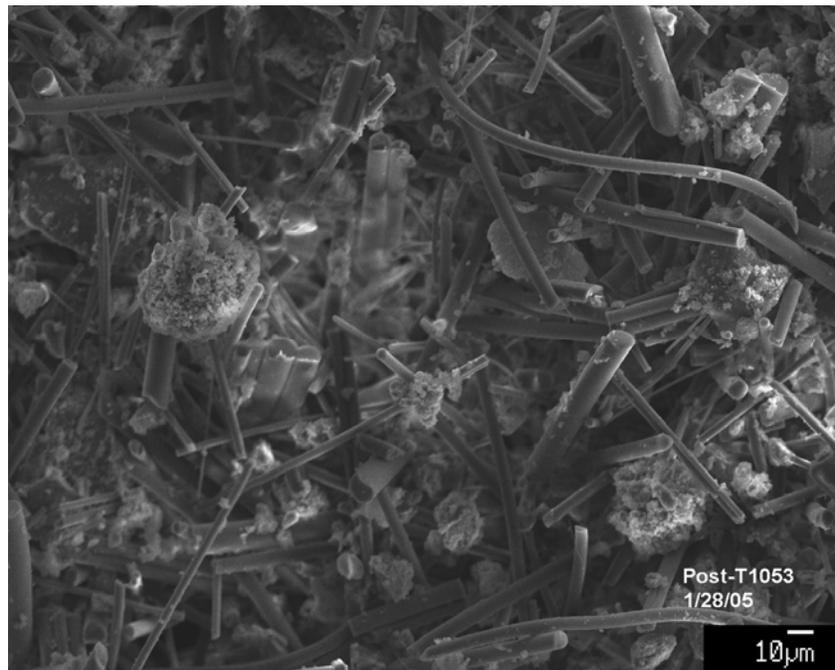


Figure 15. T1D30 tank sediment magnified 370 times focused on two large particles in Figure 14.

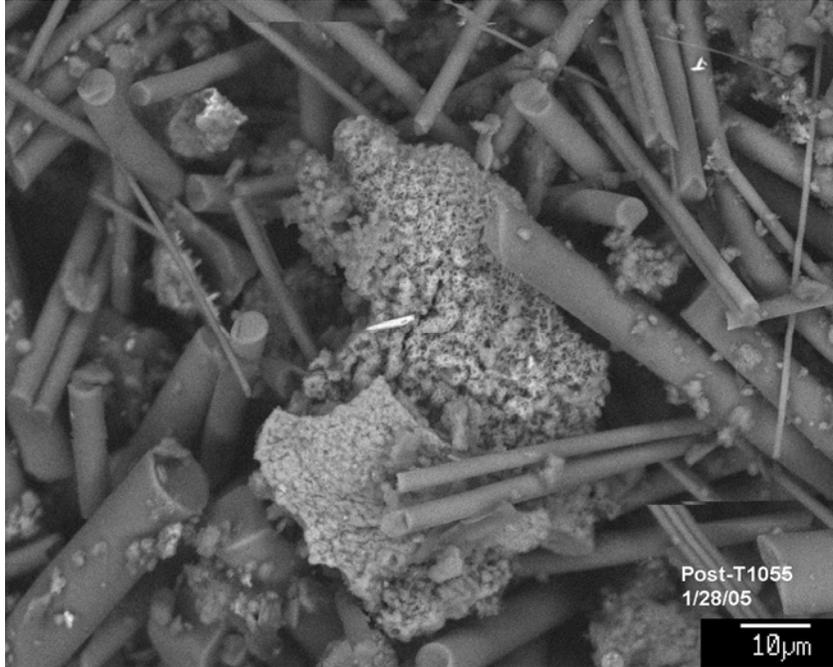


Figure 16. T1D30 sediment magnified 1000 times on a typical fuzzy particle as shown in Figure 15.

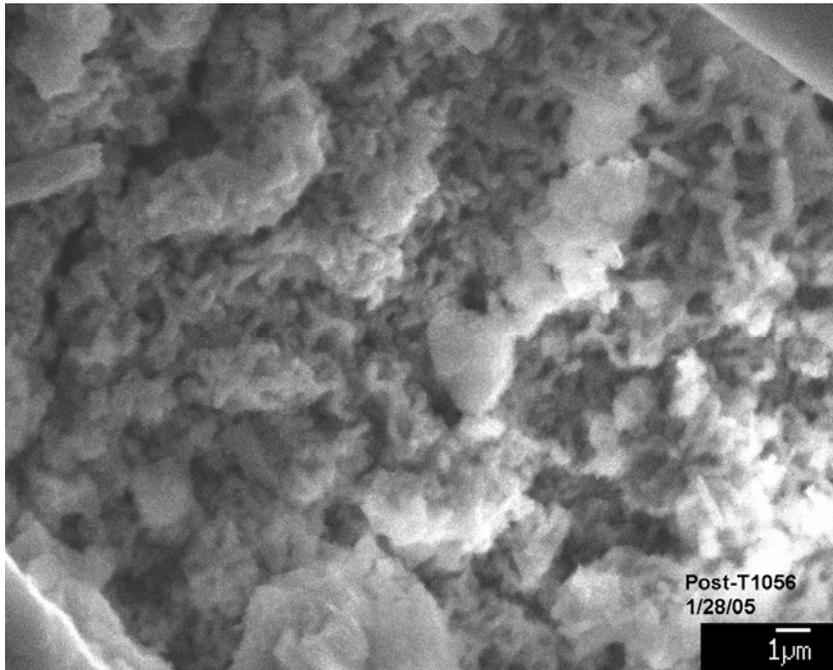


Figure 17. T1D30 sediment magnified 5000 times on the particle shown in Figure 16.

Figure 18 and Figure 19 illustrate the variety of elemental compositions observed in the tank sediment. Note that a sputter coating of gold (Au) and palladium (Pd) is applied during SEM sample preparation, so these elements are always present in the spectrum. Given the presence of crushed concrete aggregate and common dirt present in the tank, it is not surprising to find a wide variety of mineral constituents.

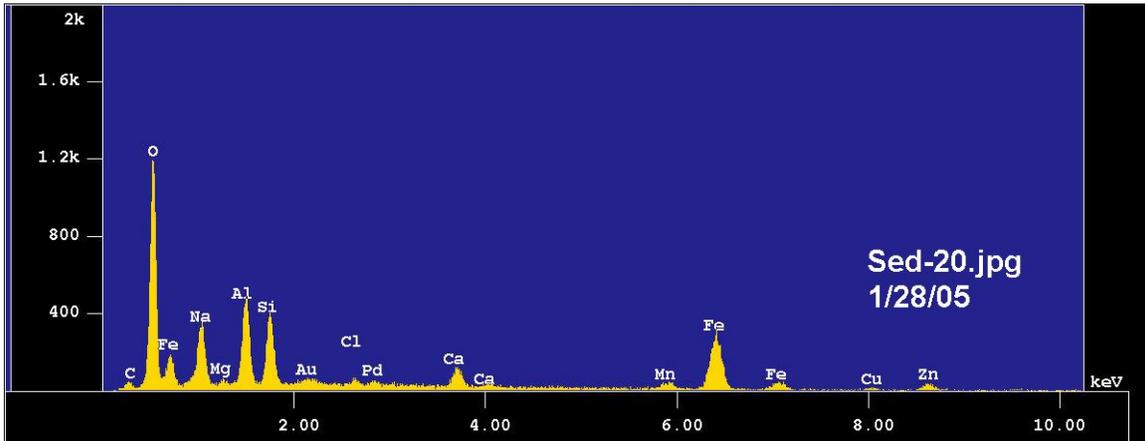


Figure 18. EDS spectrum for the particle shown in Figure 17.

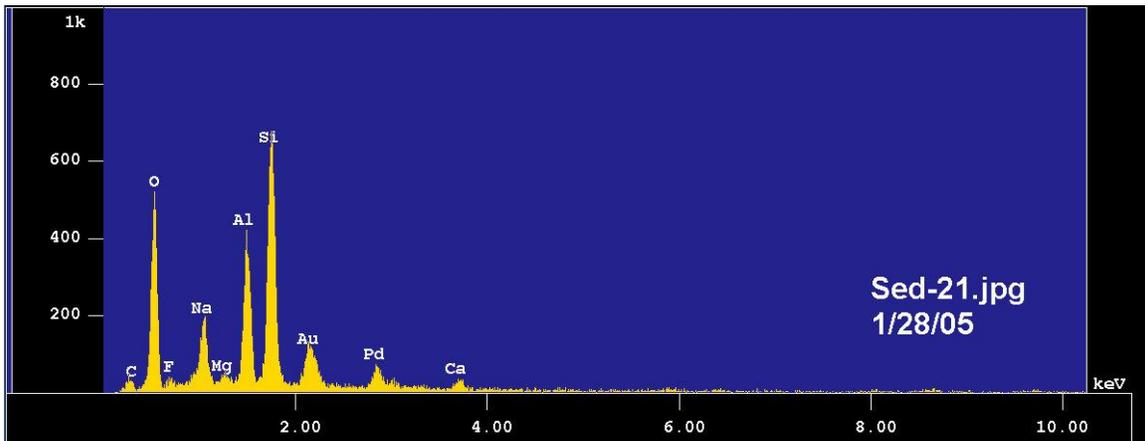


Figure 19. EDS spectrum for another representative particle present in T1D30 tank sediment.

Figure 20 illustrates another typical T1 sediment sample containing minerals like quartz and possible chemical products. Points EDS-23 and EDS-24 marked in the figure exhibit dominant proportions of oxygen, sodium, silicon and aluminum consistent with the composition of white precipitant observed in T1 water samples when cooled (see Figure 21). It is impossible to determine whether these flakes originated in the sediment bed or were dislodged from other surfaces while draining the tank.



Figure 20. T1D30 tank sediment magnified 40 times showing the presence of fiber, minerals (quartz) and possibly chemical products (EDS-23 and EDS-24).

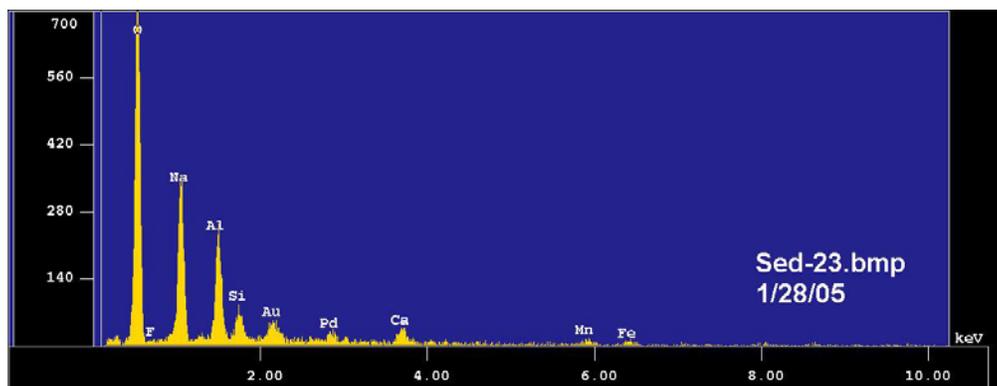


Figure 21. EDS spectrum of point EDS-23 shown in Figure 20 containing oxygen, sodium, aluminum and silicon ratios similar to T1 precipitant.

Figure 22 and Figure 23 present a pair of sediment image and EDS spectrum from T2. The sediment debris is qualitatively much different from that observed in T1. Either there is much less fiber present in this bed, or the fiber has been obscured by a layer of chemical product. There may, in fact, be less fiber because there was significantly less agitation of the submerged sample rack when loading the T2 assembly. Regardless of the absolute quantities that may be present, it is impossible to estimate from these figures alone the relative proportions of fiberglass and other material in the T2 sediment bed. Identical quantities of latent debris were added to this test, and yet the variety of elemental mineral constituents is not contributing greatly to the spectrum. The presence of phosphorus in this spectrum is consistent with the pH buffer of trisodium phosphate (TSP) that was used for T2.

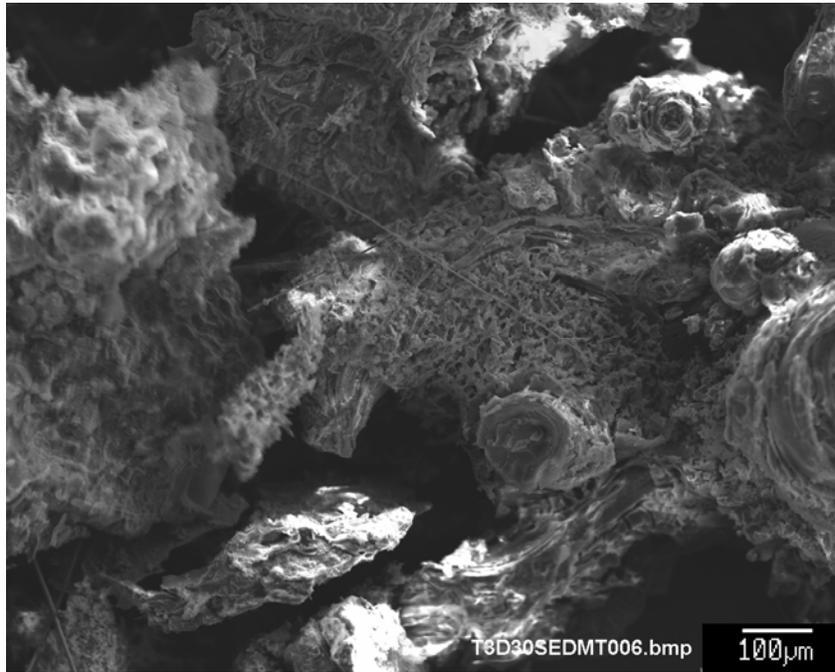


Figure 22. SEM image for a Test 2 Day-30 sediment sample.

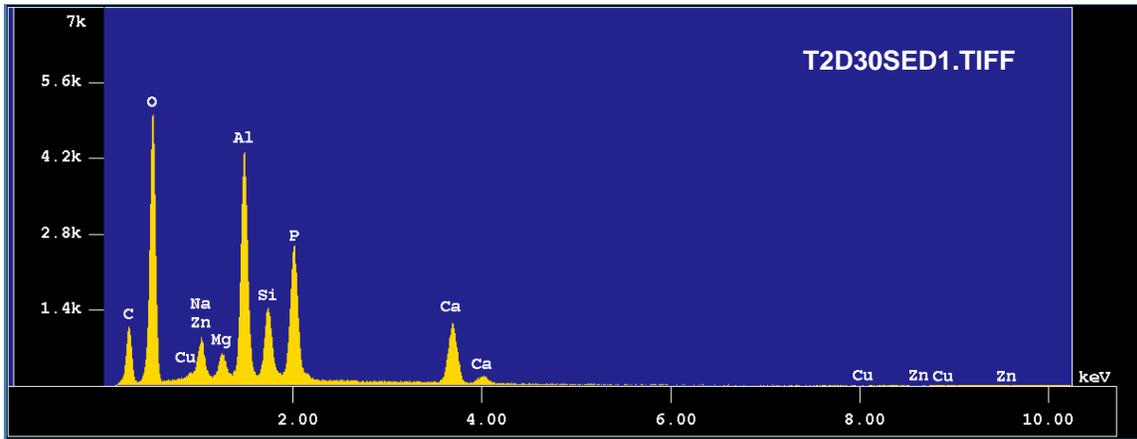


Figure 23. EDS counting spectrum for the circularly layered material near the right edge of Fig. 22.

Figure 24 and Figure 25 provide a higher magnification and an additional EDS spectrum of the same T2 sediment shown in Figure 22. Underlying fibers are visible in this image, and the dominant elemental constituents are similar, but the proportions are somewhat different. At this magnification, the spongiform deposits are clearly foreign from the particulate and fibrous debris that was initially introduced to the tank. Structures of this form also permeate the fiberglass samples that have been examined for T2.

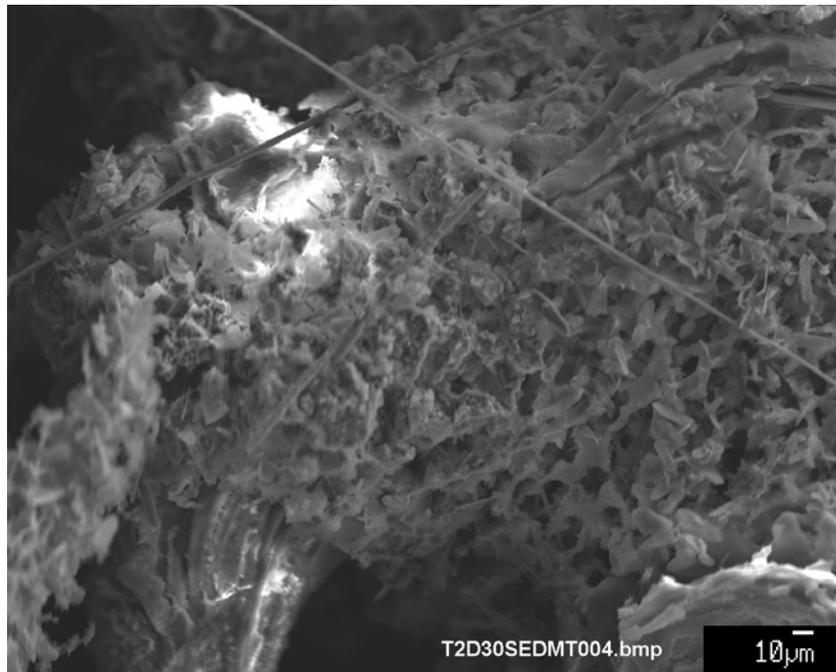


Figure 24. SEM image for a Test 2 Day-30 sediment sample with a higher magnification.

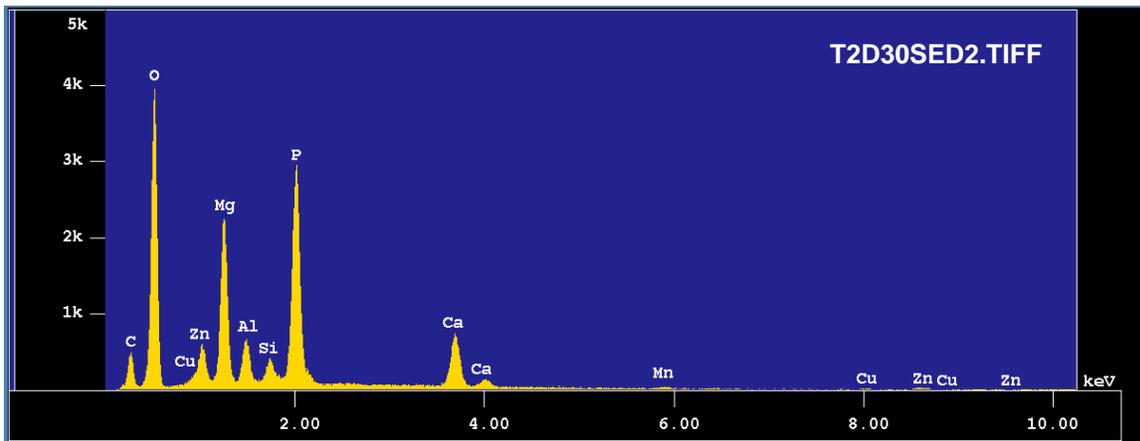


Figure 25. EDS counting spectrum for the porous structured material shown in Figure 24.

4 Elemental Composition of T1 Precipitant

The most physically homogeneous samples extracted from the ICET experiment are those of the white chemical products formed in T1 solution upon cooling. This material is generically referred to as a “precipitant,” but the exact physical formation mechanism has not been confirmed. Though consistent in appearance with a chemical flocculent formed via precipitation, the white material may also be formed by aggregation of smaller particles that are not visible at the test temperature or by nucleation upon small particles of other compounds that reside in solution at the test temperature.

The elemental composition of this material has been investigated by EDS, x-ray fluorescence (XRF), and inductively coupled plasma (ICP) spectroscopy. Substantial variability in measured elemental concentrations is observed between samples analyzed with the same method and between diagnostic methods applied to the same sample. A survey of these measurements was performed to recommend suitably averaged mass proportions for the dominant constituents that are observed (see Table 2). This estimate of composition is based largely on EDS results for precipitate collected during high-volume filtration and not from the daily water samples because there were more independent samples and more self-consistent proportions from this diagnostic than from any of the other methods individually. Mass percentages that have been confirmed by independent methods are noted in the table.

Table 2. Elemental composition (mass %) of T1D30 high-volume precipitant based on EDS analyses.

Element	Mass %
O	~46
Al	~11*
Ca	~1**
Na	~20**
B	~20***
Other	~2
* Confirmed by ICP and XRF	
** Confirmed by XRF	
*** Confirmed by ICP	

High-magnification electron micrographs of the precipitant reveal that while the material may have a characteristic size for agglomeration or clumping (see Figure 26), it may in fact be composed of much smaller elements that are loosely aggregated in networks or chains (see Figure 27). It is unlikely that this material will behave in the same manner as more familiar particulates like iron oxide and silica-based soil with respect to its inherent head-loss properties, and it would be difficult to estimate these properties based on geometric approximations based on particle size.

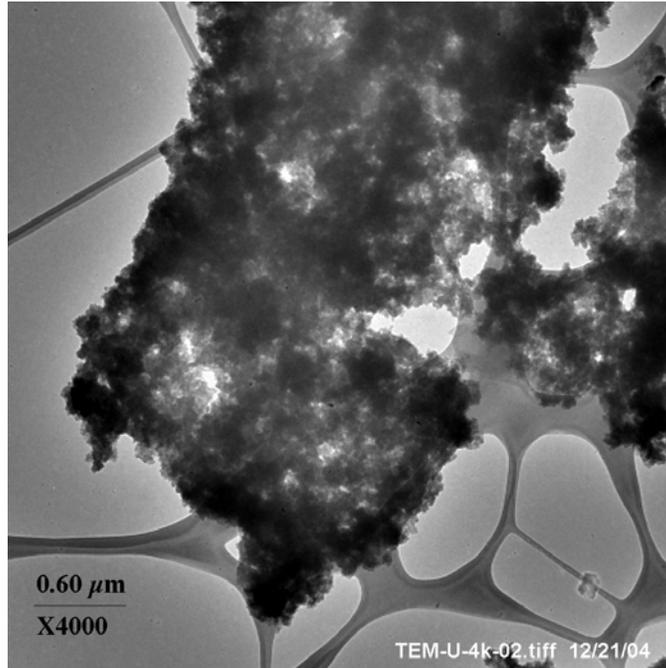


Figure 26. T1 precipitant observed at a magnification of x4000. The scale bar in this image is 0.6 μm in length.

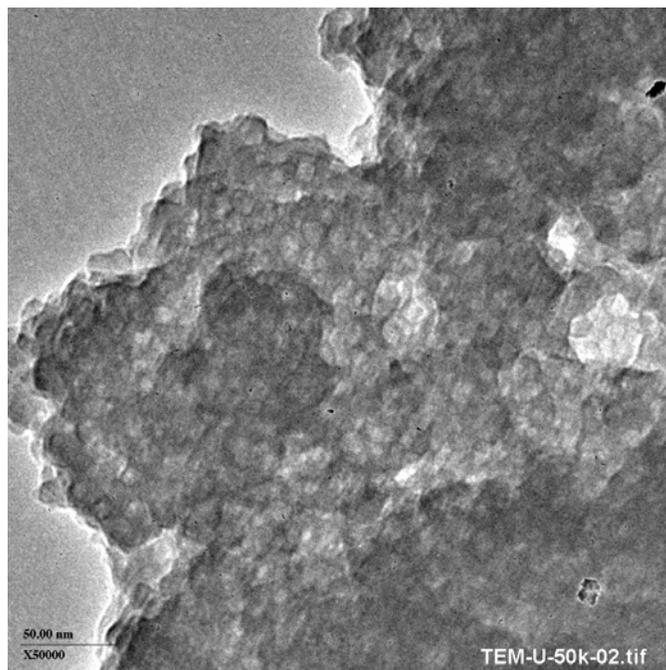


Figure 27. T1 precipitant observed at a magnification of x50,000. The scale bar in this image is 50 nm in length.

5 Deposits in Fiberglass

One of the more unexpected chemical products observed in the ICET series that deserves further consideration is the formation of deposits inside of the fiberglass debris samples. The fiberglass debris is encased in stainless steel mesh bags to minimize migration throughout the tank. Small mesh envelopes approximately 4-inch square containing approximately 5 g of fiber are pulled out of the tank periodically for SEM examination. These sample envelopes are placed in a range of water flow conditions, but none have direct water flow through the fiber. All are thoroughly immersed in the test solution until they are recovered from the tank. Figure 28 illustrates the appearance of clean fiberglass before exposure to the chemical environment. After exposure for some period of time, deposits are formed throughout the fiber matrix that appear to be of chemical origin. In general, the deposits appear to develop more completely with time and to be present throughout the fiberglass medium. Figure 29 and Figure 30 show deposits observed in desiccated T1 fiber samples at Day 15 and Day 30, respectively. Figure 31 and Figure 32 illustrate deposits observed in T2 fiber samples at Day 4 and Day 30, respectively. The deposits observed in both tests appear to be capable of changing the head-loss characteristics of a fiber bed, if they can actually form under flow. Additional work is ongoing to characterize the chemical composition of these deposits.

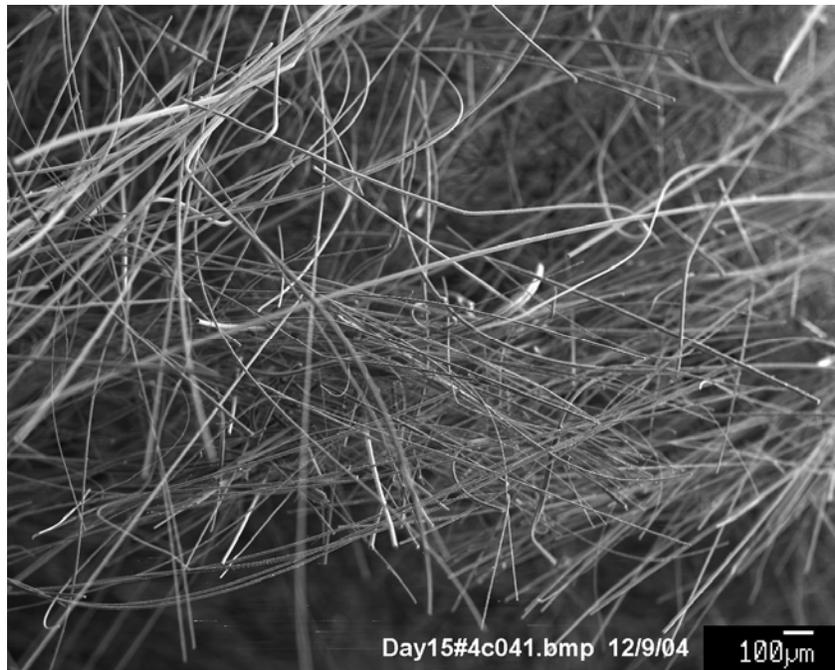


Figure 28. Clean fiberglass before exposure to test chemicals.

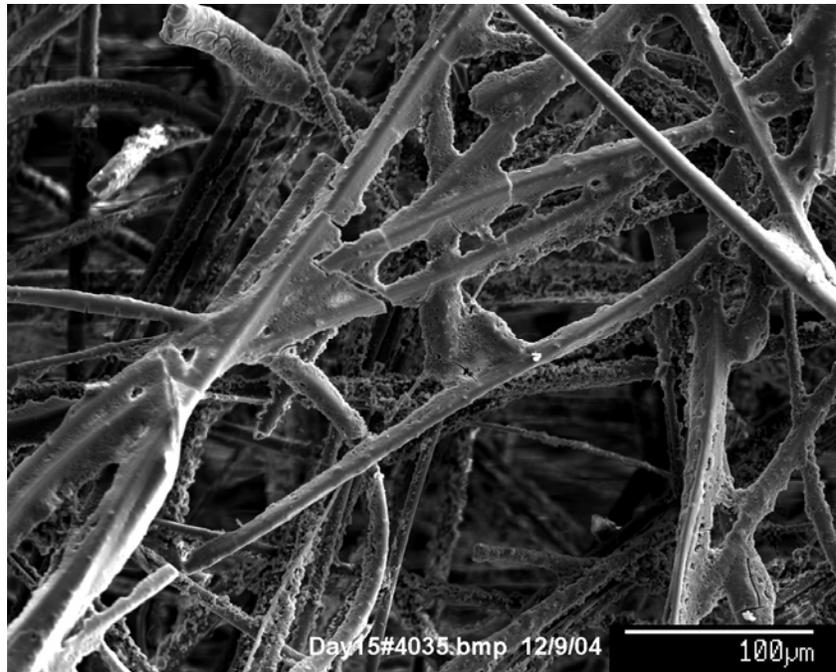


Figure 29. T1D15 deposits on surface of desiccated fiberglass sample.

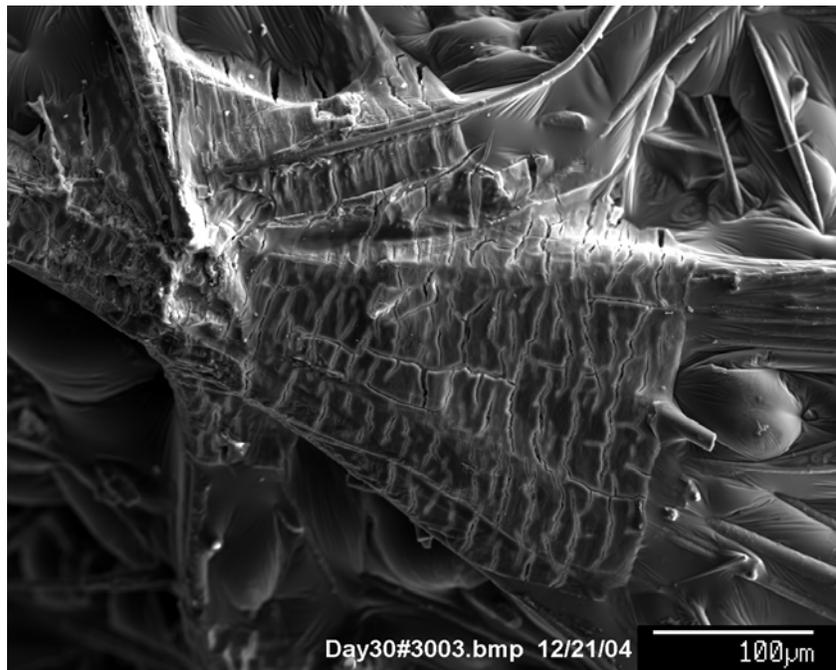


Figure 30. T1D30 deposits on surface of desiccated fiberglass sample.

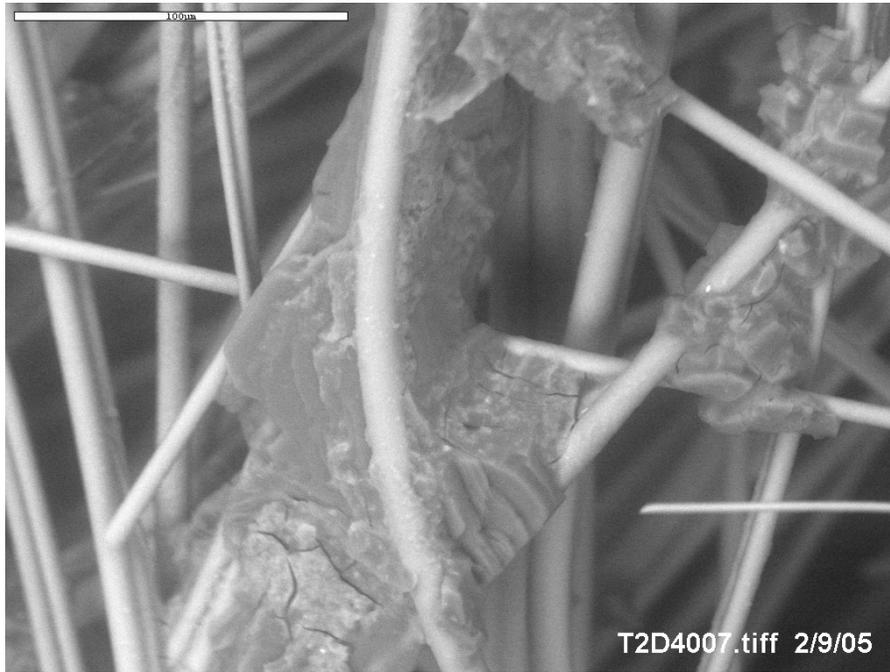


Figure 31. T2D4 deposits in hydrated fiberglass.

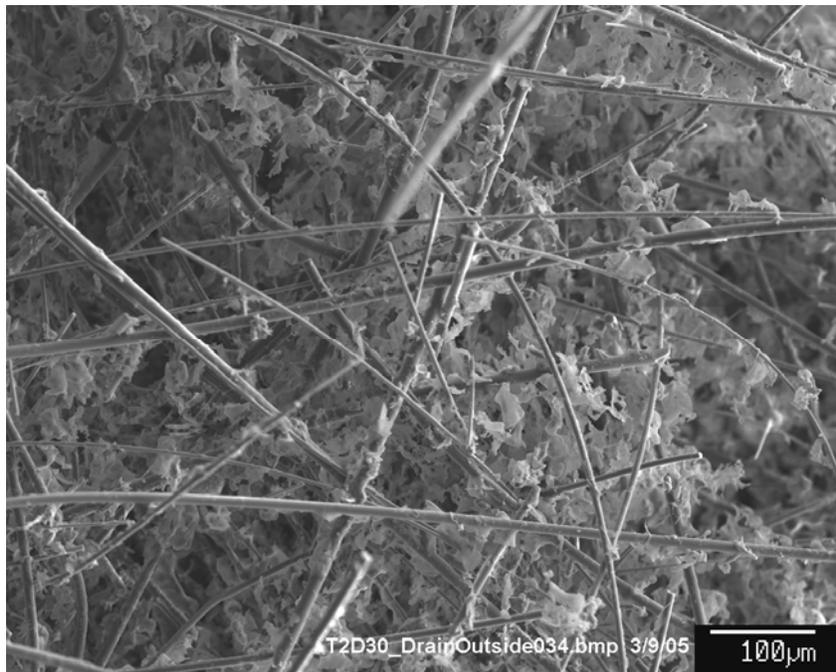


Figure 32. T2D30 deposits in hydrated fiberglass.