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Engineering-Scale Demonstration of DuraLith and Ceramicrete® Waste Forms

GB Josephson
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September 2011

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Abstract

To support the selection of a waste form for the liquid secondary wastes from the Hanford Waste Immobilization and Treatment Plant, Washington River Protection Solutions (WRPS) has initiated secondary waste form testing on four candidate waste forms. Two of the candidate waste forms have not been developed to scale as the more mature waste forms. This work describes engineering-scale demonstrations conducted on Ceramicrete and DuraLith candidate waste forms.

Both candidate waste forms were successfully demonstrated at an engineering scale. A preliminary conceptual design could be prepared for full-scale production of the candidate waste forms. However, both waste forms are still too immature to support a detailed design. Formulations for each candidate waste form need to be developed so that the material has a longer working time after mixing the liquid and solid constituents together. Formulations optimized based on previous lab studies did not have sufficient working time to support large-scale testing. The engineering-scale testing was successfully completed using modified formulations. Further lab development and parametric studies are needed to optimize formulations with adequate working time and assess the effects of changes in raw materials and process parameters on the final product performance. Studies on effects of mixing intensity on the initial set time of the waste forms are also needed.

Summary

The Hanford Site in southeast Washington State has 56 million gallons of radioactive and chemically hazardous wastes stored in 177 underground tanks (DOE 2010). The U.S. Department of Energy (DOE), Office of River Protection, through its contractors, is constructing the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to convert the radioactive and hazardous wastes into stable glass waste forms for disposal. Within the WTP, the pretreatment facility will receive the retrieved waste from the tank farms and separate it into two treated process streams. These waste streams will be vitrified, and the resulting waste canisters will be sent to offsite (high-level waste [HLW]) and onsite (immobilized low-activity waste [ILAW]) repositories. As part of the pretreatment and ILAW processing, liquid secondary wastes will be generated that will be transferred to the Effluent Treatment Facility (ETF) on the Hanford Site for further treatment. These liquid secondary wastes will be converted to stable solid waste forms that will be disposed in the Integrated Disposal Facility (IDF).

To support the selection of a waste form for the liquid secondary wastes from WTP, Washington River Protection Solutions (WRPS) has initiated secondary-waste-form testing work at Pacific Northwest National Laboratory (PNNL). In anticipation of a down-selection process for a waste form for the Solidification Treatment Unit to be added to the ETF, PNNL is conducting tests on four candidate waste forms for stabilizing and solidifying WTP liquid secondary wastes:

- Cast Stone Portland-cement-based waste form
- Ceramicrete phosphate-bonded ceramic
- DuraLith alkali-aluminosilicate geopolymer, and
- Fluidized Bed Steam Reformer (FBSR) granular product encapsulated within a geopolymer waste form.

Of these candidate waste forms, the Ceramicrete and DuraLith have been developed at the laboratory scale while the Cast Stone and FBSR waste forms have been demonstrated at the engineering to pilot scales. An engineering-scale demonstration of the Ceramicrete and DuraLith waste forms was therefore conducted to gain some knowledge of the scale-up and processing issues associated with the two waste forms prior to any waste form down-selection process.

The objectives of the engineering-scale demonstrations were to evaluate 1) the mixing steps in which the dry materials and liquid wastes are blended, 2) the pourability of the resulting slurry, 3) heat generation during curing, 4) voids and layering in the final product, and 5) any residual free liquids.

The engineering-scale testing focused on the final dry-solids/liquid-waste blending and container-filling steps of the Ceramicrete and DuraLith flowsheets. Because both waste form flowsheet concepts identified ribbon mixers for the solids/liquid blending, a ribbon mixer was selected for the engineering-scale tests. A hydraulic turbine, in-drum mixer was also used with the DuraLith waste form. The waste simulants were prepared in polyethylene tanks with in-tank mechanical agitators. The dry materials were pre-blended in the ribbon mixer and were stored in 55-gallon drums. During the mixing demonstrations, the simulants were transferred manually and the dry solids were added to the ribbon mixer via a conveyor belt. The final waste form containers included polyethylene 55-gallon drums and 2' high × 2' wide × 3' long steel boxes. The drums and boxes were filled through a bottom drain in the ribbon mixer.

A baseline secondary waste simulant used in the laboratory-scale testing, but without minor constituents such as iodine, technetium, and the heavy metals specified in the Resource Conservation and

Recovery Act, was used in the engineering-scale tests. Based on laboratory-scale optimization work, the Ceramicrete demonstrations used a 1 M sodium simulant and the DuraLith demonstrations used a 6 M sodium simulant. Demonstrations were planned with the nominal simulant loading and with high and low solids loadings to investigate possible process variability.

Before the engineering-scale demonstrations, bucket-scale tests were conducted with each waste form. Through these bucket tests, the potential for early setting of each waste form was identified. Formulation adjustments were made to both the Ceramicrete and DuraLith dry materials blends to prolong the workability time for the engineering-scale tests.

The low-shear batch ribbon mixer was inadequate to achieve good mixing of the dry solids and the waste simulant as indicated by dry materials caking on the mixer shaft and unreacted lumps in the freshly poured batches. The in-drum turbine mixer provided some improvement over the ribbon mixer in the DuraLith test but alternatives need to be identified and tested.

Both the Ceramicrete and DuraLith readily flowed when poured from the ribbon mixer, easily filling the drums (Ceramicrete and DuraLith) and boxes (Ceramicrete).

The cured waste forms were generally homogeneous from top to bottom of the drums characterized. Densities were consistent among cores taken from the top, middle and bottom of each drum. There were some small pockets of unreacted materials. The low-solids (higher water content) DuraLith drum did show some segregation of granular material at the bottom of the drum that was not observed in the high-solids drum. A soft friable layer was observed on the top of one of the Ceramicrete boxes.

One Ceramicrete and one DuraLith drum were instrumented with thermocouples to measure the temperature profile during curing. The Ceramicrete maximum temperature of 84.7°C was reached approximately 8 hours after filling the drum. The DuraLith maximum temperature of 59.5°C was reached approximately 20 hours after filling the drum.

Free liquids were observed in the closed Ceramicrete containers a day after the drum and box were poured. This is most likely condensate from the elevated temperatures as the Ceramicrete cured. Any residual water evaporated once the containers were opened, leaving residual salts.

Cores taken from the Ceramicrete and DuraLith drums were characterized with respect to waste form properties. Compressive strengths easily met the minimum 3.45 MPa (500 psi) target. Sodium diffusivities were less than the maximum, 1×10^{-6} cm^2/s. Densities were consistent from top to bottom and were less than those measured for laboratory-scale specimens. The mineralogy of the waste forms from the engineering-scale demonstration was consistent with that from the laboratory-scale specimens.

The engineering-scale tests demonstrate that both the Ceramicrete and DuraLith processes can be conducted at above laboratory scale. Additional work is needed on both the waste form formulations and the engineering processes to provide consistently good waste forms on a production scale. The formulations must be adjusted to improve the working time for mixing the dry materials and aqueous wastes and pouring into the waste containers. Adjustments in formulation will require additional characterization with respect to waste form properties and performance characteristics. Other dry solids/liquids mixing technologies need to be evaluated to improve the time and extent of mixing. Curing conditions for each waste form need to be defined with respect to humidity, temperature, and container size for implementation on a production basis.

The engineering-scale tests were conducted by MSE Technology Applications, Inc. of Butte, Montana, under the direction of PNNL.

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Acronyms and Abbreviations

ANL	Argonne National Laboratory
ASTM	American Society for Testing and Materials
BFS	blast-furnace slag
EDS	energy dispersive X-ray spectroscopy
EPA	Environmental Protection Agency
ETF	Effluent Treatment Facility
FA	fly ash
FBSR	fluidized bed steam reformer
HLW	high-level waste
HSW	Hanford secondary waste
IDF	Integrated Disposal Facility
IHLW	immobilized high-level waste
ILAW	immobilized low-activity waste
LI	leachability index
MSE	MSE Technology Applications, Inc.
PNNL	Pacific Northwest National Laboratory
RCRA	Resource Conservation and Recovery Act
SEM	scanning electron microscopy
STU	Solidification Treatment Unit
TCLP	Toxicity Characteristic Leaching Procedure
VSL	Vitreous State Laboratory at the Catholic University of America
WRPS	Washington River Protection Solutions
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XRD	X-ray Diffraction

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1.0 Background

At the Hanford Site in southeast Washington State, over 55 million gallons (Rodgers 2011) of radioactive and chemically hazardous wastes are stored in 177 underground tanks. The U.S. Department of Energy, Office of River Protection, through its contractors, is constructing the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to convert the radioactive and hazardous wastes into stable glass waste forms for disposal. Within the WTP, the pretreatment facility will receive the retrieved waste from the tank farms and separate it into two treated process streams. The pretreated high-level waste (HLW) mixture will be sent to the HLW Vitrification Facility, and the pretreated low-activity waste (LAW) stream will be sent to the LAW Vitrification Facility. The two WTP vitrification facilities will convert these process streams into glass, which will be poured directly into stainless steel canisters. The canisters of immobilized HLW (IHLW) will ultimately be disposed of at an offsite federal repository. The canisters of immobilized LAW (ILAW) will be disposed of onsite in the Integrated Disposal Facility (IDF).

In addition to the primary IHLW and ILAW glass waste forms, the processing of the tank wastes will generate secondary wastes, including routine solid wastes and liquid process effluents. Liquid wastes may include process condensates and scrubber/off gas treatment liquids from the thermal waste treatment processes. The liquid-effluent secondary wastes will be sent to the Effluent Treatment Facility (ETF) for further treatment and solidification before disposal at the IDF.

The ETF is a Resource Conservation and Recovery Act (RCRA) permitted multi-waste treatment and storage unit that can accept dangerous, low-level, and mixed wastewaters for treatment. The ETF receives, treats, and disposes of liquid effluents from cleanup projects on the Hanford Site. Plans are to increase the capacity of ETF to process the increased volume of secondary wastes when the WTP begins waste treatment and immobilization operations. A Solidification Treatment Unit (STU) will be added to the ETF to provide the needed additional capacity.

Washington River Protection Solutions (WRPS) has been chartered to move forward with the design and construction of the STU for ETF. The ETF upgrades need to be operational by 2018 to receive secondary liquid wastes from the WTP. The schedule of activities includes beginning conceptual design in September 2011, pending DOE approval. There will be a formal decision on the waste form for the secondary liquid wastes including agreement with the Washington State Department of Ecology (Ecology) by 2012.

The current baseline calls for solidification of the ETF evaporator concentrate in a cement-based waste form. However, alternative secondary waste forms are being considered. In 2006, Pacific Northwest National Laboratory (PNNL) completed for DOE an evaluation of three low-temperature technologies for the immobilization of mixed radioactive and hazardous waste. That testing program showed that DuraLith (alkali-aluminosilicate geopolymer) and Ceramicrete® (phosphate-bonded ceramic) showed potential as a waste form for the liquid secondary waste stream from WTP based on Toxicity Characteristic Leaching Procedure (EPA 1999), compressive strength, and sodium leachability index requirements.

To support the selection of a waste form for the liquid secondary wastes from WTP, WRPS has initiated secondary waste form testing work at PNNL. In 2009, preliminary screening of waste forms was conducted to assess the viability of each for the solidification of the liquid secondary wastes. Additional testing conducted in 2010 further developed and optimized Cast Stone, DuraLith, and Ceramicrete for the projected liquid secondary waste compositions.

Wastes intended for disposal in IDF must meet requirements of DOE Order 435.1 (DOE 1999) and permit requirements established by the Washington State Department of Ecology (Ecology 2008). These requirements are captured in the waste acceptance criteria for IDF. Included are criteria with respect to free liquids, compliance with land disposal restrictions, compressive strength, and leachability. For the purposes of this work, the following requirements were applied:

- Free Liquids: The waste form shall contain no detectable free liquids as defined in the Environmental Protection Agency (EPA) SW-846 Method 9095 (EPA 2004).
- Leachability Index: The waste form shall have a sodium leachability index greater than 6.0 when tested in deionized water using the American National Standards Institute/American Nuclear Society method ANSI/ANS-16.1 (ANSI/ANS 2003) or EPA Method 1315 (EPA 2009). The waste form shall have a rhenium or technetium leachability index greater than 9.0.
- Compressive Strength: The compressive strength of the waste form shall be at least 3.54E6 Pa (500 psi) when tested in accordance with American Society for Testing and Materials (ASTM) C39/C39M (ASTM 2010).

In addition to these requirements, acceptance criteria for the IDF also included meeting the land disposal requirements in 40 CFR 268 (40 CFR 2010) by meeting the universal treatment standards in 40 CFR 268.48 via the TCLP test. Meeting TCLP standards has not been a problem for the candidate treatments; therefore it was not expected to be a discriminator for the down-selection. Including in the formulations the heavy metals specified in the Resource Conservation and Recovery Act (RCRA 1976) would add raw-material costs and significantly add to the cost of disposing material from the testing. Therefore, for this engineering-scale test RCRA metals were excluded and the TCLP criterion not imposed.

2.0 Introduction

The Hanford Tank Farm contractor, Washington River Protection Solutions (WRPS), is scheduled to make a preliminary down-selection of a secondary waste form to begin conceptual design of the Effluent Treatment Facility (ETF) upgrades for a supplemental treatment unit. The candidate waste forms under consideration are:

- Cast Stone
- Fluidized Bed Steam Reforming (FBSR) product
- DuraLith alkali-aluminosilicate geopolymer
- Ceramicrete phosphate-bonded ceramic.

WRPS is sponsoring testing to collect performance data on each of the waste forms to support the down-selection decision. Laboratory testing is being conducted on each of the waste forms to quantify the release of contaminants of concern and understand the fundamental chemistry to support long-term release predictions that are necessary for the performance assessment. Performance of the waste form is a key criterion for the down-selection. Additionally, the down-selection will consider operability of the processes to produce each of the waste forms. Among the candidate waste forms, DuraLith and Ceramicrete are less mature and do not have information available to assess their process operability at full-scale. The other two processes are more mature for assessing the operability at full-scale.

The Studsvik treatment facility in Erwin, TN utilizes a fluidized bed steam reforming process to immobilize radioactive waste and provides a basis for assessment of the operability of a full-scale system based on FBSR. Full-scale preliminary designs of the Cast Stone process have been prepared for Hanford and a similar process has been implemented for low-activity waste processing using the Saltstone process on the Savannah River site. These activities provide a basis to assess the operability of a full-scale Cast Stone process.

Neither Ceramicrete nor DuraLith have conducted operations at larger than laboratory scale. The primary development of the Ceramicrete waste form has been conducted at Argonne National Laboratory; and DuraLith has been developed at the Vitreous State Laboratory (VSL) at the Catholic University of America. The laboratory-scale development of both products has been funded by the U.S. Department of Energy (DOE), and Pacific Northwest National Laboratory (PNNL) has acted as an impartial intermediary, communicating site needs and performance objectives to the developers, testing the candidate products, and preparing data packages to support WRPS down-selection decisions.

Both developers have prepared initial conceptual designs for a full-scale facility to prepare their waste forms (Russell et al. 2006; Gong et al. 2006; Maloney et al. 2006). Their designs provided a basis for the planning of this engineering-scale test. Specifically, both design concepts included a “ribbon mixer” in the flow sheet to achieve the mixing of the liquid containing secondary waste and powdered waste formers. The full scale design concepts are more fully described in Appendix A.

2.1 Engineering-Scale Flowsheet

The engineering-scale testing documented here focused on the final dry-solids/liquid-waste blending and container-filling steps of the Ceramicrete and DuraLith flow sheets. Figure 2.1 shows the key components. Because both waste form flowsheet concepts identified ribbon mixers for the solids/liquid blending, a ribbon mixer was selected for the engineering-scale tests. A hydraulic turbine, in-drum mixer was available as a second option, and was used for the DuraLith wastes when the ribbon mixer proved inadequate to achieve full mixing. The waste simulants were prepared in polyethylene tanks with in-tank mechanical agitators. Simulant transfers from the tank to the ribbon mixer were done manually using 5-gallon buckets. The dry materials were pre-blended in the ribbon mixer and were stored in 55-gallon drums. During the mixing demonstrations, the dry solids were added to the ribbon mixer via a conveyor belt. The final waste form containers included polyethylene 55-gallon drums and 2' high × 2' wide × 3' long steel boxes. The drums and boxes were filled through a bottom drain in the ribbon mixer. A forklift and an overhead crane were used to move the tanks, drums, and boxes.

Figure 2.1. Ribbon Mixer, Simulant Tank, and Dry-Materials Conveyor Belt for Engineering-Scale Demonstration

Developers for both waste forms, Ceramicrete and DuraLith, are still optimizing their products. Each developer provided their “best current” formulation (recipe) for their waste form and provided instructions for make-up at a larger scale so that raw materials could be procured to prepare for the engineering-scale testing. It would have been better for both of the waste forms to have developed further at the laboratory scale, but the down-selection timetable for implementation at Hanford could not allow more time before information on scale-up was collected. The developers of Ceramicrete felt sufficiently strongly that their technology was not ready for the scale-up testing that they chose not to attend the test, although the principal investigator did provide valuable guidance to overcome issues as they were encountered. The developers of DuraLith attended the engineering-scale testing and their contributions were key to successfully demonstrating their product at engineering scale. The larger-scale testing also proved very valuable to the developers by demonstrating the key importance of the working time as a critical criterion in formulation development.

This report contains results of testing conducted at bucket scale (~5 gallon), drum scale (55 gal), and at a ½-dimensional engineering scale (1/8th volumetric scale). The results include observations of operability, issues that arose during the scaled testing, lessons learned for full-scale design and physical and performance data of the products. The information will support the waste form down-selection and provide input to the conceptual design should either Ceramicrete or DuraLith be selected.

PNNL contracted for the conduct of the engineering-scale testing through a competitive solicitation. MSE Technology Applications, Inc. (MSE) of Butte, Montana, was selected to conduct the scaled testing and prepare the scaled waste forms. Samples collected during the testing and core samples extracted from the final cured products were sent to PNNL for testing and characterization.

3.0 Objectives

Ceramicrete has been demonstrated on the drum scale and DuraLith has been demonstrated at the bench scale with a 6-inch by 12-inch cylinder. To support a final down-selection and put these two less mature waste forms on a more even basis with Cast Stone and FBSR, both materials were produced at an engineering scale using a process and equipment representative of that identified in the pre-conceptual designs for cement-like materials (Russell et al. 2006; Gong et al. 2006; Maloney et al. 2006). The engineering-scale test demonstrated:

- the mixing steps in which the dry materials and liquid wastes are blended,
- the pourability of the resulting slurry,
- heat generation during curing,
- voids and layering in the final product, and
- any residual free liquids.

During the execution of the testing at each scale, several tests were conducted that could provide a semi-quantitative measure of the processability of the material. The in-process tests were derived from more standardized tests developed for grouts and cements. However, because the materials behave differently, the results were often outside the bounds prescribed for the tests. The results cannot be compared quantitatively to standards. Nevertheless, the results are enlightening and useful to compare one process to another. The in-process tests were:

- **Initial Relative Consistency (based on ASTM C187 (ASTM 2011))**—This test used a Vicat test apparatus and was used to determine the relative consistency (“thickness”) of the blended slurry and how the consistency changed as the slurry set (“hardened”) with time. A weighted 10-mm plunger was allowed to settle into the material for 30 seconds. Tests were repeated as the material hardened until the plunger would penetrate less than 25 mm into the material. When the material got harder the 10 mm plunger was replaced with a 1-mm plunger to determine the “initial set”.
- **Initial Setting Time –** based on ASTM C191-08 (ASTM 2008)—This test used the same Vicat apparatus as the Relative Consistency test, but with a smaller diameter plunger. Testing was repeated until the 1-mm plunger would only make a small dent (<0.5 mm) in the surface of the hardened waste form. The material was then considered set or hardened.
- **50-Cent Rheometer Slump Test—**(developed for smaller samples by Pashias (1996); loosely related to ASTM C143/C143M (ASTM 2010a)—This test uses an open cylindrical sleeve, called the 50-Cent rheometer. The test cylinder mold was filled with the sample and then the cylinder was pulled away from the sample allowing the sample to slump. The change in height of the sample when the cylinder mold was pulled away from the sample is the slump height, which is a parameter used to measure the samples’ slumping behavior.
- **Working Time –** based on ASTM C308 (ASTM 2005)—This test was intended to determine how long the material would flow until it became too stiff. Approximately 25 grams of the sample material were placed on clean, dry, freezer paper and then the material was troweled across the paper. The test was to be repeated until the material began to curl behind the spreading trowel, which indicated the material no longer flowed and the working time was over. This test was eliminated

early because it was discovered that Ceramicrete was shear sensitive and the test itself made Ceramicrete flow and spread. Repeated testing kept the material "workable" while samples that were undisturbed had long since hardened.

The in-process rheology tests are more fully described in Appendix B.

The waste form products generated during testing at MSE were shipped to PNNL, where they were characterized with respect to their physical, chemical, and performance properties.

4.0 Summary of Tests

4.1 Simulant

The amount of secondary waste (with accompanying water) in the final immobilized waste form is a key processing variable for the full-scale plant. The Effluent Treatment Facility (ETF) is expected to have an evaporator and theoretically could produce a waste stream at the needed concentration to optimize operation of the plant. A waste form that can include more waste solids (has a high waste loading) and retain contaminants to meet all disposal requirements is preferred over a material that can only meet disposal requirements when the waste loading is low. Determining an optimum waste loading is one of the key optimization variables from the lab-scale testing. When the "best current" formulations were needed from the developers to support the engineering-scale testing, Ceramicrete and DuraLith were at different development stages with respect to determining an optimum waste loading. The "best current" formulation for Ceramicrete was based upon a simulant at a 1M Na concentration (Singh et al. 2011) and DuraLith was based upon a 6M Na concentration simulant (Gong et al. 2011). Simulants of both concentrations were prepared to support both materials. The simulant make ups are in Table 4.1.

Table 4.1. Simulant Recipes to Make 500 L

		1M Na^+		6M Na^+	
Component	Chemical Formula	Weight Percent	Weight	Weight Percent	Weight
Water	H_20	93.3	490.6 kg	67.0	428.0 kg
Aluminum Hydroxide	$Al(OH)_3$	0.70	3.66 kg	3.44	21.97 kg
Sodium Chloride	$NaCl$	0.125	657.5 g	0.62	3.94 kg
Sodium Carbonate	Na_2CO_3	0.23	1.21 kg	1.14	7.25 kg
Potassium Nitrate	KNO_3	0.006	29.42 g	0.03	176.5 g
Sodium Nitrate	$NaNO_3$	2.65	13.94 kg	13.1	86.63 kg
Sodium Nitrite	$NaNO_2$	0.079	414.0 g	0.39	2.49 kg
Sodium Hydroxide	$NaOH$	1.51	7.96 kg	7.48	47.76 kg
Monosodium Phosphate	$NaH_2PO_4 \cdot 2H_20$	0.102	535.8 g	0.503	3.22 kg
Sodium Silicate	Na_2SiO_3	0.022	114.7 g	0.108	688.4 g
Sodium Sulfate	Na_2SO_4	0.060	313.2 g	0.294	1.88 kg
Sodium Oxalate	$Na_2C_2O_4$	1.11	5.86 kg	5.50	35.13 kg
Oxalic Acid	$H_2C_2O_4 \cdot 2H_2O$	0.078	409.7 g	0.39	2.46 kg
Sodium Perrhenate	$NaReO_4$	0.00047	2.47 g	0.00233	14.80 g

4.2 Ceramicrete Testing

MSE conducted four bucket-scale tests, one 55-gallon drum test, and three 1/8th-scale box tests with Ceramicrete. Test numbers were assigned sequentially as the tests were conducted. Table 4.2 describes the Ceramicrete tests.

Table 4.2. Ceramicrete Tests

Test #	Scale	Description
1	4.5-gal bucket	5% higher water than baseline
2	4.5-gal bucket	Baseline water + 0.5 wt% boric acid
3	4.5-gal bucket	Baseline water
4	4.5-gal bucket	Baseline water + 0.25 wt% boric acid
5	55-gal. drum	Baseline water + 0.5 wt% boric acid, covered during initial 24-hr cure
6	1/8th-scale box	Baseline water + 0.5 wt% boric acid, not covered
7	4.5-gal bucket	High solids + 0.5 wt% boric acid
8	2' × 2' × 6' box	Baseline water + 0.5 wt% boric acid, covered during initial 24-hr cure
9	1/8th-scale box	5% higher solids + 0.5 wt% boric acid, not covered

4.2.1 Bucket-Scale Testing

The initial plan for the bucket-scale testing was to prepare the baseline recipe recommended by the developer and two variations that would represent normal process variability. The solids:water ratio was considered to have the most impact on the processability of the material, so recipes with 5% higher solids content and 5% higher water content were also planned to bracket the value. The recipe with higher solids content was expected to be more viscous, more difficult to mix, and to generate more heat, which could affect the workability of the material. The recipe with higher water (lower solids) was expected to be thinner, easier to mix, generate less heat, and possibly have poorer product performance.

For the bucket tests all of the solid materials (powdered) were pre-weighed and blended using the double-vortex mixer shown in Figure 4.1.

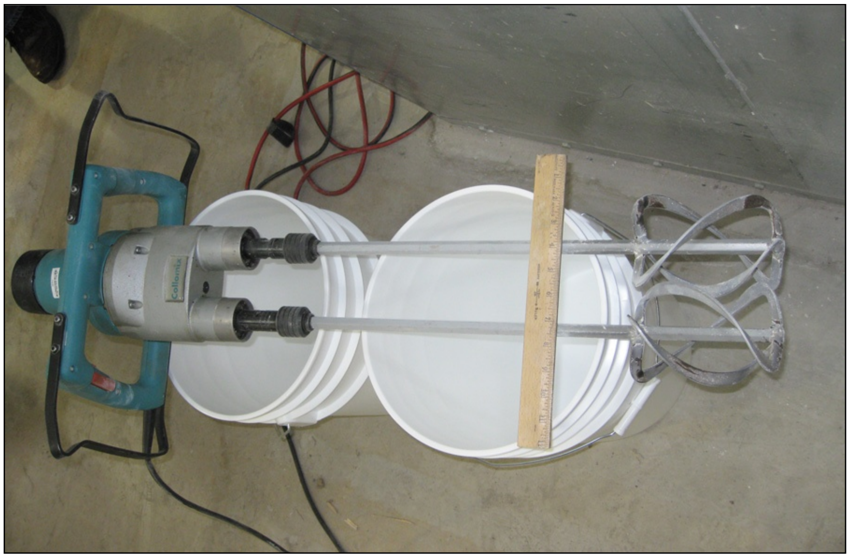

Figure 4.1. Double-Vortex Mixer Used to Blend Solids and Mix Bucket-Scale Samples

To prepare the waste-form test samples, all of the liquid materials were added to the test bucket; then, with the mixer operating, the blended solids were added to the liquid as fast as possible without accumulating dry solids on top of the mixing material. It usually took 4-5 minutes to add all of the solids. After the last solids were added the "mixing time" was started. For Ceramicrete, the samples were mixed for 20 min after the last solids were added or until the mixture heated to 40°C, whichever came first.

The make-up formulations and summary test results are shown in Table 4.3.

Table 4.3. Component Weights for the Ceramicrete 4.5-gal Bucket-Scale Samples (kg)

Component	Sample #1 High-Liquids 4.5-Gal	Sample #2 Baseline 4.5-Gal + 0.5%[a] Boric Acid	Sample #3 Baseline 4.5-Gal	Sample #4 Baseline 4.5-Gal + 0.25%[a] Boric Acid	Sample #7[b] High-Solids 4.5-Gal + 0.5%[a] Boric Acid
Test Makeups					
1-M Na^+ Simulant	7.01	6.68	6.68	6.68	6.42
MgO	3.25	3.25	3.25	3.25	3.28
KH_2PO_4	11.04	11.04	11.04	11.04	11.15
ASTM Class C Fly Ash	11.69	11.69	11.69	11.69	11.81
$SnCl_2 \cdot 2H_20$	0.51	0.51	0.51	--	0.51
Ground Zeolite™ 5A	0.37	0.37	0.37	0.37	0.37
Supplemental H_20	0.53	0.53	0.53	0.53	0.51
Boric Acid	--	0.134	--	0.067	0.135
Totals	**34.40**	**34.20**	**34.07**	**33.63**	**34.19**
Test Summary Results					
Mixing Time	20 min	20 min	20 min	20 min	20 min
Max. Temp. After Mixing	54°C @ 28 min	53°C @ 70 min	69°C @ 46 min	72°C @ 62 min	55°C @ 77 min
Time to Initial Set[b]	NA	NA	28 min	24 min	>200 min
Working Time Assessment	Too short	Adequate	Too short	Too short	Adequate

(a) Boric acid addition is wt% of formulation solids components, does not include weight of simulant or supplemental H_2O.

(b) Sample numbers are sequential as tests were conducted at MSE. This bucket-scale test was conducted after the drum-scale test (#5) and first 1/8th-scale box test (#6) to validate the high-solids formulation using boric acid.

By accident, the first bucket scale make-up had 5% higher water content and the material set (hardened) much more rapidly than expected. After all the solids were added, the slurry was mixed for 20 minutes. At the completion of mixing the slurry was very fluid, but within four minutes the slurry began to thicken. At 17 ½ minutes, the mold for the slump test was removed and there was no slump. There was insufficient working time to complete a large-scale mixing test. Therefore, modifications were made to prepare a formulation with more working time. Based upon phone discussions with the principal developer (Singh 2011), 0.5 wt% boric acid was added to the formulation to retard the setting time and give more working time for the larger-scale tests. The modification was successful in that an adequate working time was achieved to assure mixing at the larger scale and the material would not set too fast and set up in the mixer. The effect of the boric addition on the performance of the material was not evaluated before conducting the drum scale and 1/8th scale box tests. Significant lab work would be needed to determine the optimum method of retarding the Ceramicrete set time sufficiently to provide adequate working time for large scale operation.

4.2.1.1 Observations from Ceramicrete Bucket-Scale Tests

Ceramicrete is shear thinning. During the bucket scale testing, it was observed that the initial gelling or setting of the material could be reversed by shearing the material. That is, if material was mixed after it had initially started to “thicken,” the material would become more fluid and less viscous with mixing. Full implications of this shear-thinning behavior and effects on the final setting and material performance still need to be determined. However, for purposes of the testing the shear-thinning nature of the material added confidence that the larger-scale testing could be conducted without putting the large-scale equipment at risk of being filled with a solid mass of Ceramicrete. Keeping the slurry mixed should keep the material thin and workable for a long enough time to add the solids to the full-scale mixer even though it would take longer to do so at the larger scale.

Ceramicrete reactions are exothermic. As the bucket-scale test samples were setting, temperature was monitored and periodically recorded. As material set, the temperature increased and materials that set faster rose to higher temperatures. These observations are consistent with a mechanism of exothermic reactions that account for binding water, thereby removing water as a mobilizing fluid and causing the slurry to solidify. The relationship between slurry temperature and setting was carried forward to the drum-scale test as a condition for the mixing. Mixing was continued until the material reached 40°C, then material was dumped into the receiving container (drum or box).

Ceramicrete excretes a salt solution. The samples of Ceramicrete excreted a cloudy liquid that gelled and eventually solidified. Figure 4.2 shows the gelled liquid that oozed from under the sample cylinder caps and formed on that precipitated on top of the test sample in the bucket. Samples of the deposits were taken and analyzed. Results indicate that they contain potassium and phosphate with lesser amounts of sulfur, sodium, and tin.

Figure 4.2. Congealed Liquid and Precipitated Salts Excreted by Ceramicrete

4.2.2 Ceramicrete Drum-Scale Testing

The drum-scale test was performed to validate bucket-scale Ceramicrete formulations and to provide a curing temperature profile for a large cylindrical waste form. Power requirements for the ribbon mixer were also monitored during mixing. It was agreed that the drum sample would be mixed until the slurry temperature reached approximately 40°C or until the power drawn by the mixer increased dramatically, indicating that the material was thickening and slowing the mixer motor.

One 55-gal batch was generated using the Ceramicrete baseline formulation with the addition of 0.5% boric acid to prolong the working time. Table 4.4 lists the component weights used to generate the drum-scale sample. Fifty-five gallons of the waste form were generated for the 55-gal drum sample so that there would be enough extra to collect post-generation samples and account for any holdup in the ribbon mixer.

The bulk dry powders (except for ground zeolite and $SnCl_2$) were weighed and all of the powders blended for approximately 30 min in the ribbon mixer. The blended solids were then dumped from the ribbon mixer and divided into 5-gallon buckets. The prescribed amounts of 1-M Na^+ simulant and supplemental water were weighed into 5-gallon buckets, added to the ribbon mixer, and mixed. Weighed portions of the $SnCl_2$ and ground zeolite were also added to the liquids in the mixer. The dry materials were dumped from the 5-gallon buckets onto the belt conveyor and rapidly fed into the ribbon mixer. Time $t = 0$ to start the test was when addition of solids began. The addition of bulk dry materials was completed in a little over four minutes (4:14). After all the dry materials were added, mixing was continued and the temperature of the mixer monitored. When the temperature in the mixer reached an estimated 40°C the drain valve on the bottom of the mixer was opened and the blended Ceramicrete slurry poured into the plastic 55-gallon drum. The total elapsed time for blending the Ceramicrete was 24 minutes (24:05) from the start of solids addition, 20 minutes (19:51) after the last solids were added to the start of the pour. During the pour, flow was interrupted temporarily to partially fill a 5-gallon bucket with a sample for slump tests and to fill 2"-diameter × 4" sample containers.

Table 4.4. Ceramicrete Baseline Formulation with 0.5% Boric Acid

Component	Drum-scale formulation Baseline+ 0.5% Boric Acid Component Weight (kg)
1-M Na^+ Simulant	81.6
MgO	39.7
KH_2PO_4	135.0
Class C Fly Ash	142.9
$SnCl_2 \cdot 2H_20$	6.2
Ground Zeolite 5A	4.5
Supplemental H_20	6.5
Boric Acid	1.6
Totals	**418.0**
Waste loading[(a)]	**0.013**

(a) Waste loading is kg waste solids/kg total waste form.

During the mixing of the Ceramicrete the power draw of the mixer motor was monitored. It was expected that the mixer motor would draw more power as solids were added to the liquid and as the material was mixed after all the solids were added. This did not occur; there was no increase in motor power. Power to the ribbon mixer stayed at 1.64 kW from before solids addition until the batch was poured into the drum. The ribbon mixer had a gearbox reduction of approximately 40:1, which reduced the rotation rate of the mixer to ~45 rpm. The gear box also gave the mixer more torque so whatever increase in effective viscosity occurred during mixing did not slow down the mixer or drag the motor. The downside of the slow rotation rate of the mixing ribbon was that it did not impart much mixing energy (i.e., turbulence).

Upon pouring, the Ceramicrete was very fluid and poured evenly into the drum.

Immediately after the drum was filled a polycarbonate sheet was inserted to divide the filled drum vertically into two halves along the central axis. The sheet allowed the final cured monolith to be easily divided for core sampling at the end of the curing period. The sheet also had seven thermocouples attached at specific locations to monitor the temperatures within the curing material. The cooling of Ceramicrete and DuraLith are discussed together in Section 5. After the polycarbonate sheet was positioned, the top of the 55-gallon drum was covered with stretch wrap to prevent evaporation and drying during the initial cure.

When samples were collected to fill the 2"-diameter × 4" sample containers at *t* = 51 min, the 5-gallon bucket of sample taken during the pour had already started to set. With some effort the partially set material was stirred. Upon stirring it became thinner, making it easier to take samples for the 2" × 4" containers. This shear-thinning behavior had been observed earlier during the bucket-scale tests.

The next morning the sample in the 2" × 4" containers had expanded significantly and popped the tops off the containers. The material at the top was soft and friable. Figure 4.3 shows the containers with expanded Ceramicrete extending above the rim of the container.

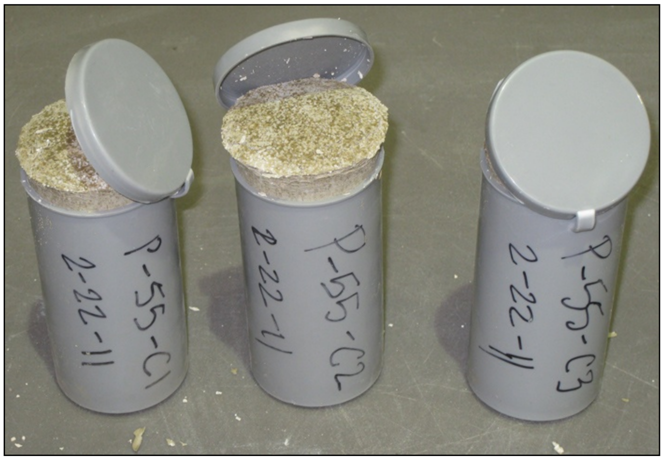

Figure 4.3. Ceramicrete Drum-Scale Test Samples Expanded Out of Container

After the first 16 hours of curing (overnight) the stretch wrap was removed from the 55-gallon drum. A thin layer of condensate had collected, covering most of the surface of the Ceramicrete. White “salts” had grown over most of the surface. The "salt" was thickest around the perimeter of the drum. In several places the top crust of the Ceramicrete was lifted up and cracked as if from pressure underneath (shown at tip of pointer in Figure 4.4, right photo).

Figure 4.4. Ceramicrete 55-Gallon Drum Test After 16 hrs of Curing While Covered

The stretch wrap was not installed again after the first night's curing and the condensation evaporated.

4.2.3 Ceramicrete 1/8th-Scale Tests

Three box samples were generated during the engineering-scale demonstration: two were poured into 2' × 2' × 3' boxes and one was poured into a 2' × 2' × 6' box. The 2' × 2' × 3' boxes were scaled so that each dimension was half that of a "standard" disposal box used for solid waste disposal at the Hanford site. The final waste-form container has not yet been decided, but previous work on secondary waste has suggested this could be a likely selection (Maloney 2006). The 6'-long box was selected for one test to determine whether the poured waste-form slurry would completely fill the farthest corners of the container.

Figure 4.5 shows Ceramicrete being poured into a 2' × 2' × 3' box.

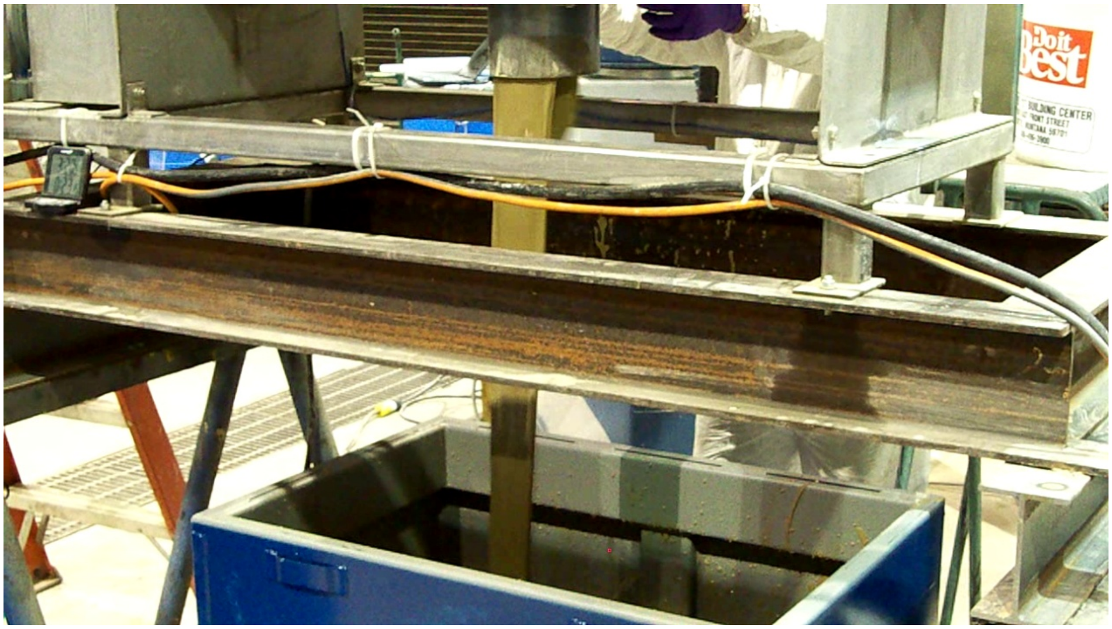

Figure 4.5. Ceramicrete Test #5 Pour

The first box was generated with an 11-ft^3 volume batch, which was the maximum that could be accommodated by the 10-ft^3 ribbon mixer. The next two boxes were generated using a 9-ft^3 volume because the 11-ft^3 volume was too large for the ribbon mixer to mix efficiently. The actual component weights for the three engineering-scale samples are listed in Table 4.5.

Table 4.5. Actual Component Weights for the Ceramicrete Engineering-Scale Samples

Component	11-ft^3 Baseline + 0.5% Boric Acid Component Weights (kg)	9-ft^3 Baseline + 0.5% Boric Acid (6' Box) Component Weights (kg)	9-ft^3 High Solids + 0.5% Boric Acid Component Weights (kg)
1-M Na^+ Simulant	122.1	99.9	96.1
MgO	59.4	48.6	49.1
KH_2PO_4	201.9	165.2	166.9
Class C Fly Ash	213.7	174.9	176.7
$SnCl_2 \cdot 2H_20$	9.34	7.64	7.70
Ground Zeolite 5A	6.79	5.56	5.61
Supplemental H_20	9.72	7.95	7.65
Boric Acid	2.46	1.94	2.03
Totals	**625.4**	**511.6**	**511.7**
Waste Loading(a)	0.013	0.013	0.012

(a) Waste loading is kg waste solids/kg total waste form.

The sequence of blending and mixing was conducted in the same manner for the 1/8th-scale tests as for the 55-gallon-drum test. However, the mixer had to be stopped several times to manually scrape off solids from the sides of the mixer. With the 11-ft^3 batch, the mixer blades never came out of the liquid, which greatly reduced the ability of the mixer to pull the solid powders down into the mixing slurry. After the first test, the batch volume was reduced to 9 ft^3 and the mixing improved, but was still inadequate to completely blend the solids into the liquid. The final poured waste form contained significant lumps. Figure 4.6 shows undispersed solids buildup on the center shaft of the ribbon mixer and lumps in the final blend. The lumps were wetted on the outside and still dry powder on the inside.

Figure 4.6. Unmixed Solids from Ceramicrete 1/8th-Scale Tests

The 2"-diameter by 4" sample containers were collected immediately from the bucket sample that had been taken partway through pouring the batch into the test box; the material was not disturbed to shear-thin the material. After sitting overnight the samples had not expanded enough to pop the tops off the containers as had occurred with the 55-gallon test samples, which had been shear thinned. However, when the samples were checked again in the afternoon the material had expanded above the top rim of the container and popped off the lids; however, the samples had not expanded as much as the 55-gallon drum samples. See Figure 4.7.

Figure 4.7. 2"-Diameter × 4" Sample Containers from the First 1/8th-Scale Test

The first test box was filled after all the solid materials were added and the slurry mixed for 22 min. The material in the ribbon mixer was then poured into the test box. The Ceramicrete was very fluid and filled the box to an even level. The box was fitted with brackets to attach a vibrator and help to achieve a volume-filling pour, but such was not needed. Figure 4.8 shows the filled test box with the polycarbonate divider installed.

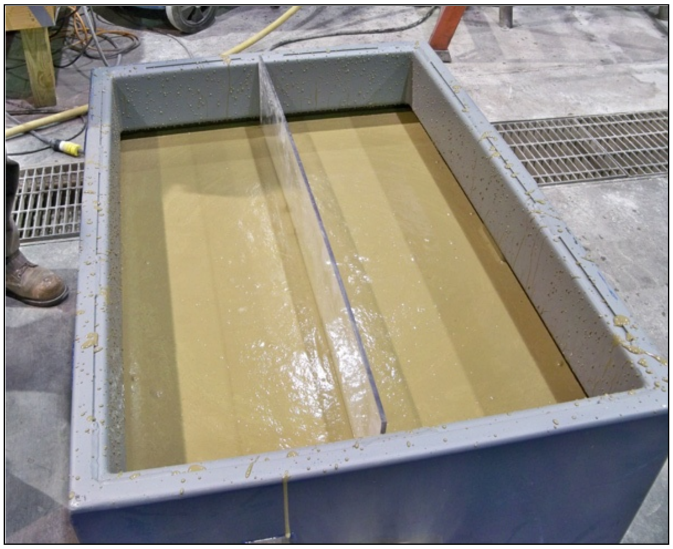

Figure 4.8. Test Box After Filling with Ceramicrete

The lid was not placed on the box and there was no accumulation of water as had been observed with the drum test. The next morning, white precipitation growths were observed on the surface. The growth accumulation was most abundant along the sample divider and around the perimeter of the box—locations that had the most water accumulation in the drum test. There were also some accumulations of white precipitate growing up from the surface like stalagmites; see Figure 4.9. Also, the Ceramicrete appeared to have swelled or expanded slightly at the surface.

Figure 4.9. First 1/8-Scale Test Box After Curing Overnight

The second 1/8th-scale test box used the 2' × 2' × 6' long test box to verify that the mixed slurry could pour the full length of a 6' box and fill the farthest corners. It did. For a more challenging test, the ribbon mixer was poured near one end of the box rather than near the middle, so the flow path was even longer than expected for full-scale operation.

The lid was placed on the second box overnight to prevent water evaporation during the initial cure and make the initial cure more comparable to the 55-gallon-drum test. The test box accumulated significant water.

The third box test used a formulation with a higher solids content (5% higher solids:water ratio). The high solids content did not cause an observable difference in the rheology of the mixed slurry. After the polycarbonate divider was added the lid was left off the third box, so its initial cure was more like the first 1/8th-scale box test in regard to water condensation or evaporation.

In addition to changes described, the second and third box tests implemented some other changes compared to the first box test:

- A smaller batch (9 ft^3 vs. 11 ft^3) was used to improve mixing.
- Solids were added at a somewhat slower rate (10 min vs. 5:35 min for Test Box #1). (There were fewer lumps and the lumps appeared to be smaller than Test Box #1.)

When the 2" diameter × 4" sample containers from the second and third box pours were examined the next morning (~18 hr after the pour), the samples had expanded out of the container and popped the lids off, similar to the drum-scale test. See Figure 4.10.

Figure 4.10. 2" Diameter × 4" Sample Containers ~18 hr After Filling Test Box #2 (left) and Test Box #3 (right)

4.2.4 Ceramicrete Observations after 55 Days of Curing

The Ceramicrete samples were allowed to cure for a period ranging from 53 days to 56 days; then the containers were removed, the monolith samples were split at the polycarbonate dividers, the monoliths were physically examined, and core samples were taken from specific locations for testing at PNNL.

Figure 4.11 shows a core sample being drilled from the top surface of the monolith from Test Box 1. The monolith from Test Box 3 is also shown.

The tops of the monoliths from both Test Box 1 and Test Box 3 were hard to the touch and showed a white salt precipitation on the surface. These two test boxes were left uncovered for the initial curing; the surfaces were dry. Test Box 1 had been prepared from the baseline Ceramicrete formulation and Test Box 3 had been prepared from the high-solids formulation. The sample from the baseline formulation had more of the white precipitate on the surface than the sample from the high-solids formulation.

Figure 4.11. Core Sampling of Monolith from Ceramicrete Test Box 1

Figure 4.12 shows the monolith from Test Box 2. This box had been covered for the initial cure and significant condensation occurred such that a layer of water collected on the surface of the monolith overnight. After the first night, the box was left uncovered and the condensation readily evaporated.

Figure 4.12. Monolith from Test Box #2, 2' × 2' × 6' (covered during initial cure)

The top of the monolith was friable and easily flaked away if touched or disturbed. Close-up pictures of the top of the monolith from Test Box #2 are shown in Figure 4.13.

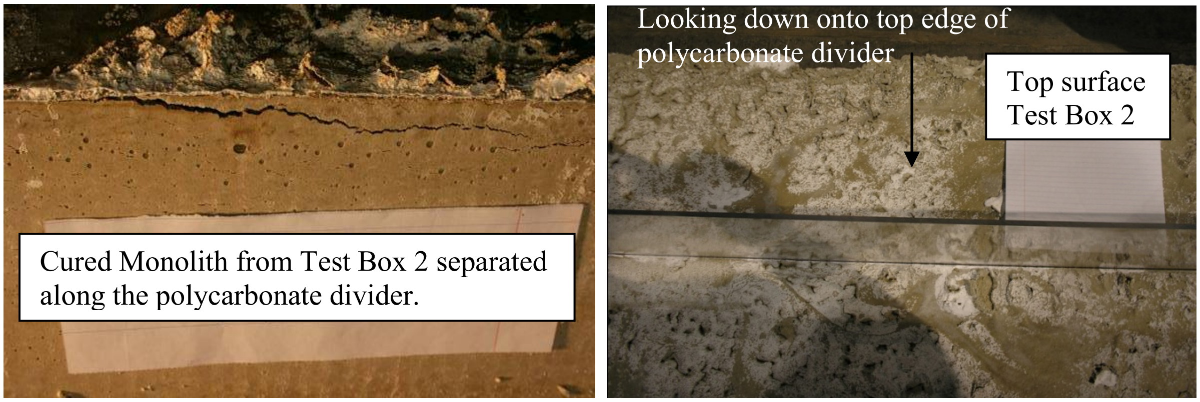

Figure 4.13. Close-Ups of Monolith from Test Box #2. Smooth face was along the polycarbonate divider.

Below the soft friable layer, the material was hard and not noticeably different from the monoliths from Test Box #1 or #3.

Figure 4.14 shows similar pictures from Test Box #3.

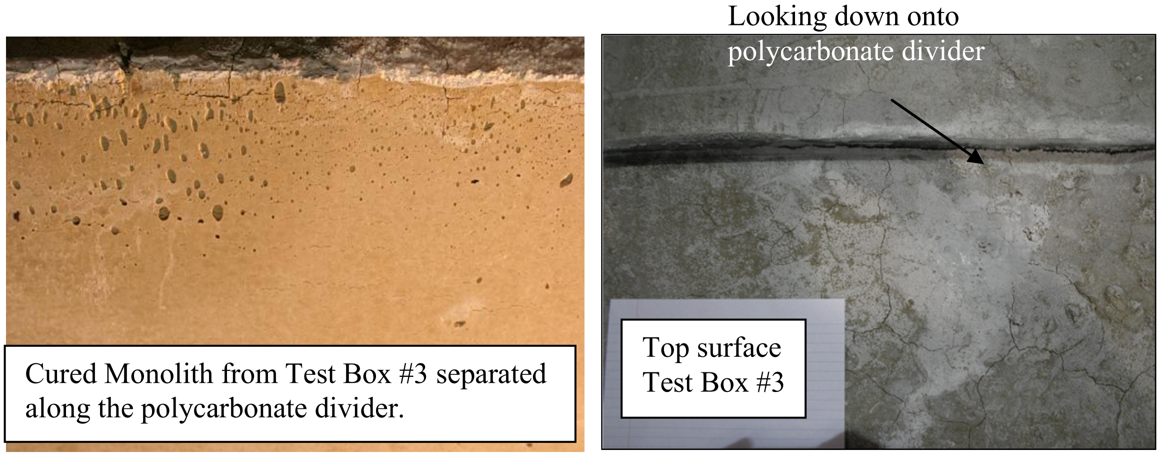

Figure 4.14. Close-Ups of Monolith from Test Box #3. The smooth face was along the polycarbonate divider.

The top of the Test Box #3 was hard and not at all friable like the top surface in Test Box #2. However, Figure 4.13 and Figure 4.14 show that both monoliths had a thin crust of material that was noticeably different color and texture than the bulk of the monolith. There was a compositional difference between the crust and bulk material for both monoliths. The soft friable nature of the crust from Test Box #2 is attributed to the accumulation of water on the surface during the first day of curing. After the first day or so the water on the surface of Test Box #2 evaporated.

Figure 4.15 shows the monolith from the drum-scale test. This material was also covered during the first day of the cure and collected a layer of water from condensate. However, the surface of the drum material was not as soft and friable as the surface from Test Box #2, although it was not as hard as the material in Test Box #3.

Figure 4.15. Drum-Scale Ceramicrete Monoliths After Cure Showing Holes Cut to Remove Core Samples

Figure 4.16 shows a close-up of the inner surface of the drum-scale monolith. Of particular note are the striations of white salt-like material and the line patterns they form on the smooth surface left from the polycarbonate divider. Where the block broke, the patterns are not visible, but the white salt-like material appears as white grains in the bulk monolith. Also note the collection of white salt at the bottom of the smooth surface; the contour of the bottom of the plastic drum is visible below the white salt layer.

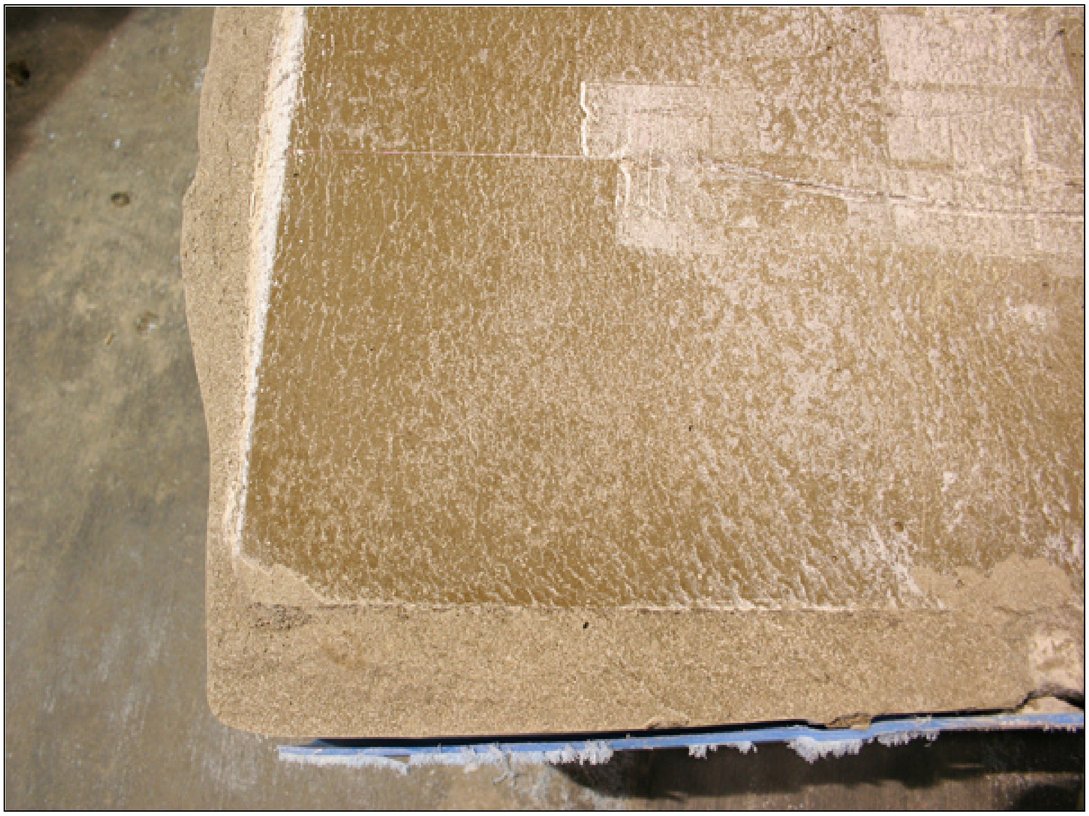

Figure 4.16. Close-Up of Drum-Scale Monolith After Curing, Broken Along Divider Sheet

Figure 4.17, Figure 4.18, and Figure 4.19 show the locations of core samples taken from Ceramicrete monoliths for subsequent laboratory performance testing conducted at PNNL.

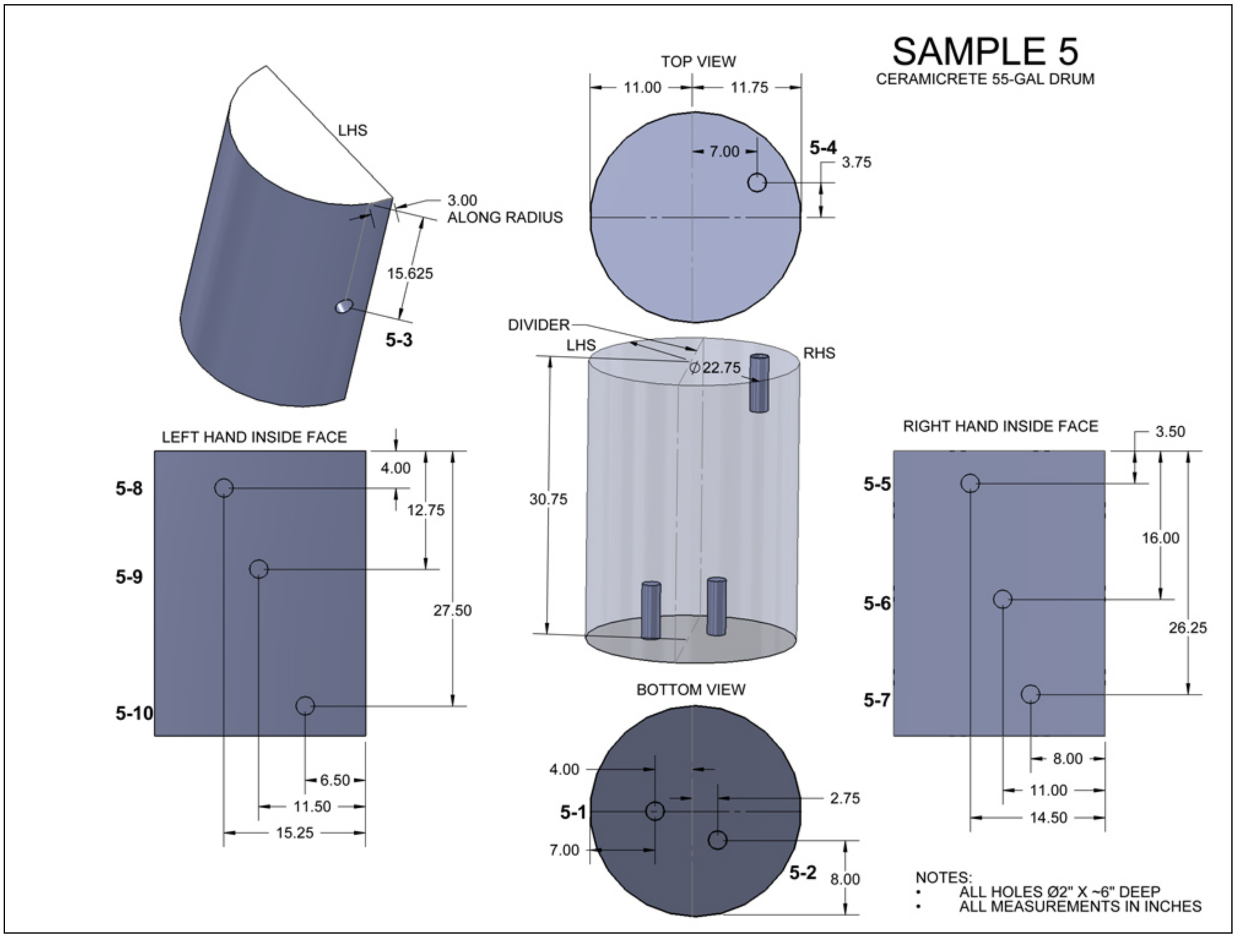

Figure 4.17. Locations of Core Samples from Ceramicrete 55-gallon Drum, Test #5[1]

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[1] From *Engineering-Scale Demonstration of Ceramicrete and DuraLith Waste Forms for the Solidification of Hanford Secondary Wastes*, MSE-294, August 2011 (Appendix E of this report).

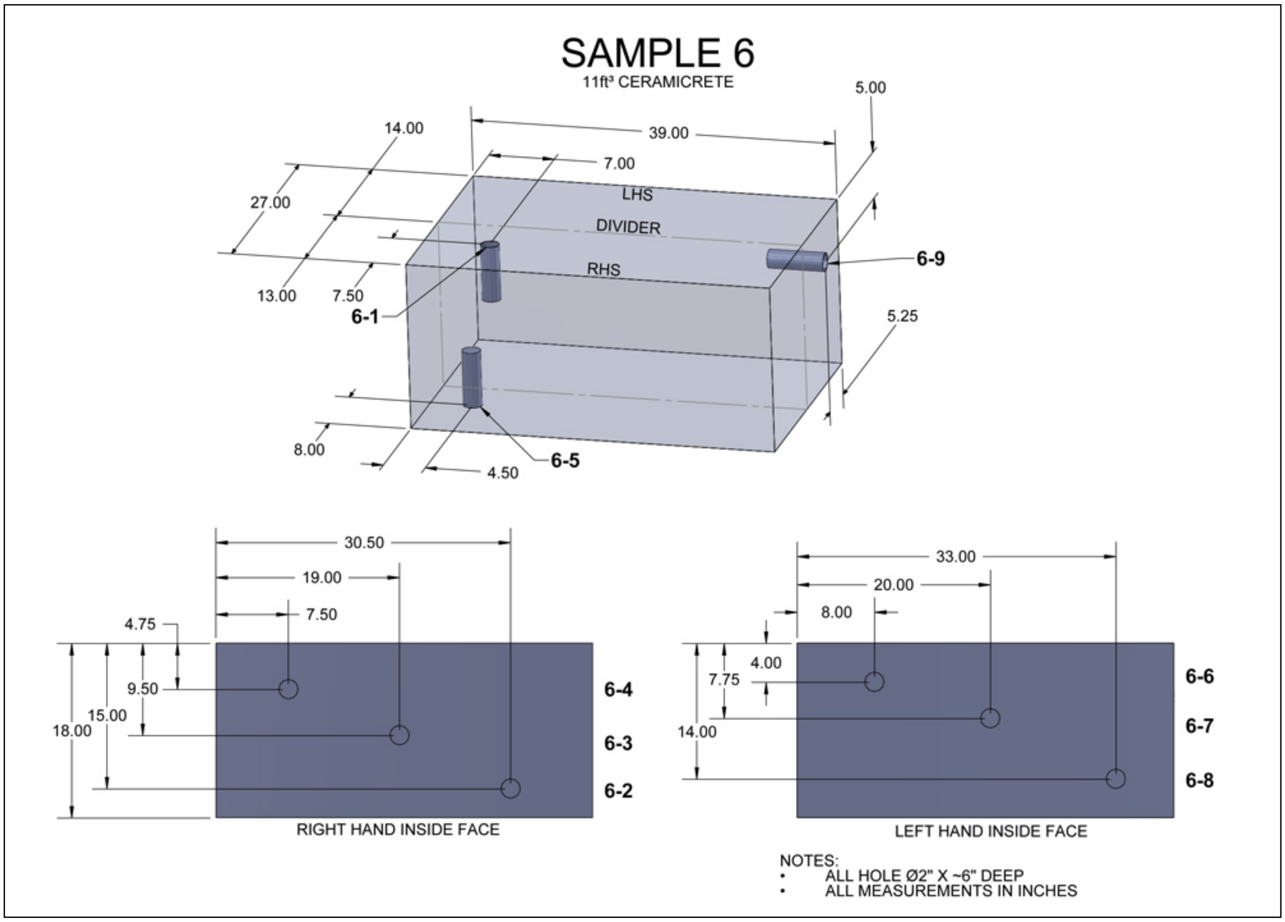

Figure 4.18. Locations of Core Samples from Ceramicrete First 1/8th-Scale Test Box, Test #6[1]

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[1] From *Engineering-Scale Demonstration of Ceramicrete and DuraLith Waste Forms for the Solidification of Hanford Secondary Wastes*, MSE-294, August 2011 (Appendix E of this report).

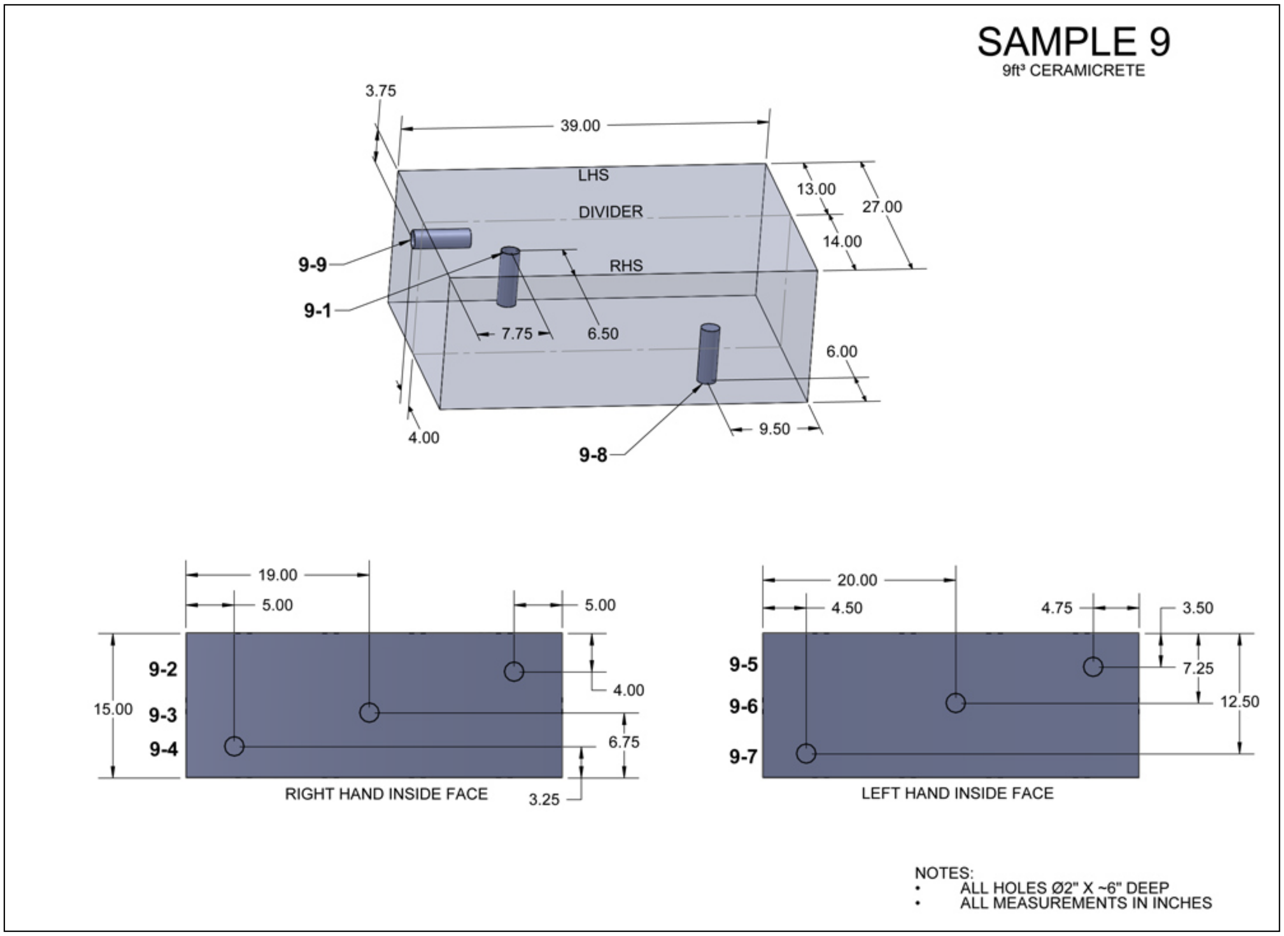

Figure 4.19. Locations of Core Samples from Ceramicrete Third 1/8th-Scale Test Box, Test #9[1]

4.3 DuraLith Testing

DuraLith testing was planned to follow the same sequence as testing with Ceramicrete, but was modified to develop more information regarding mixing. After the first drum of DuraLith was mixed using the ribbon mixer, lumps were observed in the final mix to an even greater degree than had been observed with Ceramicrete. Longer mixing time was not an option to attempt breaking the lumps and fully dispersing the solids because the materials (Ceramicrete and DuraLith) had limited working times. It was decided to use MSE's 20-hp turbine mixer to mix two additional drums of DuraLith to determine whether the additional mixer power would fully disperse the solids. The engineering-scale test using the ribbon mixer and pouring into the 1/8th-scale box was not conducted.

MSE conducted five bucket-scale tests and three drum-scale tests with DuraLith. MSE numbered the tests sequentially, following the numbers assigned to the Ceramicrete tests. Parameters for these tests are listed in Table 4.6.

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[1] From *Engineering-Scale Demonstration of Ceramicrete and DuraLith Waste Forms for the Solidification of Hanford Secondary Wastes*, MSE-294, August 2011 (Appendix E of this report).

Table 4.6. DuraLith Tests

Test #	Scale	Description
10	4.5-gal bucket	Baseline, 16.45 wt% water (all water from 6-M Na simulant, no supplemental water added)
11	4.5-gal bucket	Supplemental water, 20 wt% water
12	4.5-gal bucket	High water (20 wt%) w/70% fly ash(FA)+30% blast furnace slag (BFS)
13	4.5-gal bucket	High water _70/30:FA/BFS + 0.5 wt% boric acid
14	55-gallon drum	High water _70/30:FA/BFS, ribbon mixer
15	3.5-gal bucket	Baseline water_70/30:FA/BFS
16	55-gallon drum	High water _70/30:FA/BFS, turbine mixer
17	55-gallon drum	Baseline water_70/30:FA/BFS, turbine mixer

4.3.1 DuraLith Activator Solution

The Ceramicrete recipe only involved mixing the liquid waste simulant (and supplemental water) with the dry solidifying solids. The DuraLith recipe had an additional step: the waste simulant was first mixed with an "activator" before addition of solidifying powders. Preparing the activator solution involved several steps.

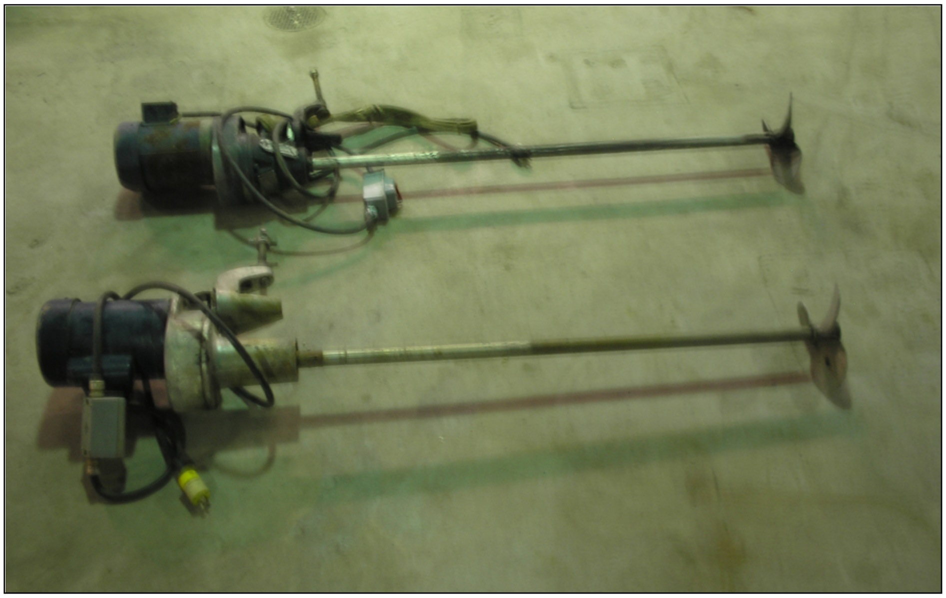
Measure the prescribed amount of secondary-waste simulant (6-M Na).

Under stirring, slowly add solid KOH and NaOH to the simulant solution and keep temperature below 60°C. Continue stirring.

Pour silica fume into the alkaline solution while stirring.

Continue stirring for at least 24 hours.

The liquid was noticeably viscous after all the silica was added, but the blade mixers were adequate to move the liquid and form a mixing vortex. After mixing for 24 hr, the solution viscosity appeared water-like. The mixers are shown in Figure 4.20.



Tank mixers
used for simulant and
activator solution:

Leeson Electrical Corp.
Grafton, WI, Model # -
GC17FC3D

½ horse power (hp)
8" propeller
4' shaft

Figure 4.20. Tank Mixers for DuraLith Activator Solution Makeup

Table 4.7 includes the activator make-ups for three batches of activator solution.

Table 4.7. DuraLith Activator Solution Make-up Weights

Component	Weight %	Batch #1 Bucket tests and Drum #1 Actual Weight (kg)	Batch #2 Drum #2 Actual Weight (kg)	Batch #3 Drum #3 Actual Weight, (kg)
6-M Na^+ Simulant	61.4	132.9	106.1	92.8
Tin Fluoride	0.61	1.27	1.02	0.94
Potassium Hydroxide	16.3	35.1	28.0	24.5
Sodium Hydroxide	2.5	5.41	4.32	3.78
Fumed Silica	19.2	41.6	33.2	29.0
Totals	100.0	216.3	172.6	151.1
Waste loading(a)		0.203	0.203	0.203

(a) Waste loading is kg waste solids/kg total activator.

Laboratory tests at VSL indicated that H_2 was generated during the fumed silica dissolution. The H_2 was attributed to residual silicon metal in the fumed silica that reacted in the highly caustic condition. Special precautions were taken during the testing to prevent accumulation of H_2 and forming an explosive condition. Bubbles were observed coming to the surface during the silica dissolution. Hydrogen concentrations were measured several times during the silica mixing. The highest concentration was measured to be 0.15% shortly after the fumed silica had been completely added (Batch #2). The Lower Explosive Limit for H_2 is 4.1%, over 25 times higher than was measured during the test. Additional laboratory tests would have to be done to establish H_2 generation rates so that appropriate safety measures could be designed for a full scale DuraLith process. Qualitatively, this test indicates that H_2 generation rates are slow. The DuraLith technology developer is investigating other sources of silica that would resolve the H_2 generation issue.

4.3.2 DuraLith Bucket-Scale Tests

Bucket-scale testing was conducted prior to the drum-scale and engineering-scale demonstrations to validate the baseline formulations provided by the DuraLith technology providers and to gather information pertaining to the scale-up formulations that were to be used during the drum-scale demonstrations. PNNL and WRPS personnel and the DuraLith technology provider were on site during the DuraLith bench-scale and engineering-scale demonstrations to observe testing and provide formulation development for the bench-scale and engineering-scale samples.

The DuraLith bucket-scale tests were conducted in the same fashion as the Ceramicrete tests. Dry binder materials weighed out, combined into a single bucket, and thoroughly mixed; the activator solution was weighed out into a 6-gal bucket and the supplemental water was added and mixed; then the binder materials were added and the entire quantity was mixed.

Table 4.8 shows weights for each of the bucket-scale tests to make up 4.5 gal of mixed DuraLith.

Table 4.8. Component Weights for the DuraLith Bucket-Scale Tests

Component	Test #10 Baseline Component Weight (kg)	Test #11 High H_2O Component Weight (kg)	Test #12 Fly Ash/High H_2O Component Weight (kg)	Test #13 Fly Ash/High H_2O+0.5% Boric Acid Component Weight (kg)	Test #15 Fly Ash/ Baseline H_2O Component Weight (kg)
Activator Solution	13.31	13.31	13.31	13.31	10.24
Binder Materials					
Blast Furnace Slag	9.91	9.91	2.97	2.97	2.28
ASTM Class F Fly Ash			6.94	6.94	5.32
Copper Slag	0.70	0.70	0.70	0.70	0.54
Metakaolin Clay	4.00	4.00	4.00	4.00	3.07
Fine Sand	6.64	6.64	6.64	6.64	5.09
Ground Zeolite 5A	0.35	0.35	0.35	0.35	0.27
Fumed Silica	0.35	0.35	0.35	0.35	0.27
Totals	21.95	21.95	21.95	21.95	16.84
Total Additional Water	164 g	1689 g	1338 g	1338 g	65.15 g
Water wt. %	16.45%	20%	20%	20%	16.45%
Boric Acid			--	114.8 g	--
Waste loading[(a)]	0.076	0.073	0.074	0.074	0.077

Note: The test numbers in this table follow the sequential test number assigned by MSE during the conduct of the testing.

(a) Waste loading is kg waste solids/kg total waste form.

The first DuraLith bucket-scale test proved that the baseline formulation that had been originally planned based upon the laboratory testing conducted by VSL had insufficient working time to allow it to be prepared at large scale. The binder materials and activator solution were mixed for 3 minutes after all the binder material had been added. Within 4–5 minutes after the mixing was complete, the DuraLith was too hard to allow insertion of the polycarbonate divider into the bucket.

Similar behavior had been observed with the Ceramicrete material; the recipe developed at lab scale did not have sufficient working time to be prepared at larger scale. Based on recommendation of the developer (Dr. Weiliang Gong, VSL) a higher-water-content formulation was tried next. This formulation set nearly as quickly as the first. The polycarbonate divider could not be inserted 6 ½ minutes after mixing was complete.

The setting of the DuraLith was very curious. Before it became hard it passed through a phase where the material seemed very "plastic" and was sticky. This behavior was very different from that of Ceramicrete, which set in a more familiar manner, like mortar or concrete. Figure 4.21 illustrates the plastic and sticky nature of the DuraLith material in the "plastic" phase.

Figure 4.21. DuraLith Deforming During Vicat Test (left) and Sticking to 50-Cent Rheometer (right)

Dr. Gong felt that the rapid setting of the DuraLith was most probably caused by a difference in composition of the blast furnace slag from the composition used in the laboratory testing to develop the formulation. He recommended that the setting could be retarded by substituting 70% of the blast furnace slag with fly ash. Fly ash was procured and two formulations were prepared based on the recommended substitution. The second formulation also added boric acid, which had successfully retarded the Ceramicrete setting time.

Water content was maintained at 20%. (Note: the lower water addition rate indicated in Table 4.8 compensated for a different batch of sand used after Test #11. The new sand had higher moisture content.)

Substituting the fly ash for the blast furnace slag significantly increased the working time for the DuraLith. A working time was qualitatively assessed by observing the rheological behavior of the 50-cent rheometer slump tests. With the fly ash formulation, the series of five slump tests showed that the material flowed with increasing resistance for a full 30 minutes after mixing was complete. After

30 minutes, the DuraLith was too stiff and sticky to pour from the cylinder. The material still demonstrated the “plastic” nature observed with the initial formulations, but the onset of the “plastic” nature was retarded and the material could be worked for about 30 minutes. Figure 4.22 illustrates how the material stiffness and stickiness progressed between 26.7 min (sample 12D) and 30 min (sample 12E).

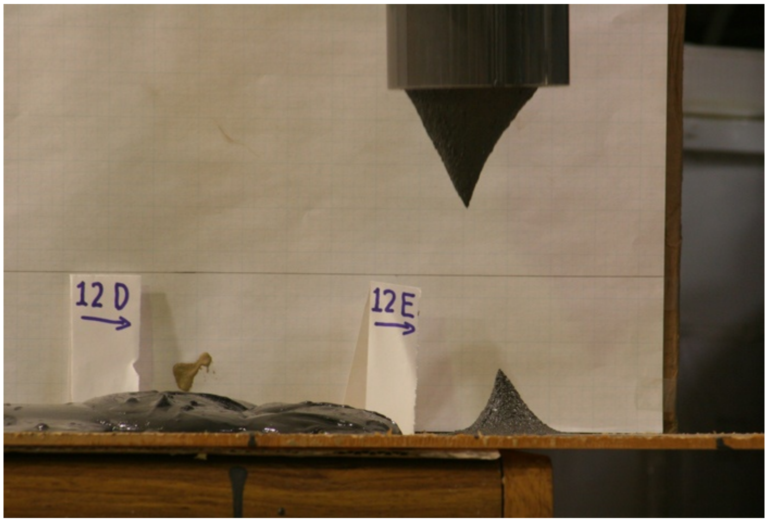


Figure 4.22. “Plastic” Phase of DuraLith Set Between 26.7 Minutes and 30 Minutes

All the 50-cent-rheometer cylinders were filled within the first 2 minutes after mixing was complete. When the polycarbonate cylinder was lifted off sample 12D 26.7 min after mixing, the weight of the DuraLith caused the material to flow and spread out on the table. A little over 3 minutes later, cylinder 12E was lifted and the material was too sticky to release from the cylinder.

The fourth bucket-scale test added 0.5 wt% boric acid to the formulation using fly ash. It was expected that the DuraLith set would be even slower, giving more working time for the larger-scale tests. No noticeable change in set time was observed after adding the same amount of boric acid that had demonstrated a big effect retarding the Ceramicrete set, 0.5 wt%.

The progression of setting for DuraLith is illustrated in Figure 4.23 with the fly ash formulation + 0.5 wt% boric acid.

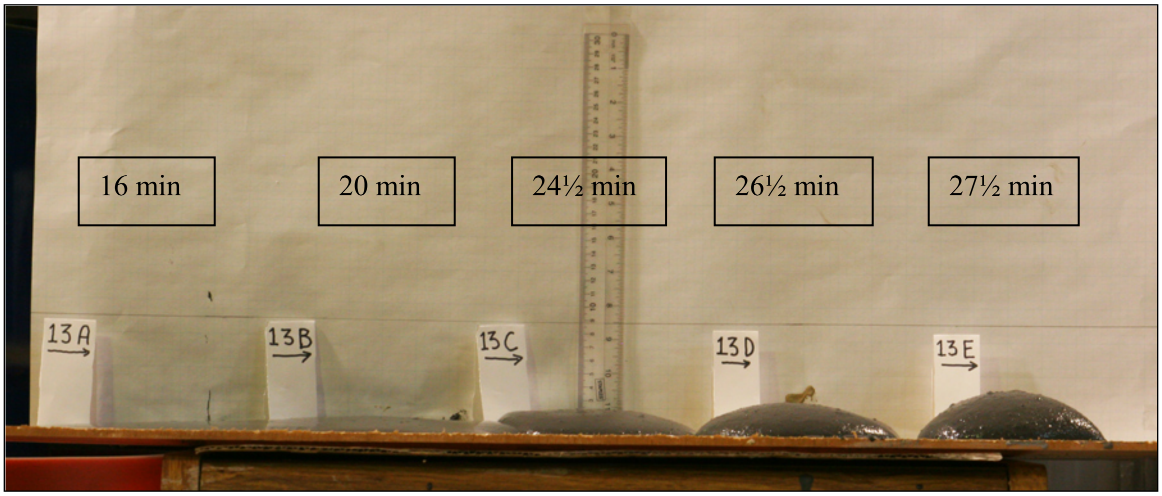


Figure 4.23. Progression of DuraLith Setting in "50-Cent Rheometer" Slump Test

After the bucket-scale tests showed that the working time of the DuraLith could be extended to 30 minutes, the modified formulation substituting Class F fly ash for 70% of the blast furnace slag with a 20% water content was tested at the drum scale. After a successful drum-scale test, the final bucket-scale test was conducted to determine the working time for the original water content (16.45 wt%) formulation with fly ash substituted for blast furnace slag.

Figure 4.24 shows the progression of DuraLith setting with the baseline water content.

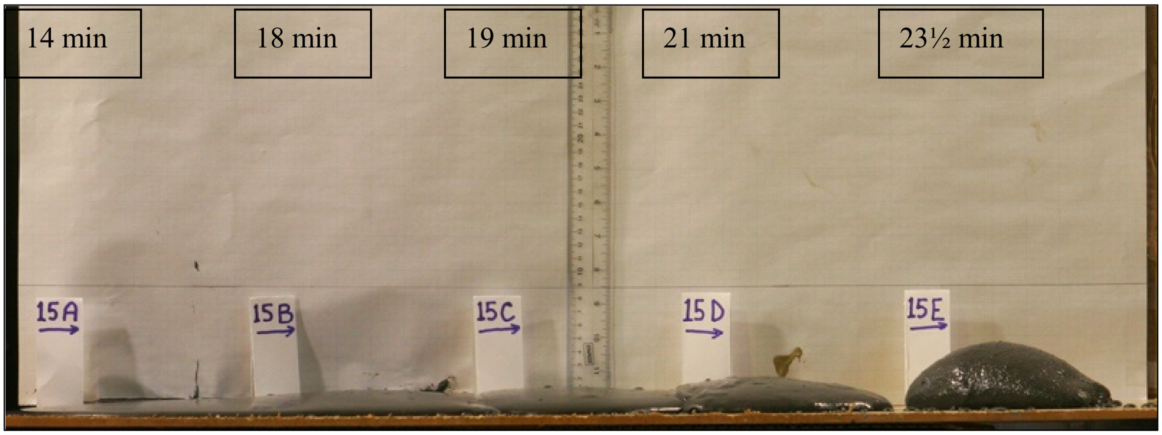


Figure 4.24. Progression of DuraLith Setting in "50-Cent Rheometer" Slump Test—Baseline Water Content

The test with lower water content demonstrated that the working time did decrease with lower water content, but remained long enough for a large-scale test.

4.3.3 DuraLith Drum-Scale Tests

Drum-scale testing was performed to validate bench-scale DuraLith formulations and to provide a curing-temperature profile for a large cylindrical waste form. Table 4.9 shows the make-up weights for all the drum-scale tests completed. Each test is described further below.

Power requirements for the ribbon mixer were monitored during mixing. The drum-scale test was conducted with the same steps as in the drum test with Ceramicrete. The prescribed solids weights were blended in the ribbon mixer and then dumped into drums to be added later using the conveyer belt. Then the supplemental water and activator solution were added to the ribbon mixer and mixed. The solids were then added via the conveyor system over several minutes (~6 min). Approximately 3 minutes into the addition, the solids addition and mixer were stopped for about a minute to clear clumps of solids from the sides and center shaft of the ribbon mixer. After all the solids were added, the full batch was mixed for another six minutes (12 minutes total) and the mixed batch was dumped into the drum. The power draw by the ribbon mixer (1.7 kW) did not change from the beginning until the mixing time was over and the batch dumped.

Immediately after the drum was filled, a polycarbonate sheet was inserted along its axis to divide the filled drum vertically into two halves. The sheet allowed the final cured monolith to be easily divided for core sampling at the end of the curing period. The sheet also had seven thermocouples attached at specific locations to monitor the temperatures within the curing material. The cooling of DuraLith and Ceramicrete are discussed together in Section 5.

Table 4.9. DuraLith Make-Ups for Drum-Scale Tests

Component	Weight %	High H_2O 21 wt% Ribbon Mixer Test #14 Component Weight (kg)	High H_2O 21 wt% High-Shear Mixer Test #16 Component Weight (kg)	Baseline 16% H_2O High-Shear Mixer Test #17 Component Weight (kg)
Activator Solution	37.2	151.11	151.11	151.11
Binder Materials				
Blast Furnace Slag	8.43	33.66	33.66	33.66
Class F Fly Ash	19.7	78.76	78.76	78.76
Copper Slag	2.00	7.91	7.91	7.91
Metakaolin Clay	11.3	45.29	45.29	45.29
Fine Sand	18.8	75.17	75.17	75.17
Ground Zeolite – 5A	0.99	3.96	3.96	3.96
Fumed Silica	0.99	3.96	3.96	3.96
Totals	100.0	399.8	399.8	399.8
Water Weight Percent (added water)		21% (21.9 Kg)	21% (21.9 Kg)	16.45% (0 Kg)
Waste loading[(a)]		0.073	0.073	0.077

(a) Waste loading is kg waste solids/kg total waste form.

After the first drum was filled, a layer of floating lumps was observed accumulating on the surface of the DuraLith slurry—even more lumps than had been observed with Ceramicrete. The left image in Figure 4.25 shows lumps floating to the surface of the drum after pouring from the ribbon mixer. The lumps could be felt within the mixed slurry. After a few minutes (before the DuraLith began to set) the depth of the layer of floating lumps is illustrated in the right image in Figure 4.25 with the gloved arm of the test director (Jody Bickford of MSE) extending up to her elbow to what felt like the bottom of the floating layer of lumps.

Figure 4.25. *Left*: Lumps in First 55-Gallon Drum of DuraLith; *Right*: Apparent Depth of Lumps

Figure 4.26 shows the size of the lumps and that the inside of the lumps contained dry powered solids.

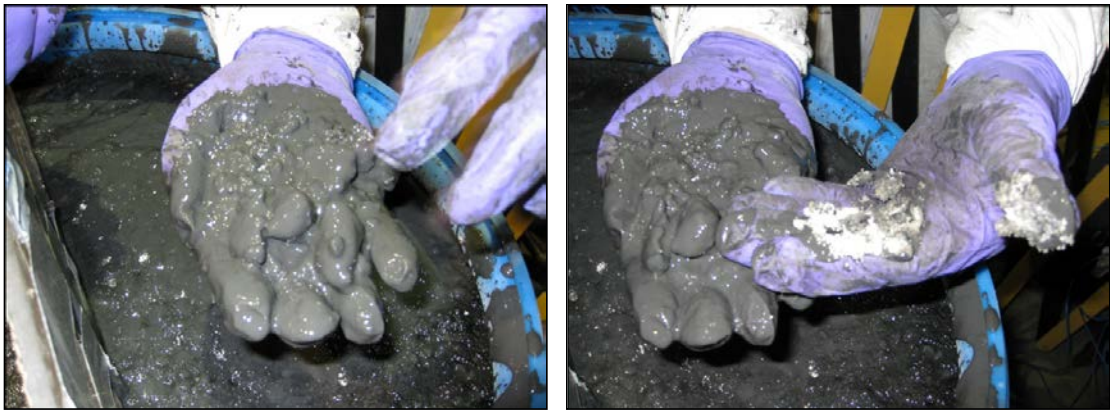


Figure 4.26. Lumps from the Floating Layer in the First Mixed DuraLith Drum. The insides of the lumps contain unwetted solid powders.

The team decided that the ribbon mixer should not be used to generate the engineering-scale demonstration samples because the drum-scale material was poorly mixed using the ribbon mixer. Like Ceramicrete, the DuraLith slurry was very fluid for most of the total working time and then became thicker and stickier. During the early working time, immediately after mixing was complete, there was no doubt the DuraLith would fill the test box volume, readily flow into the corners, and form a level top surface. The team decided to depart from the planned testing and utilize MSE's high-shear turbine mixer to determine whether additional mixing would break up the lumps and whether there would be any effect on the subsequent performance of the cured monolithic waste form. Figure 4.27 shows MSE's 20-hp hydraulic turbine mixer.

20-Hp Hydraulically Driven Drum Mixer
Hepsco Hydraulic Engineered Products – Charlotte, NC
6000 psi Working Pressure
62.5" Reinforced Shaft,
15" Propeller

Electric Fork Lift
Multiton MIC Corp. – Richmond, VA
Model SM-20, 2205-lb Capacity with Barrel-Holding Assembly

Figure 4.27. 20-Hp Hydraulic Turbine Mixer

Second Drum-Scale Test, High-Shear Mixing (Test #16). The solid powders were blended using the ribbon mixer and then loaded into buckets and transported to the building where the turbine mixer was located. Prescribed amounts of activator solution (including 6-M Na^+ simulant) and supplemental water were added to a plastic drum. The solid powders were added to the liquid over an 8-minute period. Initially the turbine mixer was rotating at 300 rpm. The speed was progressively increased three times (3 min, 6 min, and 7 min) to keep powder from accumulating on the surface. The final turbine speed was 750 rpm, as measured using a photo-tachometer.[1] After all the solids were added, the slurry was mixed for 9 minutes more.

After mixing was complete, large lumps were not visible as had been present after mixing with the ribbon mixer. Close examination of the slurry showed granular particles, which were mostly likely the sand particles and a few larger particles that were small (1/8"-1/4") clumps of powdered solids. The granular particles are still visible on the surface of the set material in Figure 4.29. The high-shear mixing significantly reduced both the number and size of the lumps but did not completely eliminate small lumps.

Comparing slump tests for the ribbon-mixed drum-scale test (Figure 4.28) and high-shear mixing test (Figure 4.29) indicates that the high-shear mixing also contributed to a longer working time.

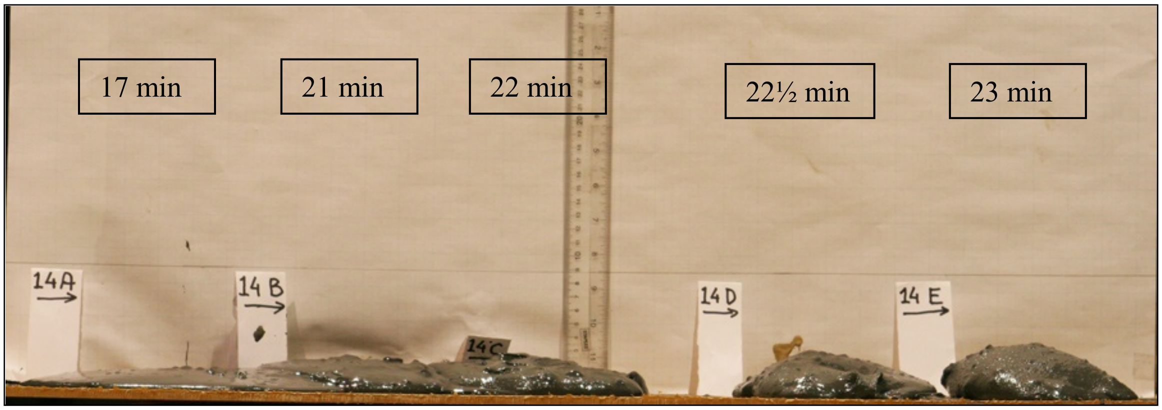


Figure 4.28. "50-Cent Rheometer" Slump Tests for DuraLith Ribbon-Mixer Drum-Scale Test (Sample #14)

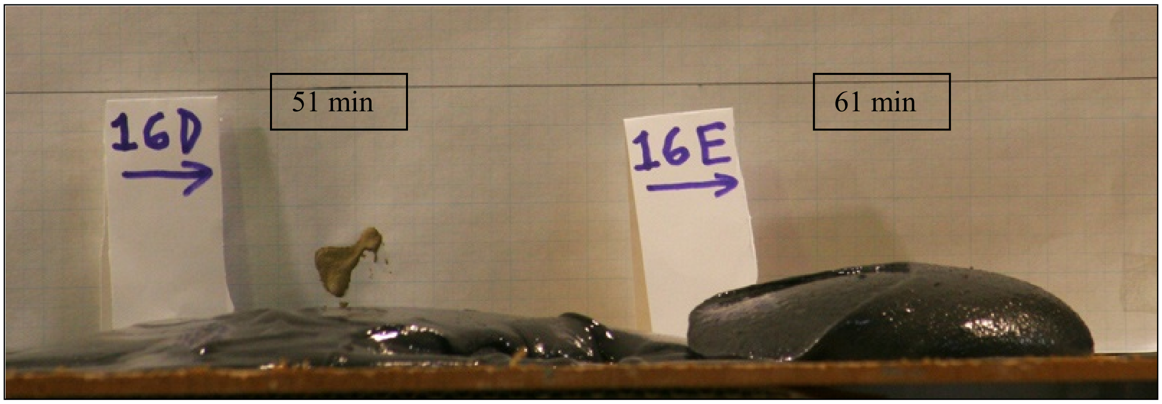


Figure 4.29. "50-Cent Rheometer" Slump Tests for DuraLith High-Shear Mixer Drum-Scale Test (Sample #16)

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[1] The turbine RPM was considered for information only. The tachometer was not calibrated instrumentation.

Based upon the observation of a longer working time with the high-shear mixing, a third drum-scale test was conducted using the baseline (16.45 wt%) water content instead of the high water content (21 wt%). The prescribed amount of simulant was added to the drum, (no supplemental water was added), and the powdered binder materials added over a period of 9 minutes. The mixer speed was 290 rpm initially and then was increased as buckets of material were added to keep solids from accumulating on the top of the slurry. By the end of the solids addition, the mixer was operating at 1300 rpm. Mixing continued at 1300 rpm for 10 minutes after all the solids were added.

Figure 4.30 shows the 50-cent rheometer test results with the higher solids content and high shear mixing.

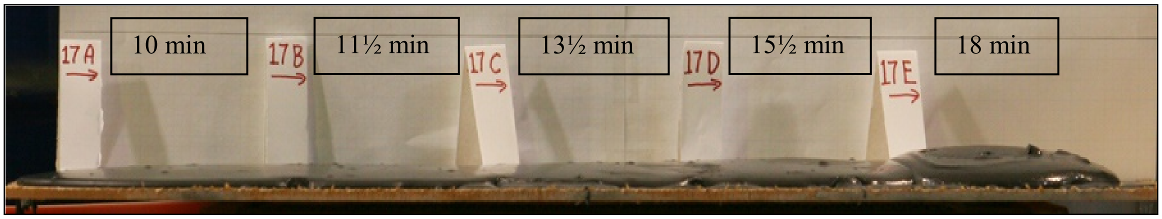

Figure 4.30. "50-Cent Rheometer" Slump Tests for DuraLith High-Shear Mixer, Baseline Water (Sample #17)

It appears that the lower water-content mixture was setting faster, as one would expect, but the times for the slump tests between the high water-content and baseline water-content mixtures were very different, making direct comparison difficult.

4.3.4 DuraLith Observations after 41 Days of Curing

The DuraLith samples were allowed to cure for periods ranging from 40 days to 42 days; then the containers were removed, the monolith samples were split at the polycarbonate dividers, the monoliths were physically examined, and core samples were taken from specific locations for testing at PNNL.

Pictures of the tops of all three DuraLith drum-scale tests are shown in Figure 4.31.

Figure 4.31. DuraLith Drum-Scale Tests. *Left*: Ribbon Mixer/21% Water [Test #14]; *Center*: Turbine Mixer/21% Water [Test #16]; *Right*: Turbine Mixer/16.45% Water [Test #17]

Notice how irregular the top surface of DuraLith from Test #14 is compared to the top surfaces of Samples #16 and #17. The irregular top surface is attributed to the lumps of unmixed powders that floated to the top of the slurry after pouring. Despite being irregular, the surface was hard on the first drum as well as the other two. Also visible in Figure 4.31 are apparent salt deposits on the surface. Unlike Ceramicrete salt deposits, the deposits on the DuraLith had essentially no thickness and could not be removed with gentle scraping. No samples could be collected for chemical analysis.

No core samples were taken from Test #14 (ribbon mixer) because of the poor mixing. When the monolith was broken and inspected, the team was surprised at how well the sample cured; hardly any lumps were identified compared to those that were seen after the mixing process. A picture of the inside surface of Test #14 and a close-up of the top section are shown in Figure 4.32.

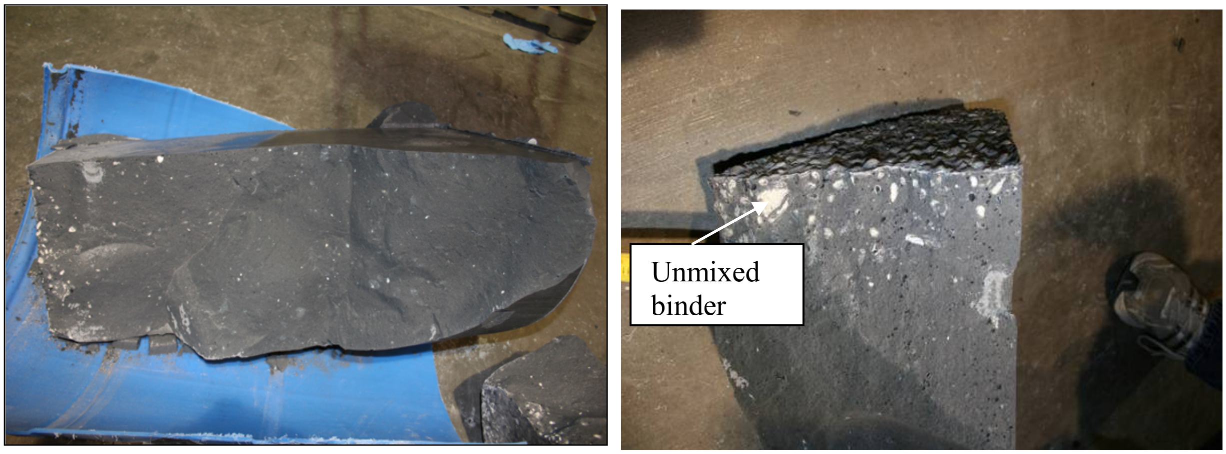

Figure 4.32. *Left*: Broken Monolith from DuraLith Ribbon Mixer Drum Test; *Right*: Close-Up of Top Layer

The close-up picture of the top section distinctly shows the light-colored remnants of the powder lumps caused by insufficient mixing in the ribbon mixer. The light areas were no longer powder, but were surprisingly hard. They could not be dislodged with a fingernail, but could be scraped with a screwdriver. The black parts of the monolith were harder and could not be dislodged with a screwdriver.

The other two DuraLith drum-scale tests used the high-speed turbine mixer. Mixing was obviously better than with the ribbon mixer and no lumps accumulated on the surface. Nevertheless, there were still a few pockets of undispersed solids that appear as white spots on the broken surfaces of both turbine mixer test samples, which are shown in Figure 4.33.

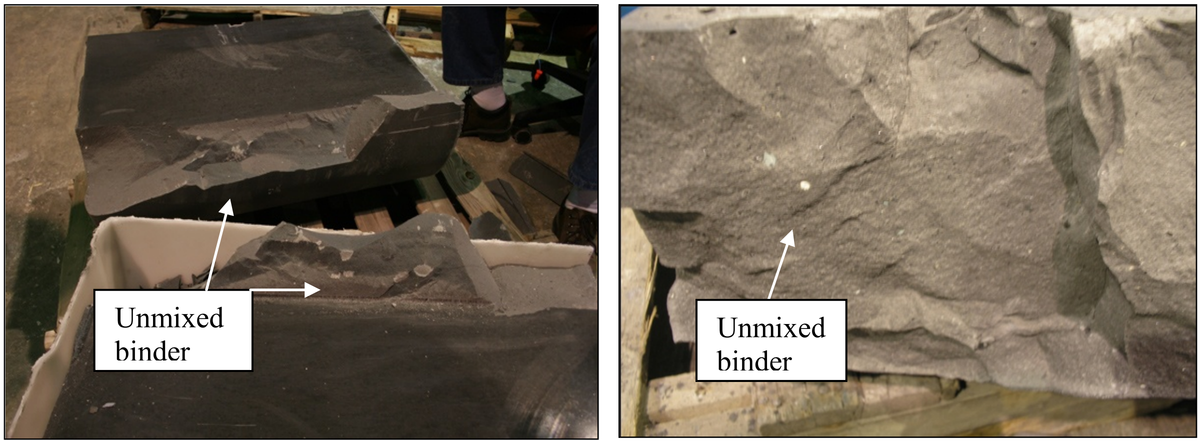

Figure 4.33. *Left*: Broken Monolith from Turbine-Mixer Test w/21% Water; *Right*: 16.45%-Water Test Mixed with Turbine Mixer

Both monoliths from the 21-wt. % water drum-scale tests also appeared to have areas that were damp and areas that were drier. A Sharpie® was used to demark one of the areas between the damp and dry areas so it could be checked the following morning to determine whether some of the sample areas actually were damp compared to the other areas that seemed drier, as shown in Figure 4.34. The top of the sample, shown on the right-hand sides of the pictures, was a lighter gray and "felt" drier than the darker gray section of the sample. The right picture in Figure 4.34 shows the same location the following morning after the sample was exposed to air; the sample had dried out, proving that during the curing time moisture had not completely equilibrated throughout the monolith.

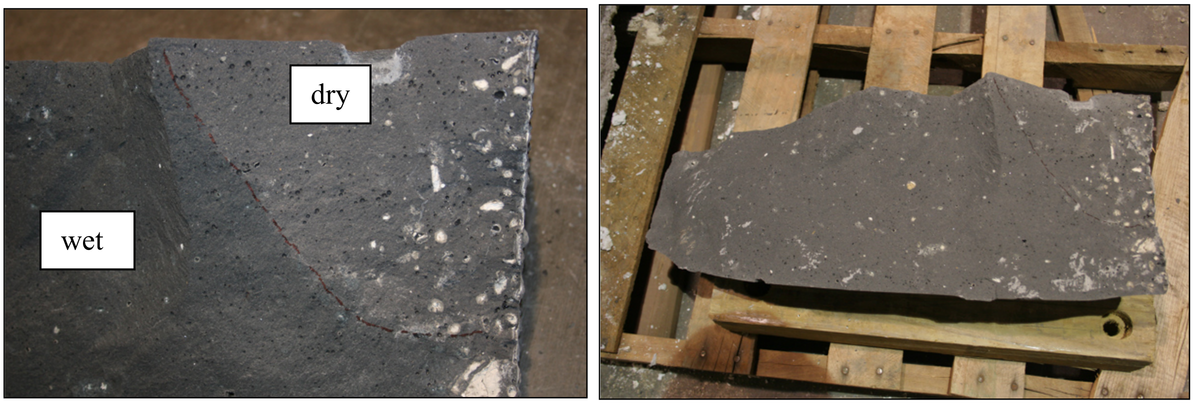

Figure 4.34. DuraLith Monoliths after Mixing with Ribbon Mixer. *Left*: Area with Moisture; *Right*: After "Drying" Overnight Broken Open, the Entire Surface is Dry.

The monolith from the turbine-mixer test with 21% water (Test #16) also appeared to have areas of the sample that were damp and areas of the sample that were drier. The monolith from the lower water-content test (Test #17) did not seem to have the "wet" areas in the broken monolith.

In all the monoliths, there were also areas with dark, shiny specks. After investigation it was determined that the specks were actually small pockets of trapped liquid. The technology developer suggests that the trapped liquid is pore water that has collected in a pocket that was formed by an air bubble. Air bubbles get incorporated into the slurry by the mixer and some do not escape before the material set up. Smaller pockets of liquid are more prevalent than larger pockets, which is consistent with air entrainment during mixing. A close-up picture of one of the large specks and several smaller specks is shown in Figure 4.35; the tan part of the picture is the fingertip of a leather glove.

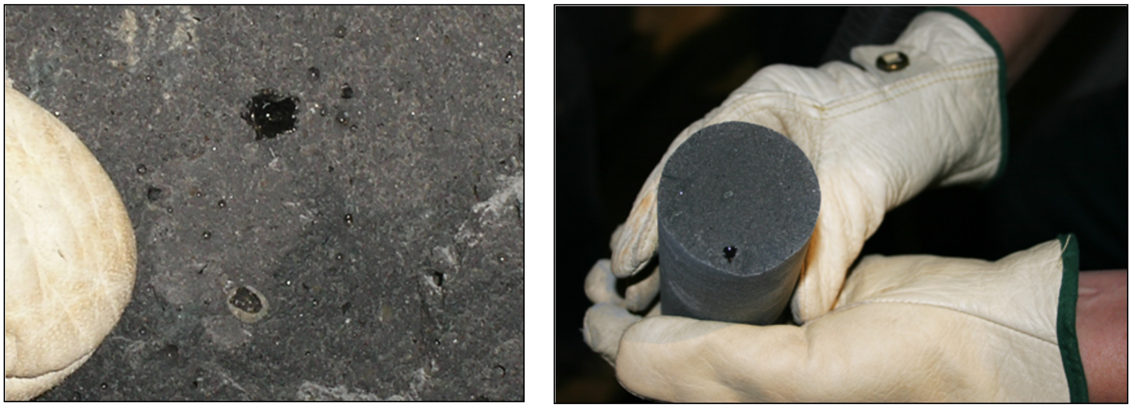

Figure 4.35. Pockets of Trapped Pore Water. *Left*: Ribbon Mixer (Test #14); *Right*: Turbine Mixer w/16.45% Water.

The turbine mixer obviously dispersed the powdered binder and mixed the activator solution; however, both turbine-mixer tests still had pockets of unmixed binder solids and unmixed activator solution. It is not known how these small volumes affect the overall performance of the monolith. To achieve homogeneous mixing will take still more mixing energy, higher power or longer times.

The 21-wt% water formulations were noticeably less viscous (more watery) than the formulation with no supplemental water (16.45 wt% water, all from simulant). A sample of the high-water formulation (Test #16) taken at the end of the mixing period measured 2450 cp viscosity (Test #16), and a sample of the 16.45-wt% water formulation taken four minutes after mixing (Test #15) measured 11570 cp. The difference in initial viscosity is consistent with settling of the coarser sand particles in Test #16, (21 wt% water, mixed with the turbine mixer) as shown in Figure 4.36.

Figure 4.36. Coarser Grain in 21-wt% Water Drum (Turbine Mixed) Attributed to Sand Settling

The test drum generated using 16.45% water (Test #17) did not show any aggregate settling at the bottom.

All of the features observed above were visible along the surface of the broken monolith. The surfaces that cured in direct contact with smooth surfaces, such as the inside surface of the drum or along the polycarbonate divider, were completely smooth, shiny, and did not display any observable features. Figure 4.37 shows the surface formed in contact with the drum (plastic) and the surface formed in contact with the polycarbonate divider.

Figure 4.37. DuraLith Monolith Surfaces Cured in Contact With Smooth Surfaces. *Left*: Plastic Drum; *Right*: Polycarbonate Divider.

Figure 4.38 and Figure 4.39 show the locations of core samples taken from DuraLith monoliths for subsequent laboratory performance testing conducted at PNNL.

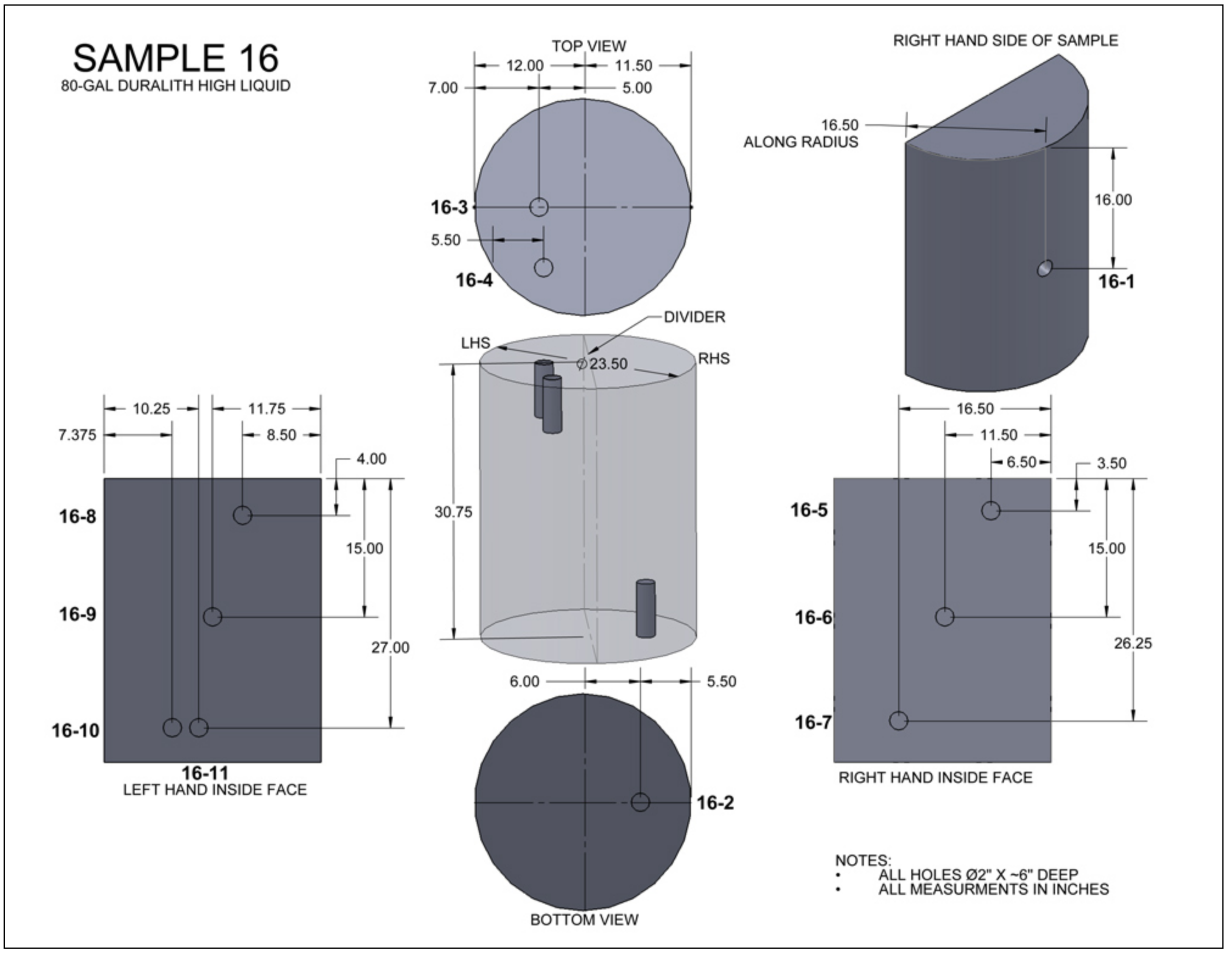

Figure 4.38. Locations of Core Samples from DuraLith High-Water (21 wt%) 55-Gallon Drum Test with High-Shear Mixing, Test #16[1]

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[1] From *Engineering-Scale Demonstration of Ceramicrete and DuraLith Waste Forms for the Solidification of Hanford Secondary Wastes*, MSE-294, August 2011 (Appendix E of this report).

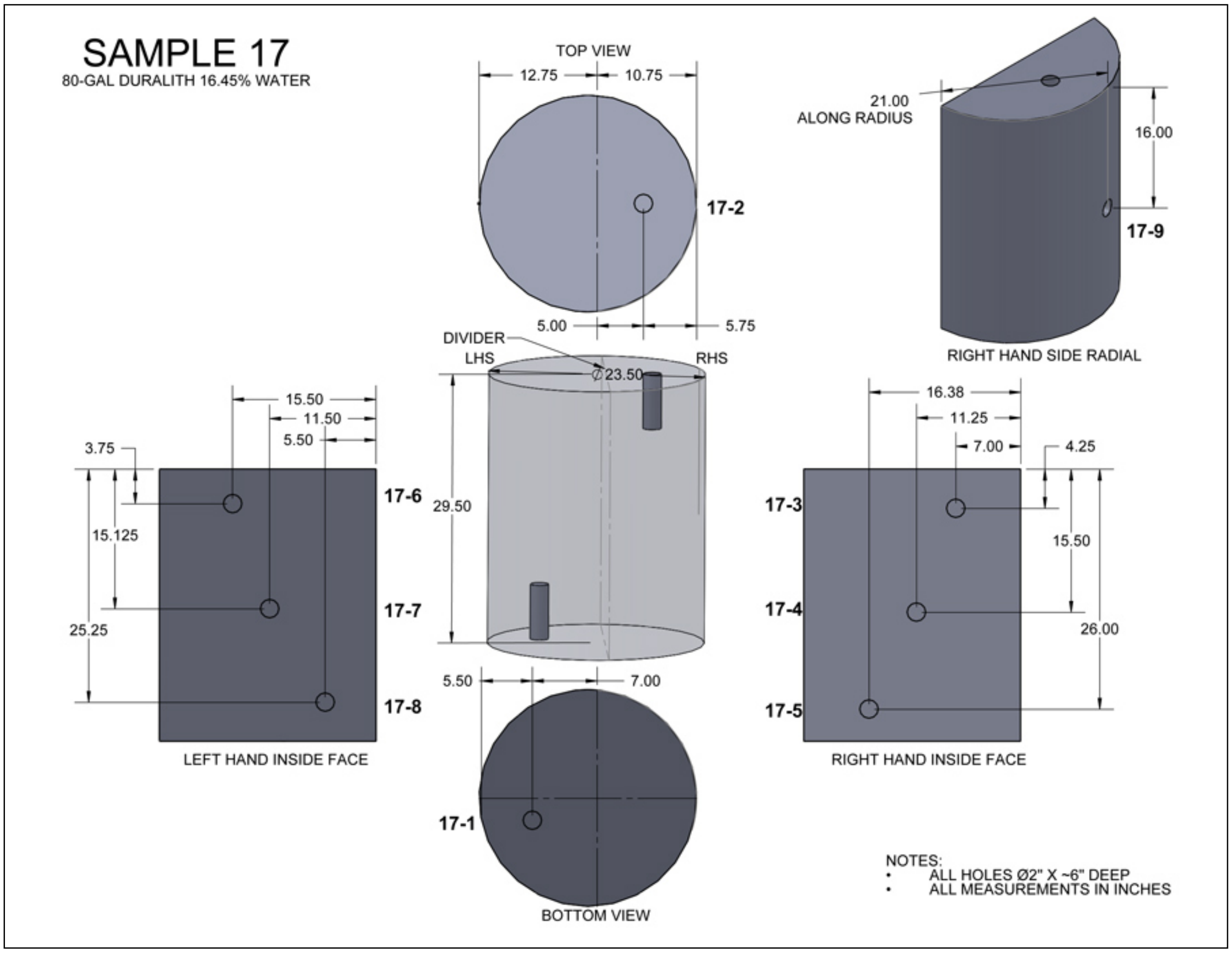

Figure 4.39. Locations of Core Samples from DuraLith Baseline Water (16.45 wt%) 55-Gallon Drum Test with High-Shear Mixing, Test #17[1]

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[1] From *Engineering-Scale Demonstration of Ceramicrete and DuraLith Waste Forms for the Solidification of Hanford Secondary Wastes*, MSE-294, August 2011 (Appendix E of this report).

5.0 Drum-Scale Cooling Tests

To obtain information on the cooling rates of Ceramicrete and DuraLith, polycarbonate dividers were fitted with thermocouples and inserted in samples of the candidate materials. Figure 5.1 shows a diagram of the thermocouple locations relative to the drum.

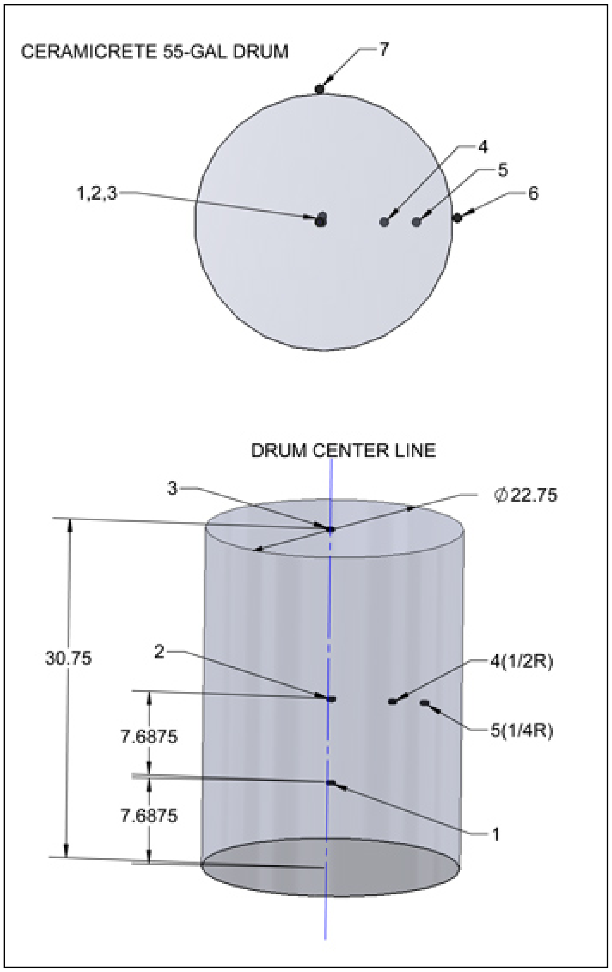

Figure 5.1. Thermocouple Locations Relative to Drum[1]

The top-center thermocouple (#3) was intended to monitor the temperature of the surface of the slurry during curing. After the polycarbonate sheet was installed in the drum, Thermocouple #3 was re-located so that the thermocouple tip was at the surface of the slurry. Thermocouples #6 and #7 were attached to the exterior of the drum at the locations indicated after the polycarbonate sheet was installed.

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[1] From *Engineering-Scale Demonstration of Ceramicrete and DuraLith Waste Forms for the Solidification of Hanford Secondary Wastes*, MSE-294, August 2011 (Appendix E of this report).

Figure 5.2 shows the temperature profile of Ceramicrete with 0.5 wt% boric acid during cooling of the 55-gallon drum. The batch was poured at approximately 37°C. The maximum temperature of 84.7°C was reached approximately 7 hours 40 minutes later.

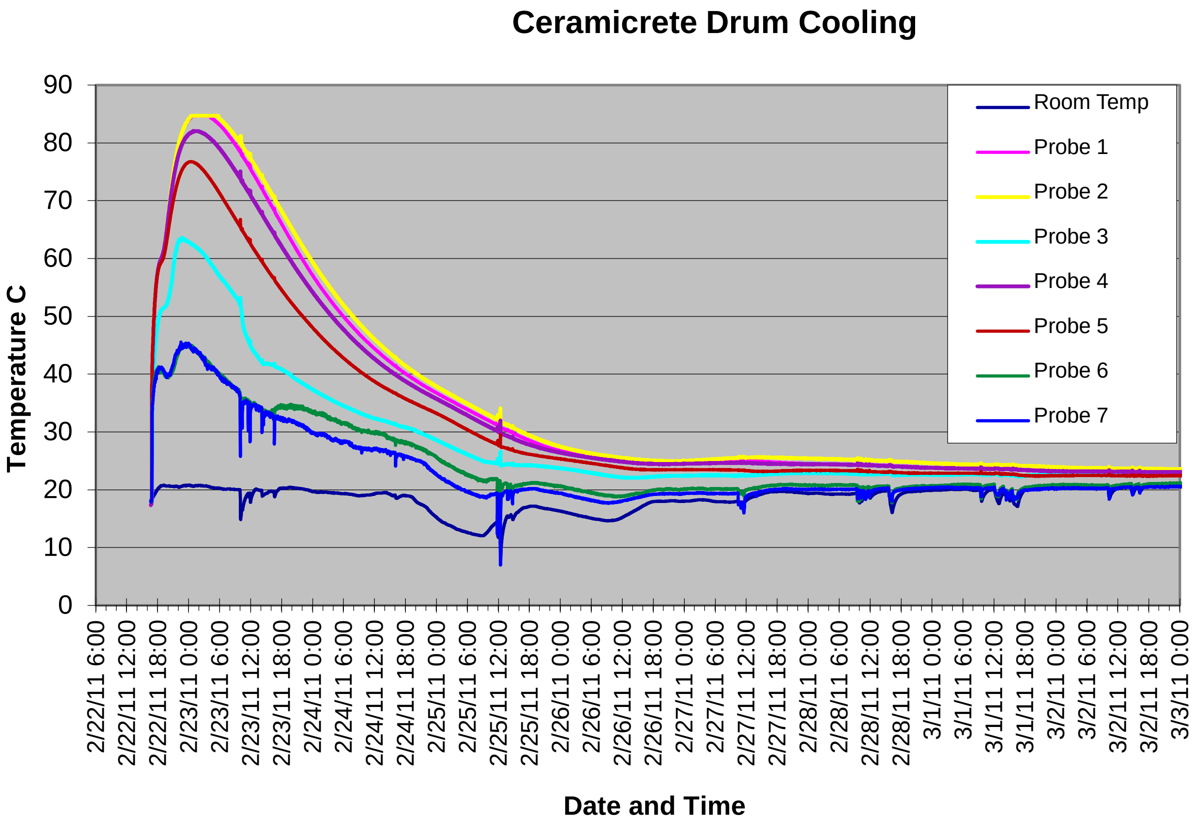

Figure 5.2. Cooling Profile of Ceramicrete 55-Gallon Drum

Figure 5.3 shows the temperature profile of DuraLith with 21 wt% water during cooling of the first 55-gallon drum (ribbon mixed). The batch was poured at approximately 21°C. The maximum temperature of 59.48°C was reached approximately 19 hours 45 minutes later.

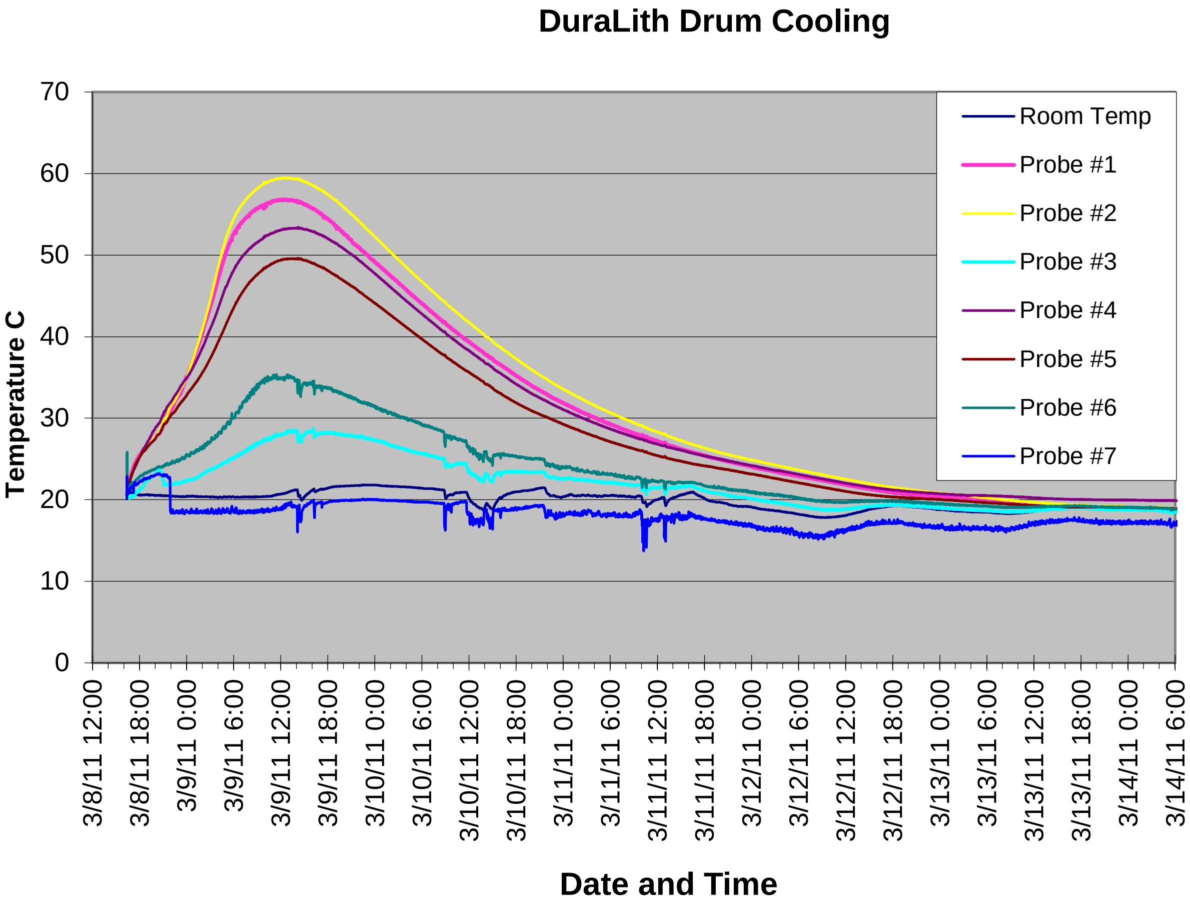

Figure 5.3. Cooling Profile of DuraLith 55-Gallon Drum

6.0 Waste Form Characterization

Specimens of the Ceramicrete and DuraLith waste forms from the engineering-scale demonstration were characterized with respect to their chemical composition and phase structure, density, compressive strength, and sodium diffusivity. This section describes the characterization methods and the results for each waste form. Where available, the results are compared to results obtained on similar laboratory-scale specimens.

6.1 Chemical Composition

Specimens of the Ceramicrete and DuraLith engineering-scale products were chemically analyzed by digesting the samples in a microwave oven using a strong-acid medium (PNNL 2011). The resulting digestate was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively-coupled plasma mass spectrometry (ICP-MS).

The Ceramicrete and DuraLith specimens were crushed and milled to <0.075 mm particle size before chemical digestion to determine the elemental composition. Microwave-assisted strong-acid digestions were conducted using 16-M HNO_3, 12-M HCl, and 29-M hydrofluoric acid (HF). The powdered samples were prepared following EPA Method 3052 (EPA 1996). The solid-acid mixture (0.25 g/14 mL) was typically reacted for 1 hour at 90 ± 5°C. Because of the presence of undissolved solids using the typical approach, a slight deviation was made: the reaction time was extended to between 2 and 3 hours, and the solid-to-acid ratio was reduced (0.1 g/30 mL). Upon complete dissolution of the sample, 3 mL of a 4.4-M H_3BO_3 solution was added to the acid solution to neutralize the fluoride. The resulting solution was filtered through a 0.45-µm membrane and analyzed for rhenium and trace metals with ICP-MS and for major cations and a limited number of nonmetals (e.g., phosphorus and sulfur) with ICP-OES.

The concentration of major cations was measured with ICP-OES (Perkin Elmer OPTIMA 3300 DV [Waltham, Massachusetts] with a Perkin Elmer AS93+ autosampler) using high-purity calibration standards to generate calibration curves and verify continuing calibration during the analysis run. Because of the differences in the leachate cation concentration, a number of dilutions, ranging from 100 to 1.01 times, were used to obtain measurable concentrations of the cations of interest. Details of this method are found in EPA Method 6010B (EPA 2000a). Inductively coupled plasma mass spectrometer (Perkin Elmer ELAN DRC II with a Perkin Elmer AS93+ autosampler) was used to measure trace-metal concentrations. These measurements were performed following the PNNL-AGG-415 method (PNNL 1998), which is similar to EPA Method 6020 (EPA 2000b).

6.1.1 Ceramicrete Chemical Composition

Chemical composition was determined for one specimen from the center of the Ceramicrete high-solids box (#9-3) and for cores from the top, middle, and bottom of the initial Ceramicrete drum (#5-5, #5-6, and #5-10). Table 6.1 provides the chemical compositions for the four samples.

Table 6.1. Chemical Compositions of Ceramicrete Drum and Box Cores

	High Solids Box (Middle, #9-3)	Drum (Top, #5-5)	Drum (Middle, #5-6)	Drum (Bottom, #5-10)
Constituent	mg/g	mg/g	mg/g	mg/g
Aluminum	36.4	36.6	36.9	37.0
Barium	2.26	2.24	2.29	2.27
Calcium	48.2	49.5	50.3	49.5
Cesium	0.00178	0.00193	0.00187	0.00203
Chloride	NM[(a)]	NM	NM	NM
Fluoride	NM	NM	NM	NM
Iodine	NM	NM	NM	NM
Iron	18.5	18.4	18.8	18.7
Magnesium	77.6	77.5	78.0	78.2
Phosphorus	90.4	86.5	88.0	86.8
Potassium	119.0	120.0	118.0	115.0
Silicon	101.0	103.0	97.1	97.1
Silver	NM	NM	NM	NM
Sodium	13.8	14.6	14.5	14.3
Strontium	1.19	1.20	1.23	1.20
Sulfur	<13.1	<13.8	<13.8	<11.1
Tin	9.45	9.51	9.93	9.78
Titanium	2.41	2.38	2.44	2.42

(a) NM = not measured.

6.1.2 DuraLith Chemical Composition

Chemical composition was determined for cores from the top, middle, and bottom of the DuraLith high-solids drum (cores #16-4, #16-6, and #16-11) and top, middle, and bottom of the DuraLith low-solids drum (cores #17-2, #17-5, and #17-7). Table 6.2 provides the chemical compositions for these six samples. Table 6.2 shows that some elements demonstrate a difference between the top, middle, and bottom of the drum that is consistent with settling of solids, as seen in Figure 4.36. The DuraLith formula mixed activator solution and solids, blast furnace slag, class C fly ash, metakaolin clay, and fine sand. Of these, the fine sand was generally more coarse than the fly ash or blast furnace slag; however, some large particles could have been included in either the fly ash or the blast furnace slag. The activator solution was primarily potassium and sodium hydroxides with dissolved silica and waste simulant. Table 6.2 indicates higher concentrations of potassium, sodium, and calcium in the cores from the upper parts of the drums. This would be consistent with settling of heavier particles, leaving a higher concentration of "activator" in the geopolymer. The higher concentration of calcium in the upper sections could come from the blast furnace slag or the fly ash to form the geopolymer—both had high concentrations of calcium. The coarse granular nature of settled material in Figure 4.36 was initially attributed to coarse sand. The higher concentration of iron is more consistent with coarse particles of blast furnace slag or fly ash, but sand can also have high iron depending upon the source. Such differences are not observed in samples from Test #17, which had less water (16 wt% vs. 20 wt%) and was noticeably more viscous. DuraLith recipes with high water content (to gain working time) may also incur settling.

Table 6.2. Chemical Composition of DuraLith Drum Sample Cores

Constituent	Drum Low Solids (top, #16-4)	Drum Low Solids (middle, #16-6)	Drum Low Solids (bottom, #16-11)	Drum High Solids (top, #17-2)	Drum High Solids (middle, #17-7)	Drum High Solids (bottom, #17-5)
	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g
Aluminum	70.1	66.0	64.7	62.0	61.2	61.5
Barium	1.45	1.41	1.38	1.38	1.37	1.41
Calcium	57.5	53.3	52.2	53.5	51.6	52.5
Cesium	0.00166	0.00168	0.00166	0.0015	0.00143	0.00155
Chloride	NM(a)	NM	NM	NM	NM	NM
Fluoride	NM	NM	NM	NM	NM	NM
Iodine	NM	NM	NM	NM	NM	NM
Iron	13.5	18.2	23.1	20.6	19.4	19.8
Lead	0.034	0.0446	0.0555	0.0447	0.0442	0.0422
Magnesium	9.69	9.18	9.02	8.86	8.65	8.68
Manganese	0.429	0.431	0.415	0.405	0.375	0.375
Phosphorus	<3.75	<3.36	<3.54	<3.24	<3.89	<3.75
Potassium	59.3	53.5	52.2	57.3	56.5	58.1
Rhenium	0.00623	0.00312	0.00287	0.0038	0.00394	0.00441
Silicon	205	225	234	187	226	227
Silver	NM	NM	NM	NM	NM	NM
Sodium	49.4	40.5	38.9	46	45.2	46.5
Strontium	0.739	0.694	0.675	0.688	0.681	0.69
Sulfur	<13.5	<12.1	<12.8	<11.7	<14.0	<13.5
Tin	2.36	2.15	2.1	2.39	2.43	2.29
Titanium	3.31	3.07	3.01	2.83	2.79	2.82

(a) NM = not measured

6.2 Phase Characterization

X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) with energy-dispersive spectrometry (EDS) analysis was performed on samples of each waste form to determine the sample mineralogy and to gain insight into the distribution of elements within the waste form.

Samples were prepared by first cutting a representative sample approximately 1.5 cm × 1.5 cm × 1.5 cm cube from the core sample using a diamond wafering saw lubricated with water. Next, the samples were ground down to a fine powder with a mortar and pestle. Crystalline Cerianite (CeO_2) was spiked in with the powdered sample at roughly 10 wt% as a standard to estimate the amount of crystals identified.

The samples were pressed into a back-mount holder to maximize random crystal orientation. A Bruker D-8 Advanced X-ray diffractometer system was used to collect the patterns. The diffractometer was configured with the following: goniometer radius of 500 mm, Cu target, Bragg-Brentano (focusing optics), 0.3° divergence slit, 2.5° Soller slits, and a position-sensitive detector with an angular range of 3° 2θ. The scan conditions used were: range of 5 to 90° 2θ, step size of 0.015° 2θ, and counting time of 1.5 s per step.

Each scan is shown with and without the background subtracted and the phase overlaid or underneath the patterns for ease of viewing and comparison. The amorphous content of the pattern is fit and removed during the background-subtraction process. The patterns are dominated by the internal standard which was spiked in at roughly 10 wt% per sample; this alone indicates the samples are dominated by an amorphous fraction. The crystalline phases identified in the Ceramicrete and DuraLith samples are quite different.

The three different cores of Ceramicrete (#5-5, #5-6, and #5-10) are very similar to each other. The following crystalline phases were identifiable by XRD in all three Ceramicrete cores: $MgKPO_4 \cdot 6H_2O$, periclase (MgO), polyhalite ($K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$), quartz ($SiO_2$), $K_4P_2O_7 \cdot 3H_2O$, $CaKPO_4$, and $KCaPO_4 \cdot H_2O$. Figure 6.1, Figure 6.2, and Figure 6.3 show the collected patterns with the background removed and the identified crystalline structures. In comparison, X-ray diffraction evaluation of laboratory-scale samples of Ceramicrete prepared for Waste Acceptance Testing showed K-Struvite ($KMgPO_4 \cdot 6H_2O$), periclase (MgO), and quartz (SiO_2) (Mattigod et al. 2011). The material is largely amorphous.

DuraLith cores (#17-2, #17-5, and #17-7) were all similar to each other. Quartz was the only crystalline phase positively identified by XRD in all three DuraLith cores. Chromium iron vanadate ($(Cr,Fe)VO_4$) was identified as a reasonable fit structurally, however the chemistry is unlikely. Microcline ($K_{0.94}Na_{0.06}Al_{1.01}Si_{2.99}O_8$) was identified as a trace phase, most notably in Core #17-5, with peaks at 21° and 27.25° 2θ. Microcline is likely an unreacted phase in the sand that was added. Lastly, zeolite A ($K_{12}Si_{12}Al_{12}O_{48}$) was loosely identified as a trace phase indicated in the patterns by leak low-angle peaks at 7.25° and 10.25° 2θ. Figure 6.4, Figure 6.5, and Figure 6.6 show the collected patterns with the background subtracted and the identified crystalline structures. In the Waste Acceptance Testing reported by Mattigod et al. (2011), quartz (SiO_2), albite ($NaAlSi_3O_8$), and calcite ($CaCO_3$) were identified in the laboratory-scale samples prepared for testing. The DuraLith is largely amorphous.

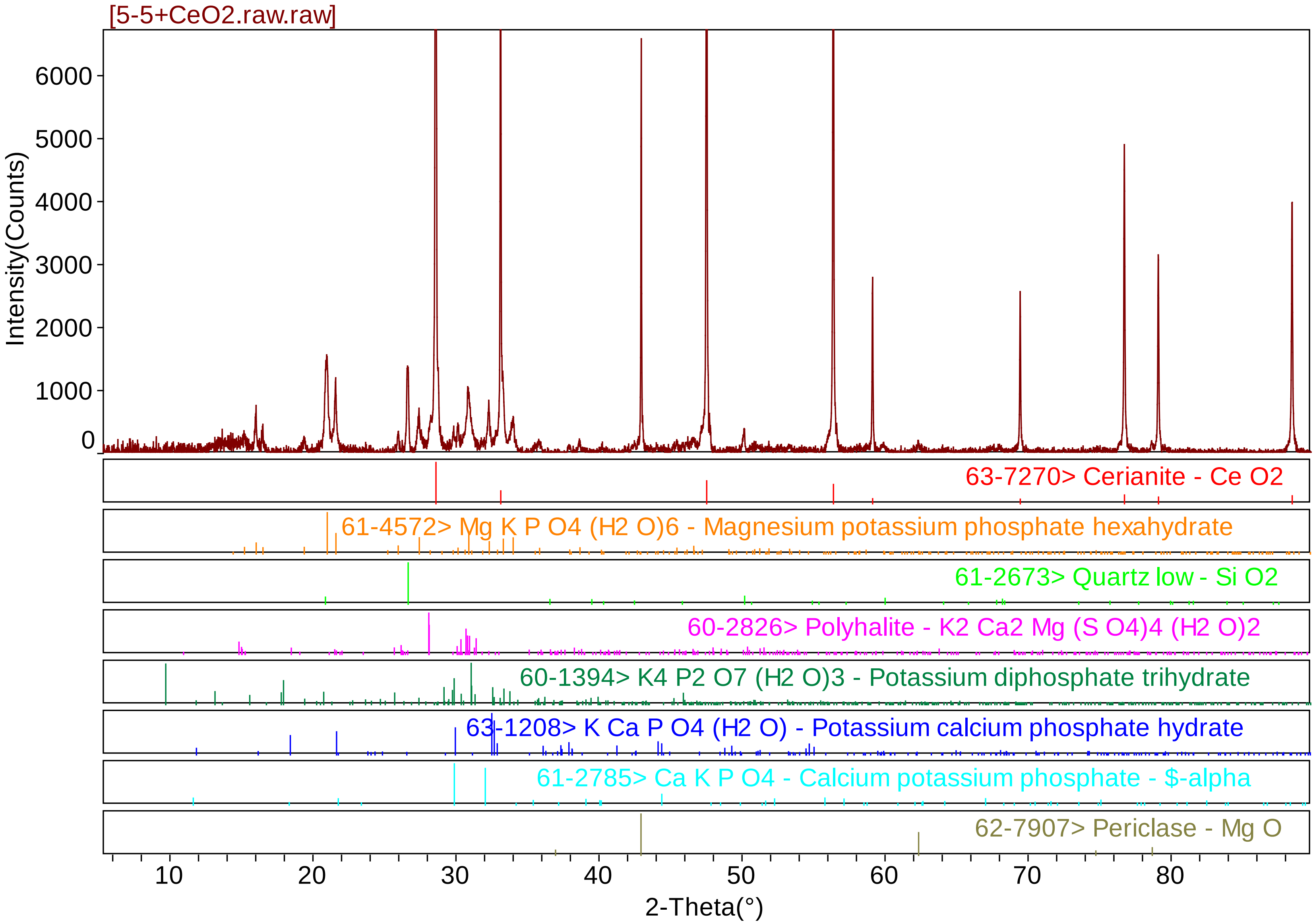

Figure 6.1. Background-Subtracted Pattern of Ceramicrete Core #5-5 with Identified Crystalline Phases

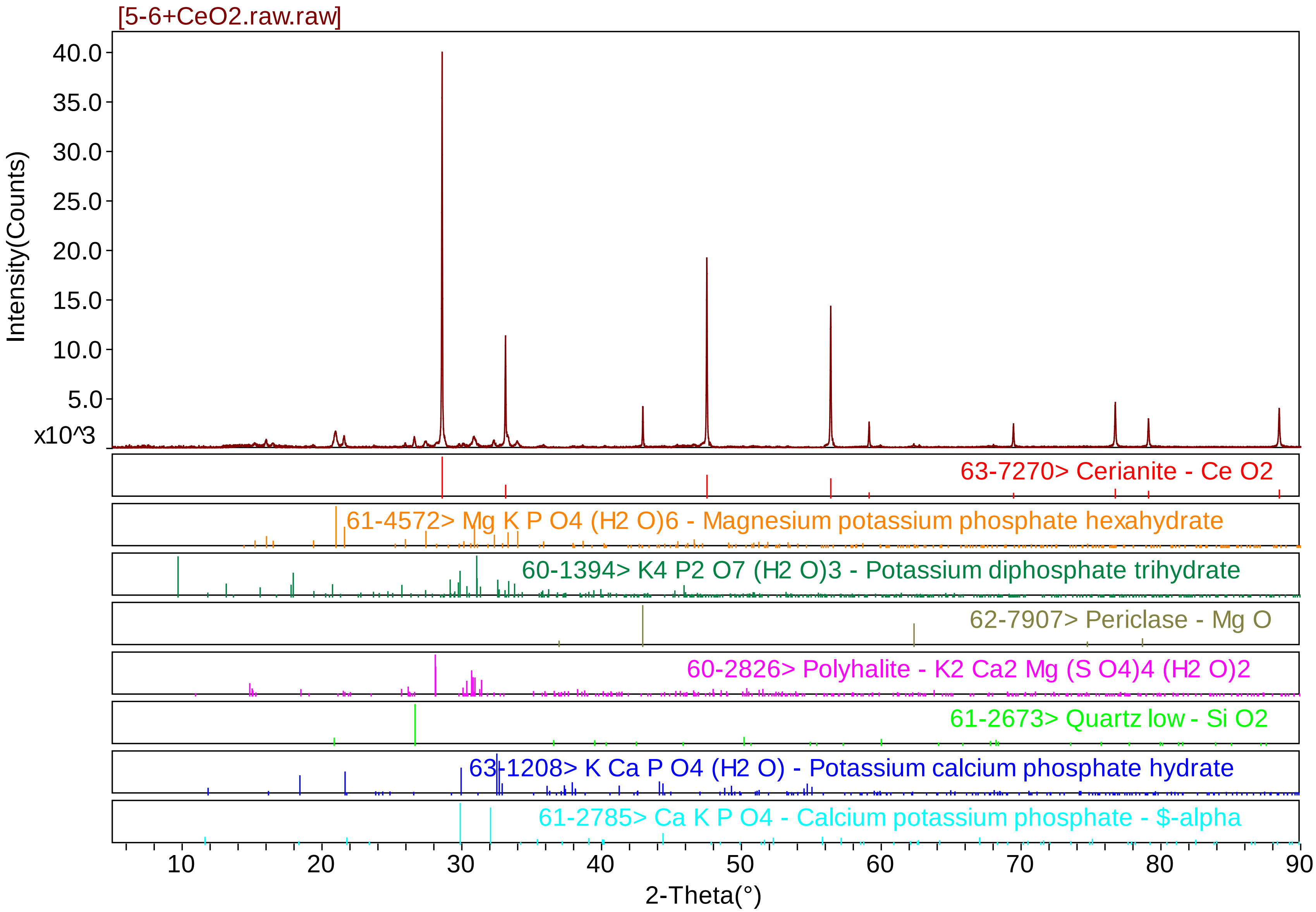

Figure 6.2. Background-Subtracted Pattern of Ceramicrete Core #5-6 with Identified Crystalline Phases

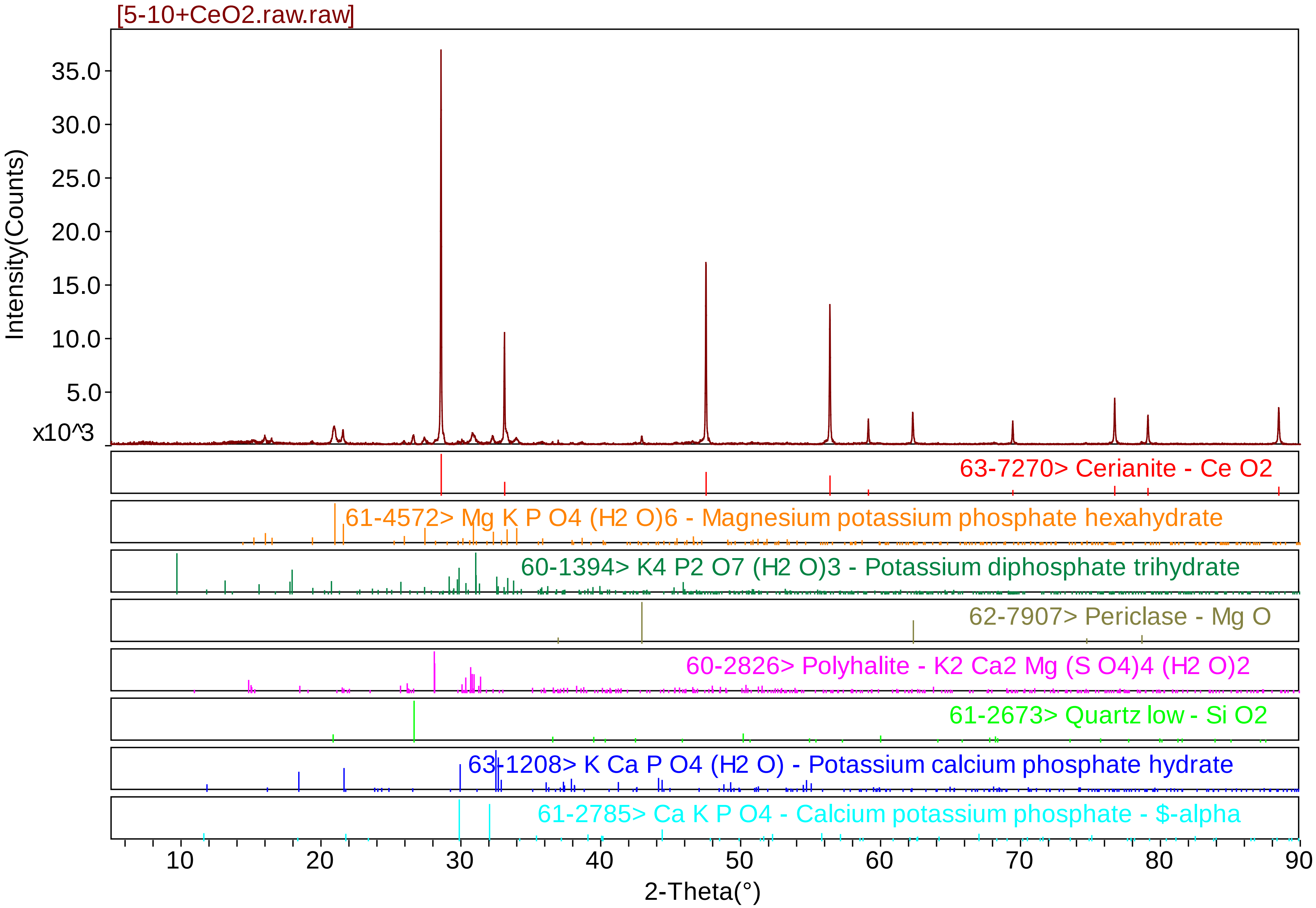

Figure 6.3. Background-Subtracted Pattern of Ceramicrete Core #5-10 with Identified Crystalline Phases

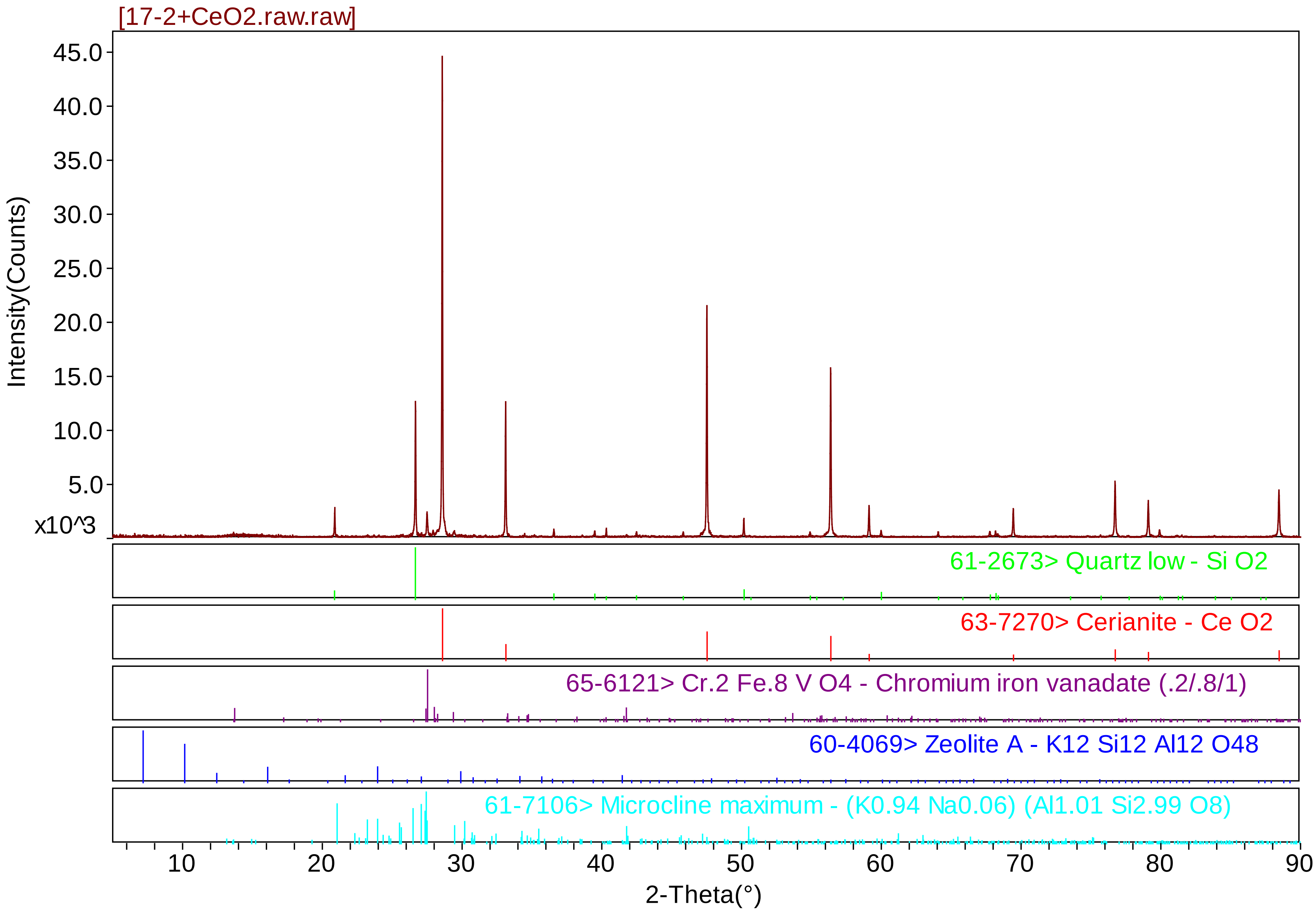

Figure 6.4. Background-Subtracted Pattern of DuraLith Core #17-2 with Identified Crystalline Phases

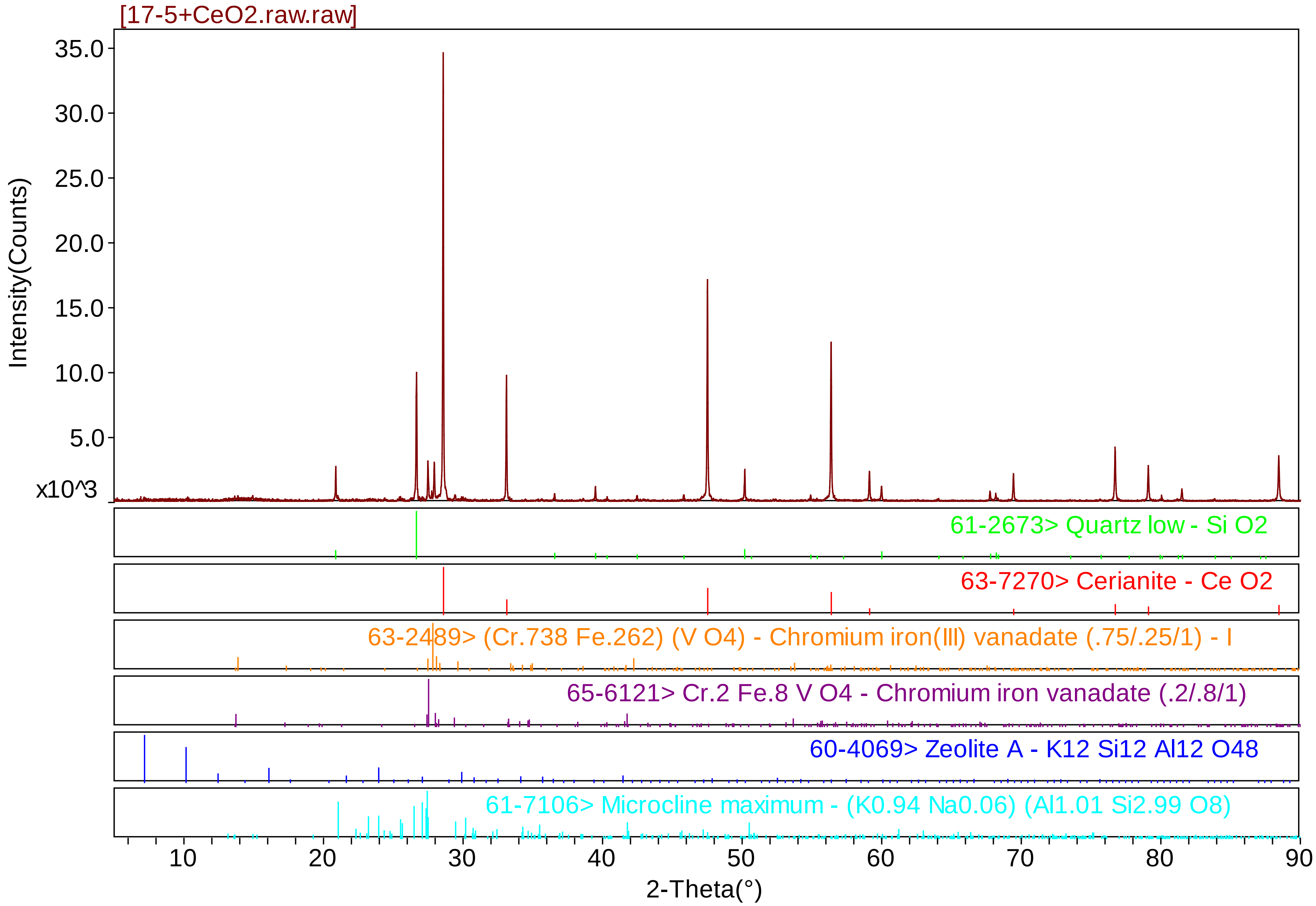

Figure 6.5. Background-Subtracted Pattern of DuraLith Core #17-5 with Identified Crystalline Phases

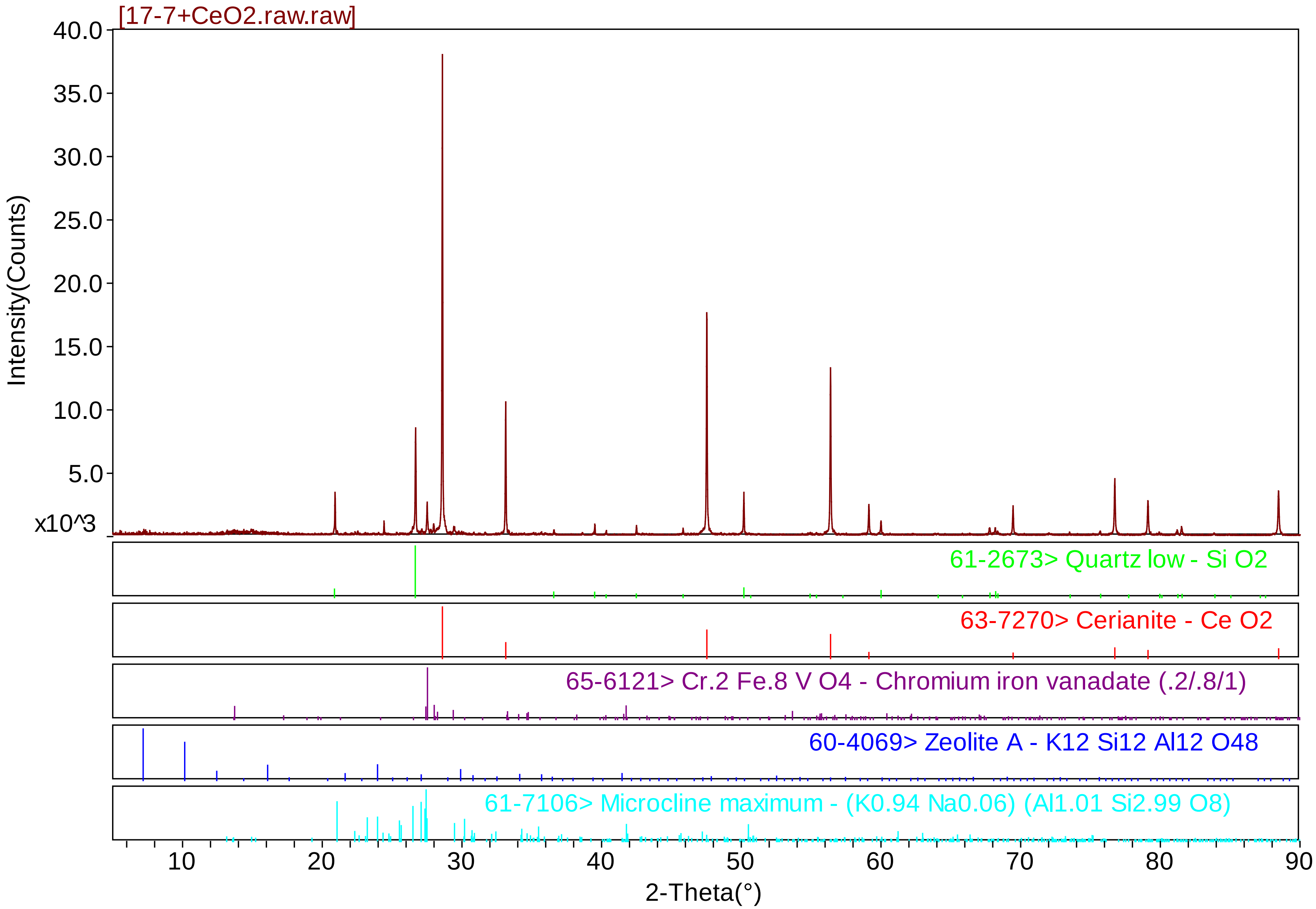

Figure 6.6. Background-Subtracted Pattern of DuraLith Core #17-7 with Identified Crystalline Phases

Figure 6.7 shows SEM images of Ceramicrete core 5-5 and Figure 6.8 shows SEM images of DuraLith core 17-2. EDS analyses were conducted on locations on each of the images to confirm the basic composition of the amorphous material that makes up most of both waste forms. XRD analyses confirmed that the solidified monoliths were mostly an amorphous solid. EDS analyses and spectra are in Appendix C.

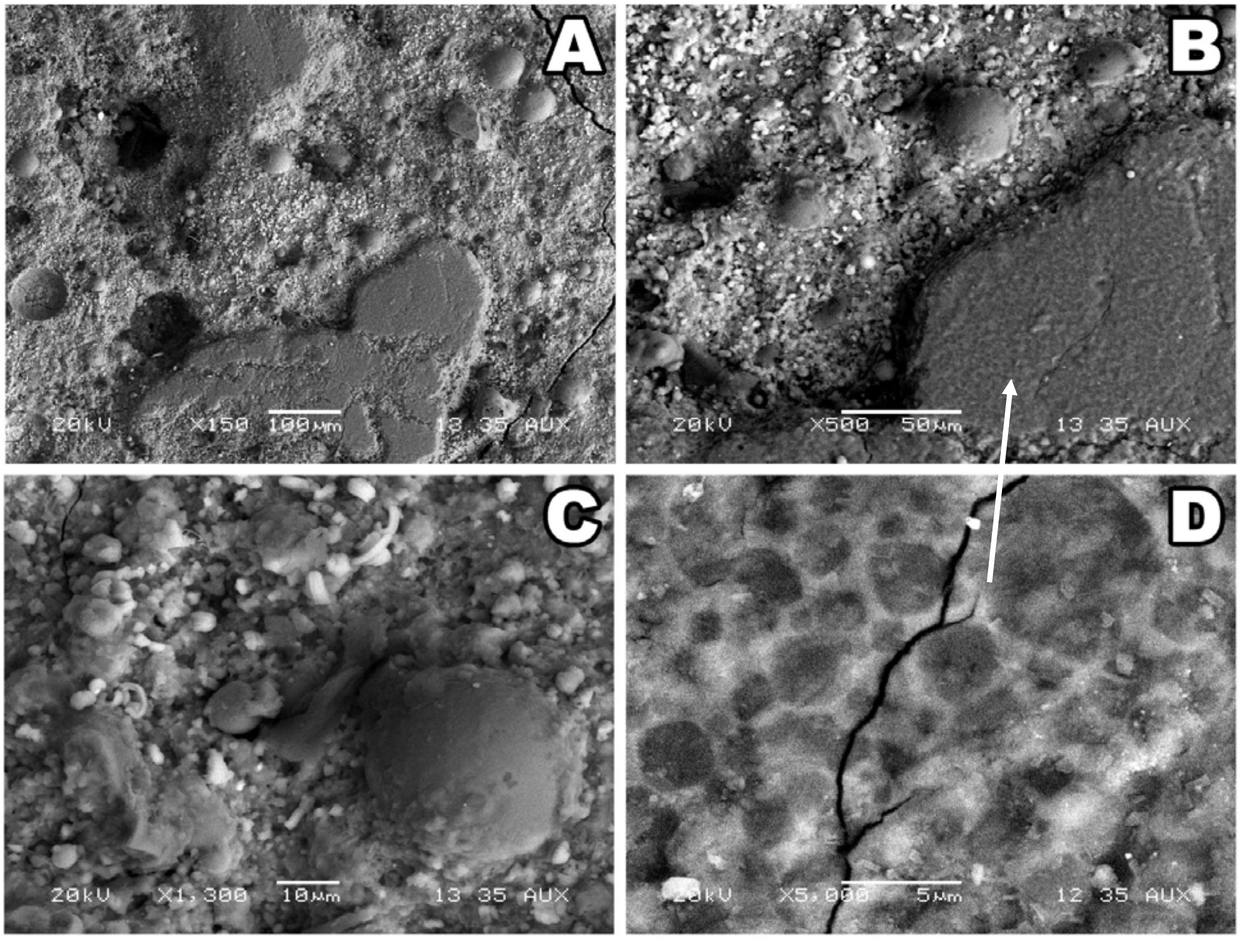

Figure 6.7. Backscatter Electron Images of Ceramicrete 5-5 in Cross Section Taken at A) 150X, B) 500X, C) 1,300X, and D) 5,000X. D) is a close-up of the large grain in the lower right of image B.

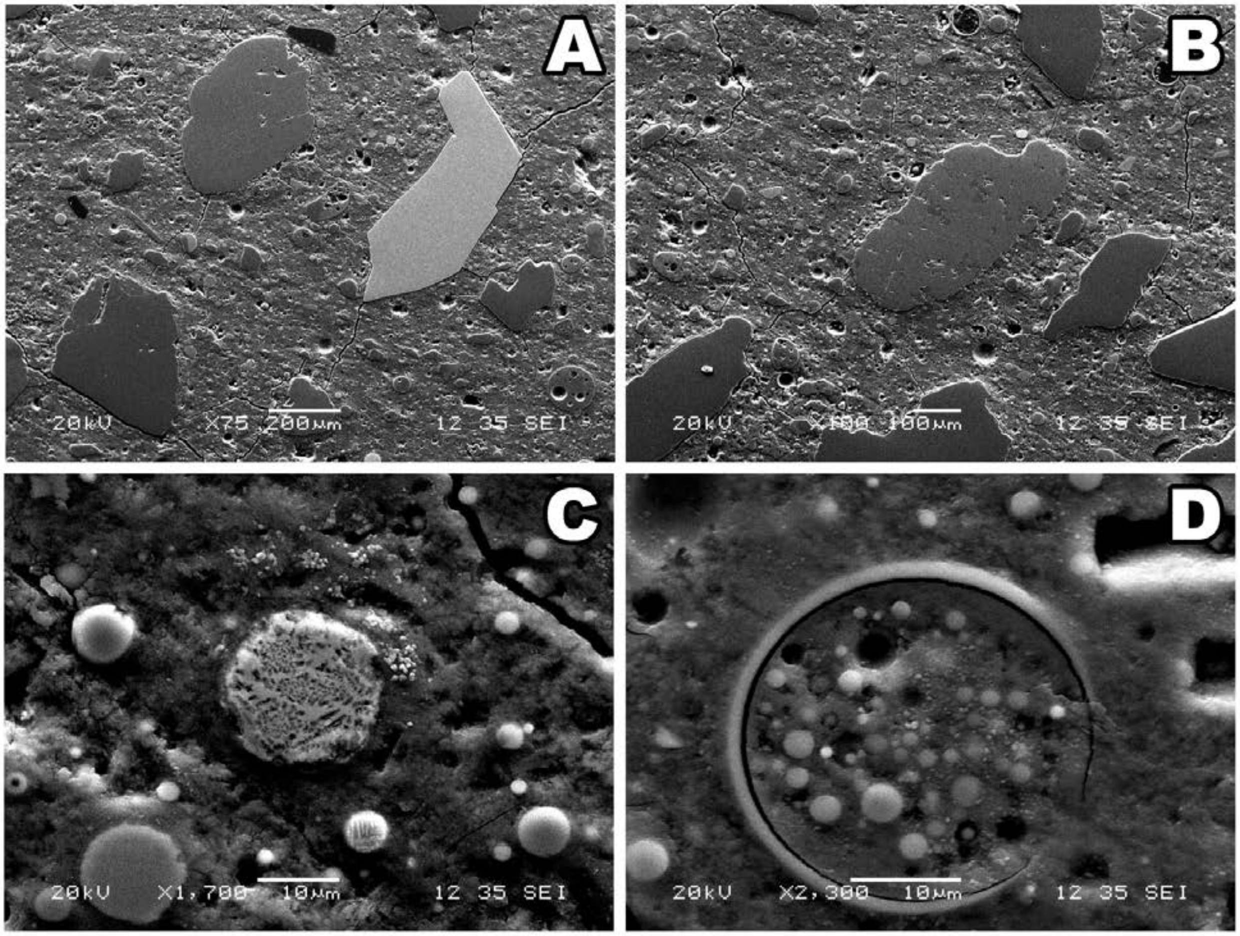

Figure 6.8. Secondary-Electron Images of DuraLith Core 17-2 in Cross Section Taken at A) 75X, B) 100X, C) 1,700X, and D) 2,300X

6.3 Compressive Strength

Compressive strength tests were conducted on Ceramicrete and DuraLith cylinders cored from the engineering-scale casting and from individual cylinders prepared by casting into 2" diameter × 4" long molds.

The compressive strength tests of the cylindrical specimens were conducted as specified by the American Society for Testing and Materials (ASTM) Standard Procedure C-39/C39M (ASTM 2010), which is used to determine the compressive strength of cylindrical samples. According to the test method, a sample is loaded into the testing apparatus so that the axis of the specimen is aligned with the center of thrust of the spherically seated block of the testing apparatus. Before testing the specimen, the load indicator is set to zero. The loading is applied continuously without any shock at a stress rate of 0.25 ± 0.05 MPa/s (35 ± 7 psi/s). The loading is maintained until the load indicator starts to decrease steadily, and the specimen displays a well-defined fracture pattern as illustrated in the C-39/C39M test method. The compressive strength is calculated by dividing the maximum load imposed on the specimen during the test by the average cross-sectional area.

The compressive strength tests were conducted using a servo-hydraulic universal test machine (Instron® MTS system). This apparatus has maximum load capacity of 20 kip (equivalent to 88.96 kN). The compressive load was applied until the complete fracture of the specimens was observed. The loading rate was set at 0.25 MPa per second (29437.5 N/min) as specified by ASTM C-39, *Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens*. Ceramicrete Compressive Strength Test Results

Table 6.3 lists the compressive strength test results for cores from the Ceramicrete drum (#5) and the Ceramicrete box with a high solids loading (#9). Also shown are compressive strength results from Ceramicrete specimens prepared by casting into 2" diameter × 4" long cylindrical molds. The compressive strengths for the core samples are fairly consistent from top to bottom of the drum and box pours with the exception of the core at the very top surface of the high-solids box #9. The sample from the top surface shows a lower compressive strength though it is still above the 3.45 MPa minimum. Densities are consistent from top to bottom at an average 1.83 g/cm^3.

Table 6.3. Compressive Strength and Density Results for Ceramicrete Tests

	Compressive Strength (MPa)	Density (g/cm^3)
Drum Core Samples (Run #5)		
5-5 RHS* Top Diagonal	13.2	1.82
5-6 RHS Middle Diagonal	13.9	1.83
5-10 LHS* Bottom Diagonal	15.0	1.82
Box Core Samples (High Solids #9)		
#9 Core #1 Top RHS	4.5	1.83
9-2 RHS Top Diagonal	15.8	1.82
9-3 RHS Middle Diagonal	11.6	1.82
9-7 LHS Bottom Diagonal	13.3	1.85
Cast Cylinders Run #6		
Test 6 P-3-223-1-C 2-23-11	2.0	1.72
Test 6 P-6-223-1-C 2-23-11	1.8	1.70
Test 6 P-8-223-1-C	1.7	1.68
Cast Cylinders Run #9		
Test 9 P-2-223-1-C 2-24-11	1.1	1.55
Test 9 P-2-223-3-C 2-24-11	1.5	1.57
Test 9 P-2-223-8-C 2-24-11	1.4	1.54
Laboratory-Scale Specimens		
ANL* Ceramicrete (Singh et al. 2011)	18.6 ± 7.1	1.99
PNNL Ceramicrete, 28 Days (Mattigod et al. 2011)	6.8 ± 4.2 (9.5(a) ± 1.2)	2.07
PNNL Ceramicrete, 90 Days	19.0 ± 4.0	—

*RHS = right-hand side, LHS = left-hand side; ANL = Argonne National Laboratory

(a) Excluding two tests below 3.45 MPa.

The results for the cast Ceramicrete cylinders are affected by the swelling observed with the smaller samples cast into molds. As noted in Sections 4.2.2 and 4.2.3, these cast specimens expanded and formed a friable top. As shown in Figure 6.9, the cast specimens did not show a sharp break as was observed with the core cylinders from the engineering-scale core samples.

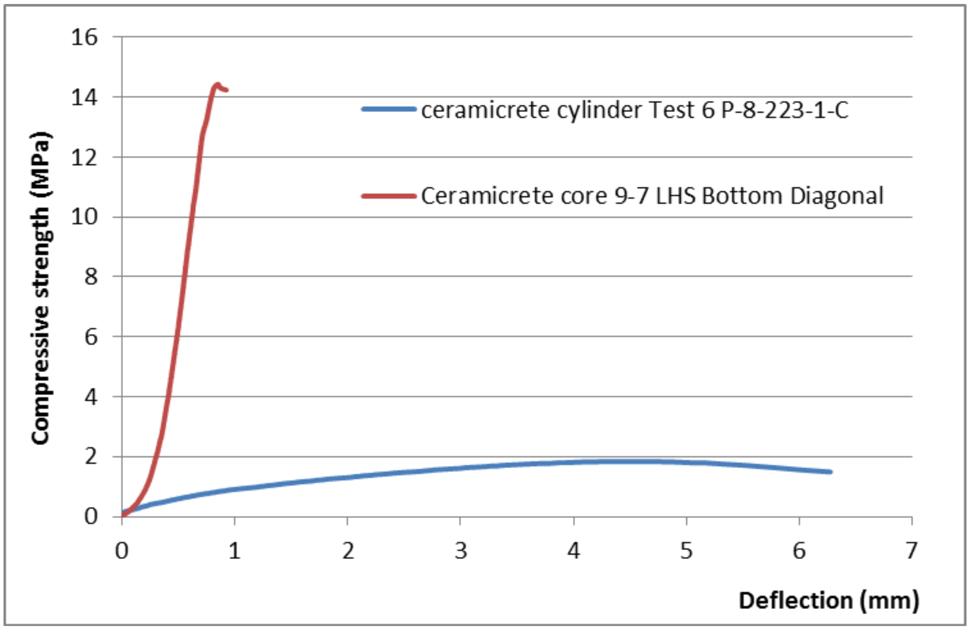

Figure 6.9. Comparison of Compressive Strength versus Deflection for Ceramicrete Core and Cylinder Specimens

6.3.1 DuraLith Compressive Strength Test Results

Table 6.4 lists the compressive strength test results for cores from the DuraLith drum tests and for DuraLith specimens cast into 2" diameter × 4" long molds. There are no observable trends in compressive strength or density from top to bottom in either of the DuraLith drums. The average compressive strength is 27.6 MPa for the Run #16 core samples and 32.3 MPa for the Run #17 core samples. The core samples with the higher solids content and greater density (Run #17) had a slightly higher strength, but the difference did not exceed 95% confidence limits. There was essentially no difference between the cast cylinders. Compressive strengths for the cast cylinders are lower than for the core samples. All samples exceeded the requirement, >3.45 MPa.

Table 6.4. Compressive Strength and Density Results for DuraLith Drum Tests

	Compressive Strength (MPa)	Density (g/cm^3)
Core Samples Run #16		
Sample 16 Core-4 LHS Top	27.6	1.85
16-6 Middle Diagonal RHS	34.0	1.81
16-7 Bottom Diagonal RHS	24.7	1.84
16-11 Bottom Diagonal LHS	24.1	1.84
Core Samples Run #17		
Sample 17 Core-2 RHS Top	39.7	1.91
17-7 Center Diagonal LHS	25.3	1.92
17-5 Bottom Diagonal RHS	31.8	1.92
Cast Cylinders Run #16		
DuraLith-1 Test 16 3-10-11	14.3	1.85
DuraLith-5 Test 16 3-10-11	13.5	1.88
DuraLith-9 Test 16 3-10-11	14.1	1.87
Cast Cylinders Run #17		
Test 17 3-18-11 DuraLith 16.45% #3	13.9	1.95
Test 17 3-18-11 DuraLith 16.45% #6	17.7	1.94
Test 17 3-18-11 DuraLith 16.45% #8	9.6	1.94
Laboratory-Scale Specimens		
CUA S1-6X5, 21 Days (Gong et al. 2011)	101	—
CUA S1-6X5, 45 Days	132	—
PNNL DuraLith, 28 Days (Mattigod et al. 2011)	23.3 ± 6.3	2.01
PNNL DuraLith, 90 Days	28.2 ± 12.5	—

6.4 Leach Testing – Waste Form Diffusivity – EPA Draft Method 1315

The draft EPA Method 1315 (EPA 2009b) is a dynamic leach experiment that consists of submerging a monolithic sample in deionized water at a fixed liquid-volume to solid-surface-area ratio. According to the method (EPA 1315) the sampling was done at fixed periods of time at cumulative leaching times 0.08, 1, 2, 7, 14, 28, 42, 49, and 63 days. At each sampling interval, the leaching solution was removed and replaced with fresh deionized water. A schematic of this process is shown in Figure 6.10.

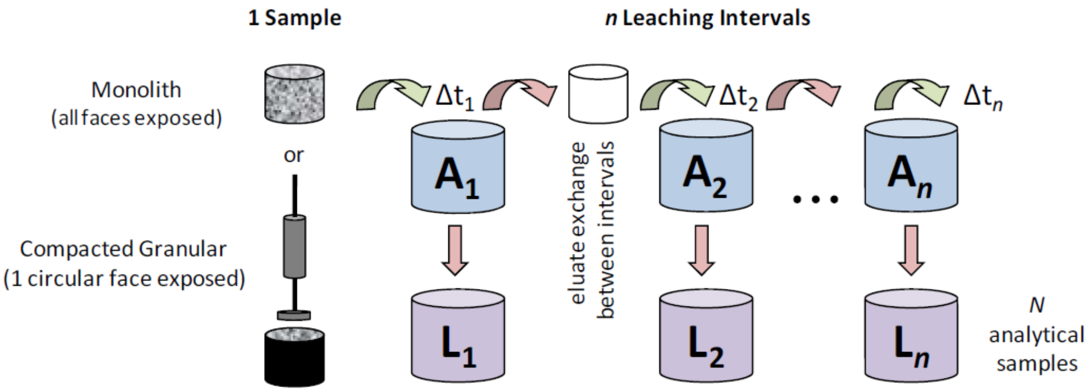

Figure 6.10. EPA 1315 Testing Scheme

The geometric surface area used in this test method is calculated based on the cylindrical dimensions of the sample. At each of the nine pre-determined leaching intervals, the sample mass was recorded, and the leaching solution was changed. This method is similar to ANSI/ANS 16.1 (ANSI 2003), but the leaching intervals are modified, and the process of mass transfer can be interpreted by more complex release models that account for physical retention of the porous medium and chemical retention at the pore wall through geochemical speciation modeling.

In this test, cylindrical monolith samples (~2" diameter by ~4" height) were placed into the centers of leaching vessels and mixed with deionized water to maintain a solid-to-solution ratio of 9 ±1 mL of leachant per cm^2 of sample. A sample stand and holder were used to maximize the contact area of the sample with the leaching solution. In between the sampling/replacement intervals, the experimental vessels were covered with lids. The solution exchanges were made at leaching times of 2 hours (0.08 day) and 1, 2, 7, 14, 28, 42, 49, and 63 days in accordance with the method. Chemical analyses of the leachates were conducted following filtration using a 0.45-µm syringe filter.

The observed diffusivity for each constituent was calculated using the analytical solution, Equation 6.1, for simple radial diffusion from a cylinder into an infinite bath as presented by Crank (1986).

$$D_i = \pi \left[\frac{M_{ti}}{2\rho C_0(\sqrt{t_i}-\sqrt{t_{i-1}})}\right]^2 \tag{6.1}$$

where:
D_i = mean observed diffusivity of a specific constituent for leaching interval, i (m^2/s)
M_{ti} = mass released per unit area of the specimen during leaching interval i (mg/m^2)
t_i = cumulative contact time after leaching interval i (s)
t_{i-1} = cumulative contact time after leaching interval $i-1$ (s)
C_o = initial leachable content (mg/kg)
ρ = sample density (kg/m^3)

The mean observed diffusivity for each constituent can be determined by taking the average of the interval observed diffusivity with the standard deviation.

The leachability index LI, the parameter derived directly from immersion-test results, evaluates diffusion-controlled contaminant release with respect to time. The LI is used as a criterion to assess whether solidified/stabilized waste is likely to be acceptable for subsurface disposal in waste repositories. The LI was calculated with Equation 6.2:

$$LI_n = -\log[D_n], \tag{6.2}$$

where LI is the leachability index and D_n is the effective diffusivity for elements of interest (cm^2/s) during the leach interval n.

6.4.1 Ceramicrete Leach Test Results

Figure 6.11 shows the Na leachability index data for three core samples and four 2" × 4" cylinders. The core samples leached were from the 55-gallon drum, and the 2" × 4" cylinders were cast when the low-solids and high-solids 1/8th-scale boxes (2' × 2' × 3') were poured.

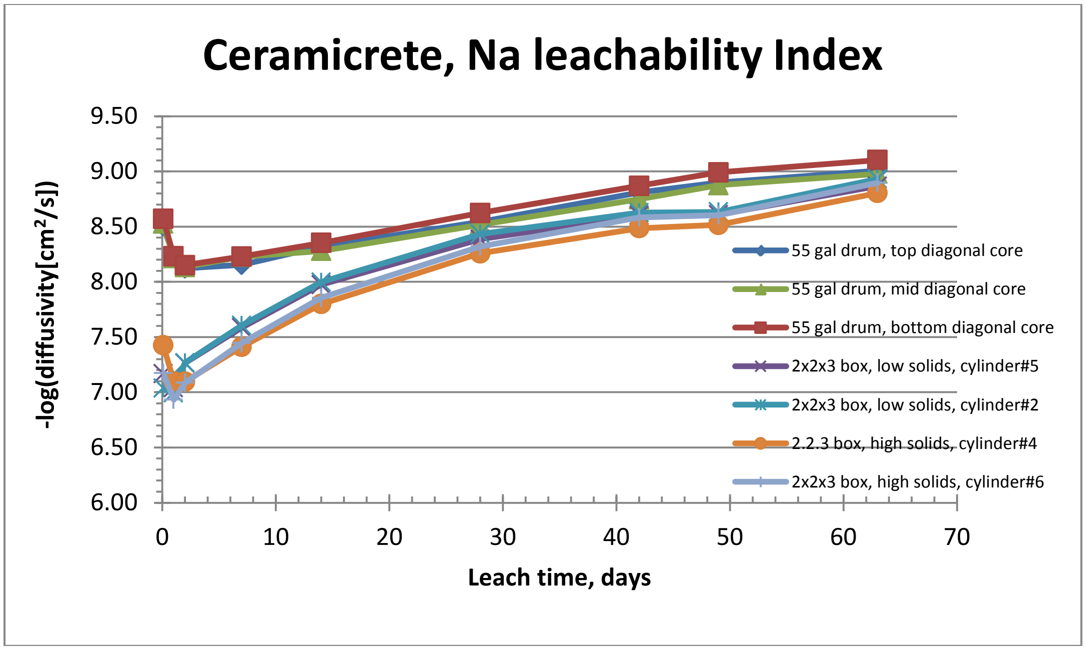

Figure 6.11. Ceramicrete, Na Leachability Index from EPA 1315 Testing

The leachability index is the negative logarithm of the diffusivity, –log(*D*). A high leachability index means contaminants leach out of the material slowly—the diffusivity is low. Other reports have shown diffusion data directly. Figure 6.12 shows the same data plotted as diffusivity rather than leachability index.

Figure 6.12 shows that the leaching results from all the engineering-scale boxes were very similar, whether for low solids or high solids. The results from the 55-gallon drum test were different from the engineering-scale boxes, but very similar among the three separate leach tests.

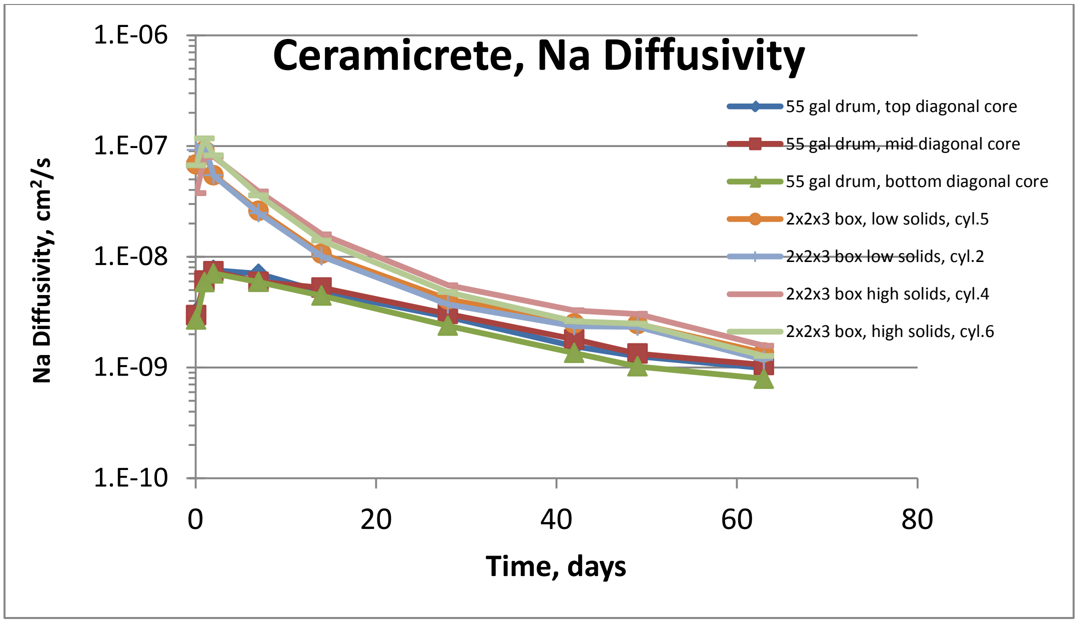

Figure 6.12. Sodium Diffusivity of Ceramicrete from EPA 1315 Testing

Figure 6.13 shows representative 55-gallon drum and engineering scale box data on the same plot with previous laboratory results collected as part of the waste acceptance testing program (Mattigod 2011). The lab results and 55-gallon drum diffusivities follow a similar path, with the 55-gallon drum Ceramicrete having a somewhat lower diffusivity than the lab tests throughout the leach. The diffusion rate from cylinders cast during the 1/8th-scale test boxes was significantly higher early in the leach test and then decreased to nearly the same as the lab tests near the end of the 63-day leach.

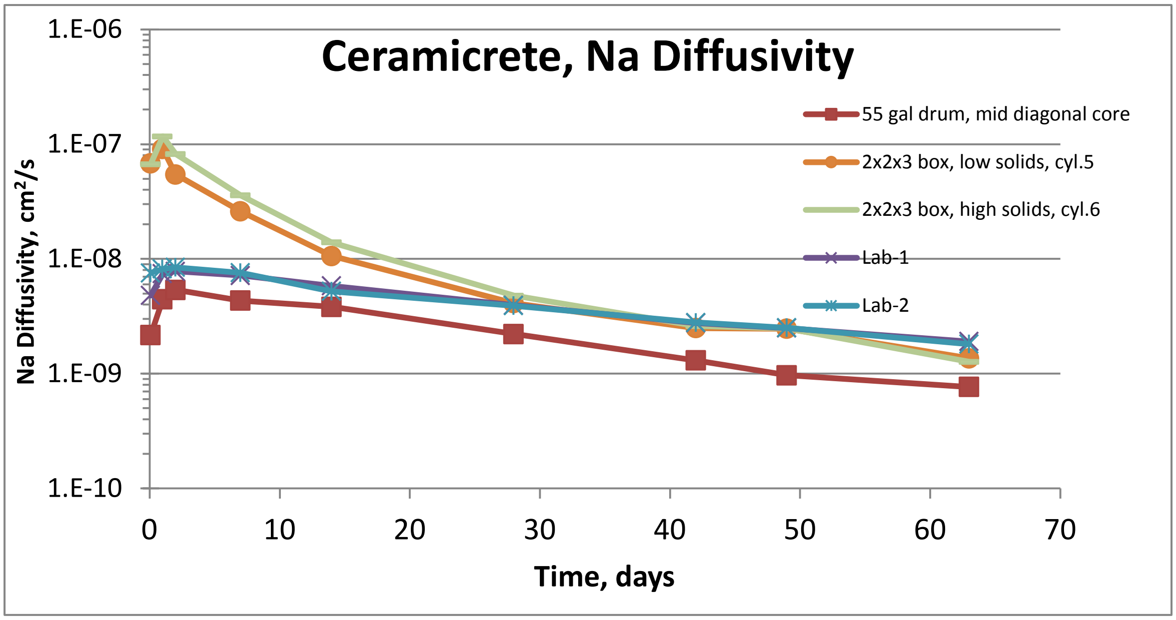

Figure 6.13. Sodium Diffusivity of Ceramicrete from Scale-Up Testing and Lab Testing

6.4.2 DuraLith Leach Test Results

Figure 6.14 shows the Na leachability index data for seven DuraLith core samples. The core samples leached were from the drum made with 16.45 wt% water (baseline) using the high-shear mixer and from the drum made with the high water content (21 wt%) using the high-shear mixer.

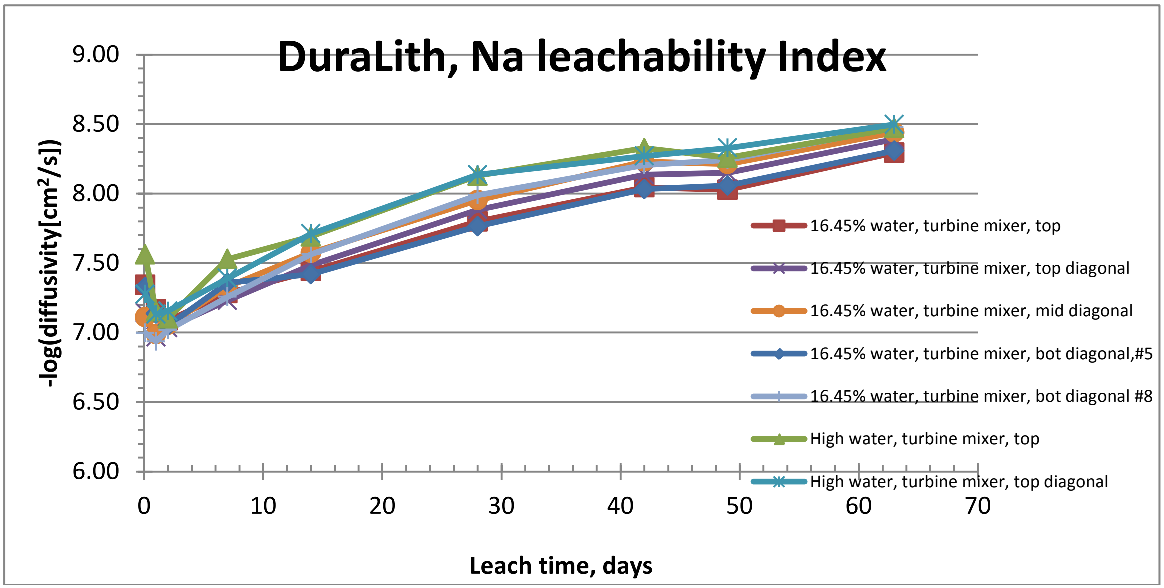

Figure 6.14. Sodium Leachability Index in DuraLith from EPA 1315 Testing

Figure 6.15 shows the same data plotted as diffusivity rather than leachability index.

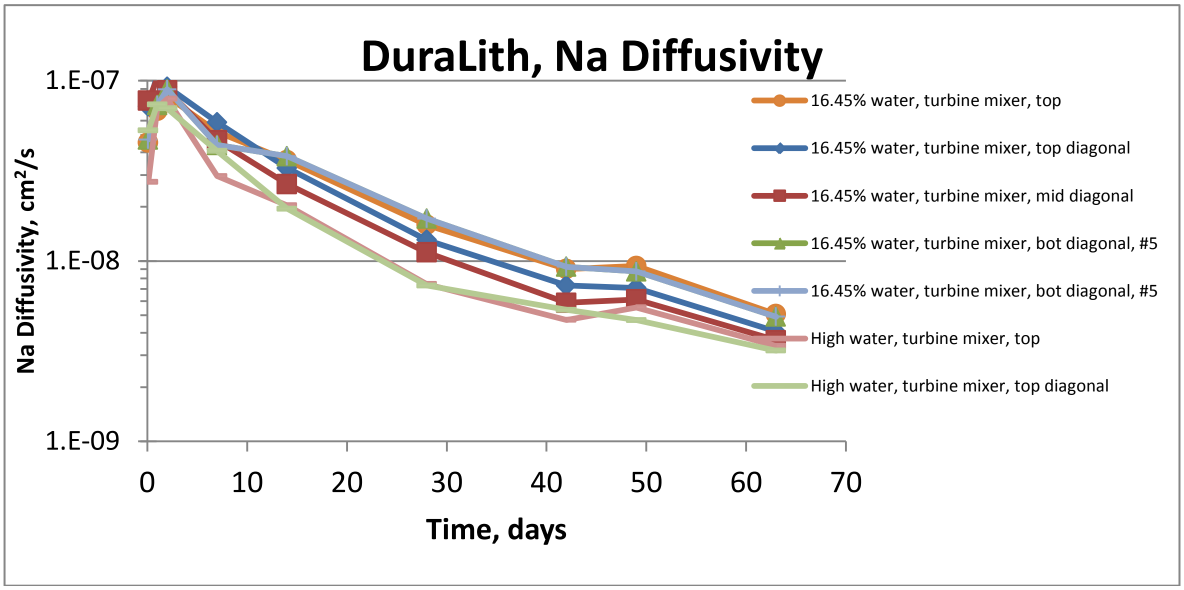

Figure 6.15. Sodium Diffusivity in DuraLith from EPA 1315 Testing

Figure 6.15 shows that the leaching results from both of the 55-gallon drum tests using the high-shear turbine mixer were similar, with the low-solids material having a bit lower diffusivity than the high-solids material.

Figure 6.16 shows high-solids and low-solids data on the same plot with previous laboratory results collected as part of the waste acceptance testing program (Mattigod 2011). Both large-scale tests with DuraLith indicated higher diffusivities than the lab tests with DuraLith.

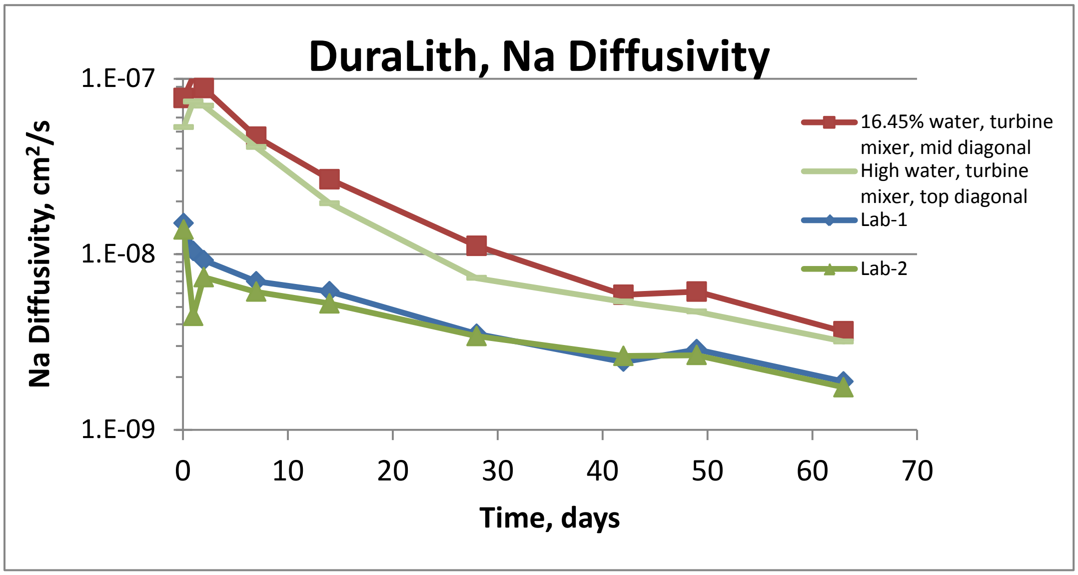

Figure 6.16. Sodium Diffusivity in DuraLith from Scale-Up Testing and Lab Testing

7.0 Simulant Analyses

Samples of the liquid simulants (1 M Na and 6 M Na) were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively-coupled plasma mass spectrometry (ICP-MS). Results of the analyses are shown in Table 7.1

Table 7.1. Chemical Analyses for 1 M and 6 M simulants.

	1 M Sodium Simulant for Ceramicrete		6 M Sodium Simulant for DuraLith	
Component	Target (g/L)	Measured (g/L)	Target (g/L)	Measured (g/L)
Na	22.990	23.1	137.94	144.7
Al	2.534	2.1	15.20	12.8
Si	0.053	<0.0655	0.32	<0.347
K	0.023	0.422	0.14	2.68
OH^-	6.766	NM	40.60	NM
NO_3^-	20.336	NM	122.02	NM
CO_3^{2-}	1.368	NM	8.21	NM
Cl^-	0.798	NM	4.79	NM
NO_2^-	0.552	NM	3.31	NM
P (for PO_4^{3-})	0.213	0.205	1.28	1.32
S (for SO_4^{2-})	0.141	0.178	0.85	0.98
Re	0.003	0.0033	0.02	0.0155
TOC	5.258	NM	31.55	NM

8.0 Results and Discussion

The primary objective of the engineering-scale demonstration was to evaluate several characteristics of the candidate secondary waste forms, Ceramicrete and DuraLith, that would affect the final design of the ETF so that down selection could be better informed and a better estimate for the cost of a treatment facility could be prepared. Below are identified results from the testing and subsequent data evaluation.

Formulation—the first result for both waste forms, Ceramicrete and DuraLith, was that the formulations developed from laboratory-scale testing did not have sufficient working time. The initial formulations provided by the developers set up too quickly to be poured into the final waste container at full scale. Ceramicrete began to set within 4 minutes and could no longer pour within 15 minutes. Within 4–5 minutes after the slurry was mixed DuraLith was too hard to insert a plastic divider into the bucket.

Both waste forms had to be reformulated to give them longer working times. The first formulations that provided sufficient working time to allow large scale testing were taken forward for the 55-gallon drum testing. The technology developers provided input to direct the reformulation but there was no opportunity to optimize either waste form. All performance results should be considered as minimum achievable performance. Improvements should be expected with further development.

Mixing—the ribbon mixer did not provide adequate mixing of the liquid and powdered solids to achieve a homogeneous mix with either the Ceramicrete or DuraLith waste forms. Both waste forms had significant amounts of undispersed solids in the form of wetted clumps of powder in the final mixed slurry. During the cure the clumps of unmixed powders became incorporated in the cured monolith. With the black DuraLith the locations of unmixed powders were identifiable as light spots, but were not otherwise significantly different. They were no longer powders; they seemed hardened similar to the rest of the monolith. In Ceramicrete the unmixed lumps were essentially the same color as the cured monolith and could not be distinguished.

The effect of the unmixed solids on the overall waste form performance could not be established by the performance testing on the cured waste forms. The unmixed solids were most prevalent at the top of the monolith, so if there were an effect the compressive strength would be expected to decrease. Samples from the Ceramicrete drum (Test #5) indicate a minor reduction in strength, 13.2 vs. 15 MPa; however, compressive strength measurements on cores taken from the 1/8th-scale test box show the top diagonal was stronger than cores taken from the middle or bottom sections of the monolith. Both differences are relatively small and not statistically significant. (Note: the Ceramicrete sample taken directly into the top of the waste form did show a significantly lower (but still above required minimums) compressive strength than the internal cores. This is attributed to the thin crust of softer salts that formed on the surface of the Ceramicrete (see Figure 4.14).

Even if the inadequate mixing did not affect the final waste form performance, it is an issue that should be addressed in the final design. The ribbon mixer employed for the engineering-scale test matched the scale-up concepts for both candidate waste forms. Prescribed amounts of waste and powdered solids could be loaded into the mixer and mixed batchwise. When the mixing was complete the entire contents of the mixer could be dumped into the final container, filling the container to the desired fill ratio. Two basic variables determine the amount of mixing that can be achieved with such a system:

mixing time and mixing intensity. For the engineering-scale demonstration mixing time was limited by the relatively short working times for both waste forms. Only with modifications could usable formulations for the waste forms be prepared. To make sure the material did not set up within the equipment, mixing times were limited to about 20 minutes. To achieve better mixing a mixer with much higher mixing intensity should be employed.

Ceramicrete and DuraLith displayed characteristics of shear thinning. That is, the setting up of the material was retarded or even reversed by shearing the slurry with either continued mixing or remixing. The effect was more noticeable for Ceramicrete. More testing would need to be conducted to determine the effect of shearing on the final formulations, especially if Ceramicrete were selected, since it appears more sensitive to shearing.

Flowability—The mixed slurries for both waste forms were initially expected to be more similar to concrete than they proved to be. A prime objective was to determine whether the mixed slurry would completely fill the final waste container or the farthest corners would remain unfilled and there would be voids within the waste. Both candidate waste forms are very fluid when initially mixed. They pour more like water than concrete. The initial concerns about completely filling the waste container were removed.

Working time—Both initial formulations provided by the technology developers had to be modified to achieve adequate working time to conduct larger-scale testing. For Ceramicrete additional working time was achieved by adding boric acid to the makeup. For DuraLith the accelerated set was attributed to a different, more reactive and finer particle-size composition of blast furnace slag. Substituting a different "cement forming" (pozzolan) binder, ASTM Class C fly ash, for 70% of the blast furnace slag extended the working time. Working time is an attribute for each material that has not been fully considered nor optimized during the lab-scale developments.

Heat Generation—Section 5 shows the cooling profiles for 55-gallon drum scale makeups of both Ceramicrete and DuraLith. Figure 5.2 shows the cooling curve for Ceramicrete and Figure 5.3 shows the cooling curve for DuraLith. The peak internal temperature for Ceramicrete was higher and developed faster than the peak internal temperature for DuraLith. The data from these curves could be modeled to determine the heats of reaction and kinetics for the curing reactions and the thermal conductivity of the waste. These parameters could then be used to model the peak internal temperature for a full-scale waste form. Such modeling will be necessary when selecting the volume (and configuration) of a final waste form. Some materials (e.g.. concrete) are negatively affected if the curing temperatures rise above some critical temperature. At this point, the critical curing temperatures for Ceramicrete or DuraLith are unknown.

Segregation—Segregation was initially imagined to occur when viscous materials filled a box and layers folded upon one another like taffy or poured glass filling a canister. Since both waste forms were very fluid during the pour, segregation via this mechanism did not occur. Visually there were some differences within the waste forms that displayed types of segregation, but segregation was not measurable as differences in density. Figure 4.14 shows the cross section of a thin crust on the top of Ceramicrete Test Box #3. Also, an accumulation of voids (pits) are seen in the upper few inches of the waste that could have been left by trapped air bubbles. Figure 4.16 shows apparent segregation of white solid phases along lines among the more prevalent tan/brown phase of the Ceramicrete. Figure 4.34 shows an accumulation of light material that are the residues from unmixed powdered solids discussed in "Mixing" above. Figure 4.35 shows pockets (aka voids or pits) within the cured DuraLith. Some of these contained collected pore water. These voids are attributed to trapped air bubbles incorporated into the slurry while mixing with the high-shear mixer Figure 4.36 shows what appears to be an accumulation of the coarser sand that settled to the bottom of the low-solids (21 wt% water) drum of DuraLith.

Free Liquids—when Ceramicrete was covered during the cure, condensate accumulated on the surface. The 55-gallon drum, Test Box #2, and all the bucket-scale tests had layers of accumulated water when the materials were covered during the initial overnight cure. When the covers were left off the condensed liquid evaporated so there were no free liquids. DuraLith did not accumulate condensate.

Leachability—Both waste forms demonstrated a sodium leachability index above 6 as required for disposal in IDF. The Ceramicrete 55-gallon drum test demonstrated a leachability index better than that achieved during waste acceptance testing at lab scale. Leach tests for the Ceramicrete 1/8th-scale boxes were conducted on the 2" × 4" cylinders collected during the pour, not on a core from the monolith. These cylinders had demonstrated an unusual expansion during the cure. The drum scale and 1/8th-scale boxes displayed some evidence of stresses that could have caused expansion (see Figure 4.5), but did not expand like the cylinder samples (see Figure 4.10). It is unknown whether the differences that caused the expansion also affected the leachability index negatively. The DuraLith leachability test results were similar to one another for all seven tests. Only core samples cut from the drum-scale monoliths were tested. A slight difference was observed between the high-solids and low-solids makeups, with the low-solids makeup unexpectedly having a better leach index. All of the large-scale DuraLith tests demonstrated a higher Na diffusivity (poorer Na leachability index) than the lab-scale sample tests for the waste qualification testing. The reason for the poorer leaching performance is not yet known. It must be remembered that both Ceramicrete and DuraLith formulations prepared for the engineering-scale testing were prepared solely to achieve a usable working time. No performance optimization had been conducted.

Mineralogy—XRD analyses of both Ceramicrete and DuraLith are consistent with the descriptions of the solidifying mechanisms described by the technology developers. In short, each waste form is essentially an amorphous solid matrix that includes some crystalline particles that were in the initial makeup, i.e., sand particles. The solid monolith is not crystalline.

Waste form performance—Both Ceramicrete and DuraLith samples met the waste form performance criteria for Na leachability (LI > 6) and compressive strength (> 3.54 MPa), and after open exposure during curing there were no free liquids. There is also a performance requirement for Tc leachability. For this non-radioactive large-scale testing, Re was used as a surrogate for Tc. The Re leachability data for both Ceramicrete and DuraLith did not comply with the model assumptions for EPA 1315 testing. During the leach tests more Re leached from the monolith than is consistent with the EPA model as a semi-infinite solid. Therefore, the data cannot really be used to determine whether the monoliths met or failed performance standards for leach resistance.

We asked the Ceramicrete waste-form developers at Argonne National Laboratory and the DuraLith waste-form developers at the Catholic University of America to provide some insights regarding the observations from the Ceramicrete and DuraLith engineering-scale demonstrations. Their perspectives are included in Appendix D.

MSE's report on the conduct of engineering-scale tests at their facility is included in Appendix E.

9.0 Conclusions

Two primary conclusions derive from the large-scale testing of Ceramicrete and DuraLith as candidate secondary waste forms:

1) **Both candidates were successfully demonstrated at larger scale**. Despite the remaining unanswered questions this should be the primary conclusion. A process can be designed for either waste form that can generate boxes of solidified waste that will meet the requirements for compressive strength, absence of free liquids, and sodium leachability. (Tc leachability could not be verified from the results of this testing, but should be achievable based upon laboratory testing.)

2) **Both candidates are still too immature to complete a detailed final design**. The process steps to prepare large volumes were conducted and understanding developed to support conceptual design of a full-scale plant. This demonstration provides some answers for a final design, but also raises questions about each candidate waste form that should be answered in the laboratory and then validated at larger scale preliminary to finalizing a design. The lessons learned and questions to be answered are described below.

Formulation development—both Ceramicrete and DuraLith had been optimized in the laboratory using laboratory equipment and laboratory raw materials. When the step was made to larger scale using other raw materials, both candidates had unexpected results. The materials had insufficient working time. Both developers believe that they understand the reasons for the short working times and within a few hours guided formulation modifications that allowed successful completion of the large-scale mixing and pouring of their materials. Optimization still needs to be completed for formulations with longer working time AND parametric studies need to be conducted to identify the effects of changes in the waste-forming solids. This testing demonstrated how changes in the raw material composition (in this case a different blast furnace slag) could affect the working time. Raw materials will always demonstrate variation. The effects of the variation need to be established. This is especially true for DuraLith.

The Ceramicrete formulation had a significantly lower waste loading than the DuraLith formulation. Waste loading directly affects volume of the waste form produced. The volume of final waste form affects the size (and cost) of the plant equipment necessary to achieve the target throughput and the volume (cost) for the final disposal. Ceramicrete needs additional formulation development to determine the effects of higher waste loading. If Ceramicrete is limited to low-waste loadings, its application costs will be high.

Operability—The final step of processing for both technologies was essentially the same. Liquids were mixed with solid powdered waste formers and the mixed slurry poured into a final waste container. Both slurries poured easily and readily filled the container without voids. Both materials required more intensive mixing than was provided by the ribbon mixer used in this testing (see “Mixing” below).

The DuraLith process required preparing an “activator” solution, which required additional mixing of solid powders with the liquid secondary waste. In addition to additional mixing steps the “activator” solution was reacted for 24 hours to fully dissolve the solids (fumed silica); executing this process in the treatment facility will add significant reactor volume. During this reaction H_2 gas is generated which must additionally be considered in designing the process to operate safely. This testing indicated that the

H_2 generation rates were slow; safety controls may not be difficult to implement, but additional work is needed to establish the ranges of H_2 generation as raw materials may vary. Other silica sources may be substituted for the silica fume to remove the potential for hydrogen generation.

Mixing—this work employed a ribbon mixer with a working volume appropriate to conduct batch mixing for a full container of the final waste form. The mixing was inadequate. Without some significant changes to the formulations, it should be considered that either of these waste forms will have a relatively short working time. Extended mixing to achieve better homogenization is not really a suitable option. Options that provide much more intensive mixing over short mixing times should be considered for the conceptual design. Additional work is needed to establish the energy requirements for mixing and what level of homogeneity is needed to assure that product performance is not compromised. Full homogeneity is probably not needed.

Both Ceramicrete and DuraLith displayed behavior that indicated mixing itself may extend the working time. The effect was more pronounced for Ceramicrete than DuraLith. Ceramicrete was shear thinning; if energy was imparted into gelled (not fully set up) Ceramicrete, the material could again be fluidized. This phenomenon needs to be more fully understood.

Product Expansion—sample cylinders of Ceramicrete expanded significantly during the curing process, but the large monoliths expanded only slightly. The technology developer has suggested a mechanism for this behavior; it had not been observed during the lab scale testing. The causes need to be understood so that they can be avoided or controlled.

Product Curing—this testing collected data from which could be derived the heat release during curing and a temperature profile during curing modeled for the final waste container size and configuration. Some cement-like materials (e.g., concrete) have maximum temperature limits during curing beyond which the performance of the material is degraded. The effects of temperature on the curing of each of these materials (Ceramicrete and DuraLith) needs to be established to support performance of the final waste form for Hanford secondary waste disposal.

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Appendix A

Ceramicrete and DuraLith Flowsheets

Appendix A

Ceramicrete and DuraLith Flowsheets

A.1 Process Flowsheets

As part of the low-temperature immobilization study (Russell et al. 2006), flowsheet concepts were proposed by the Ceramicrete and DuraLith developers. These are described briefly below.

A.1.1 Ceramicrete Conceptual Flowsheet

The Ceramicrete preparation process is relatively simple. Getter materials such a tin chloride and silver zeolite are added to the liquid waste solution. Then the magnesium oxide and monopotassium phosphate and any fillers are added. The slurry is mixed and is poured into the container to cure. The main steps in the Ceramicrete concept for Hanford secondary liquid wastes include (Russell et al. 2006):

1. Liquid waste receipt
2. Partial neutralization
3. Getters and reducing-agent addition
4. Partial dewatering by evaporation
5. Mixing waste solution and Ceramicrete dry materials
6. Waste form curing and storage

Figure A.1 shows the conceptual flow diagram to implement this process. The liquid secondary wastes would be received into one of two tanks. One of the tanks is used to receive the wastes while the other is transferring its contents to the neutralization vessel.

Partial neutralization was not included in the most recent Ceramicrete secondary waste preparation but was included in the conceptual flowsheet developed in 2006 for Hanford secondary wastes (Russell et al. 2006). In the neutralization tank, phosphoric acid is added to neutralize the caustic secondary wastes to a pH of approximately 5. The neutralization step is exothermic and the resulting heat will need to be dissipated. This neutralization step may or may not be necessary in the process. In more recent laboratory testing with simulated Hanford secondary wastes, the neutralization step is not included. Following the neutralization step, if used, stannous chloride ($SnCl_2$) is added to reduce technetium to the less mobile +4 oxidation state, and silver zeolite is added to capture iodine within the zeolite cage structure.

The next step is to dewater the aqueous waste solution using a vacuum evaporator. This step is intended to minimize the volume of the final Ceramicrete waste form. The extent of evaporation would have to be optimized with respect to equipment and energy costs relative to the savings in materials and disposal costs. Two evaporator condensate tanks are included to allow for one vessel to be sampled and discharged while the other is receiving the evaporator condensate.

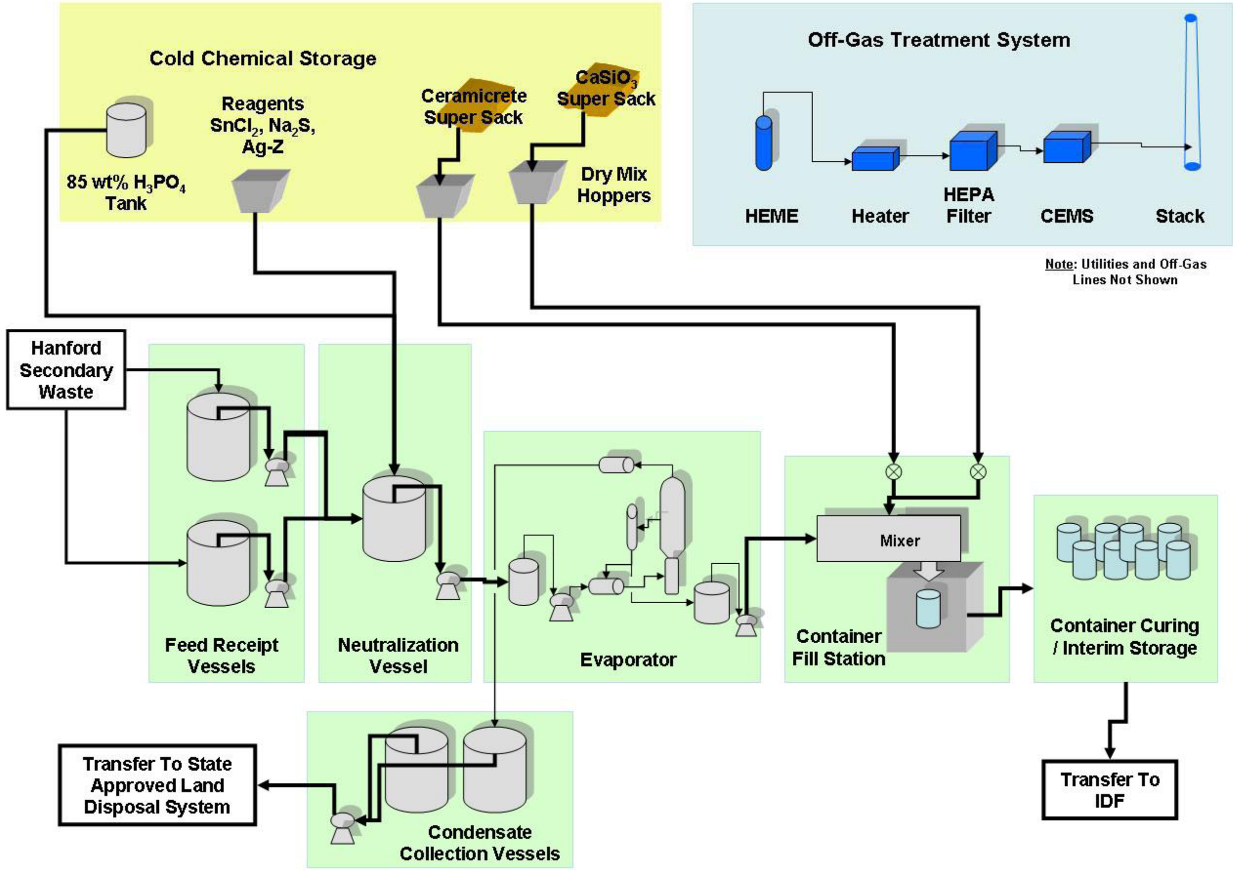


Figure A.1. Conceptual Flow Diagram for Ceramicrete Process (from Russell et al. 2006)

The concentrated waste solution is then transferred to a mixer for blending the with the Ceramicrete dry materials including the magnesium oxide, monopotassium phosphate, and filler material. A continuous, ribbon-type mixer is the proposed mixer in the conceptual flowsheet (Russell et al. 2006). The ingredients are mixed in a batch in a mixer and are discharged into the waste form container. Mixing times are on the order of 20 to 30 minutes. The mixer is sized for delivery to a single waste form container volume. A 2.04 m^3 box is proposed as a compromise between minimizing the number of containers produced on a daily basis and allowing for heat dissipation during the Ceramicrete curing process.

The Ceramicrete should set within a couple of hours and should be cured within 24 hours although heat dissipation may take longer, depending on the size of the containers. Storage will be needed for the curing process and interim storage will be needed until the containers can be received in IDF.

Ancillary systems include chemical storage for the dry materials including the getters and Ceramicrete ingredients and a storage tank for the phosphoric acid for neutralizing the caustic secondary wastes. An off gas treatment system would also be required.

A.1.2 **DuraLith Conceptual Flowsheet**

The DuraLith process (Figure A.2) is designed to receive the Hanford secondary waste (HSW) continuously, process it, generate monoliths and treat the resulting liquid, solid, and gaseous effluents (Gong et al. 2006). Lag storage tanks for HSW are recommended so that the DuraLith facility is decoupled from WTP operations. The waste (liquid and suspended solids if any) will then be transferred to the DuraLith process tank. The alkaline waste can be processed through an evaporator to concentrate it and to achieve higher waste loading, thus reducing the capital cost of the facility and also decreasing the number of monoliths to be produced. If a waste concentration process is used, the condensate generated from the evaporator overheads would need treatment. The condensate is expected to be low concentrations of radioactive constituents that can be treated by the existing onsite liquid effluent treatment facilities.

The first step in the process (Figure A.2) is to transfer the waste to the mixing tanks. For treating the HSW, the mixing tanks are designed to operate in parallel so that the feed process can be operated as a continuous batch process. The mixing tanks are initially fed with concentrated HSW, and chemical enhancers, such as tin fluoride and silver mordenite, are mixed in followed by solid caustic (KOH and NaOH) addition. This is immediately followed by adding silica fume, and it is mixed thoroughly to produce a homogeneous activator solution. The mixing tanks are equipped with cooling coils to control the heat generated from the exothermic reaction. The activator solution will be mixed continuously for 24 hours to make sure that the silica fume completely dissolves before the process of alkali activation begins.

The blended dry ingredients, consisting of BFS, metakaolin, sand, copper slag, Type 5 zeolite, Ionex® Ag 900, and the filler silica fume, are stored in a supply hopper. The alkali activation process is initiated by pumping small batches of fully mixed activator solution and mixing with the appropriate quantities of dry blend in a ribbon blender. Blending is conducted until a fluid, pourable DuraLith paste has formed. The total blending time should not exceed 10 minutes. The mixture is discharged from the ribbon blender to steel molds. The molds are vibrated to achieve a uniform fill and to remove any gaps and air pockets that may occur during the fill operation. Once the ribbon blender is empty, it is immediately filled with another batch of activator solution from the mix tank to prevent any residual paste from the previous batch from hardening in the ribbon blender. Although the flowsheet depicts just one ribbon blender, three ribbon blenders are recommended to provide needed operational flexibility.

The suggested steel molds are commercially available square containers, each with a capacity of about 48 cubic feet (1.75 cubic yards) of the freshly blended DuraLith paste.

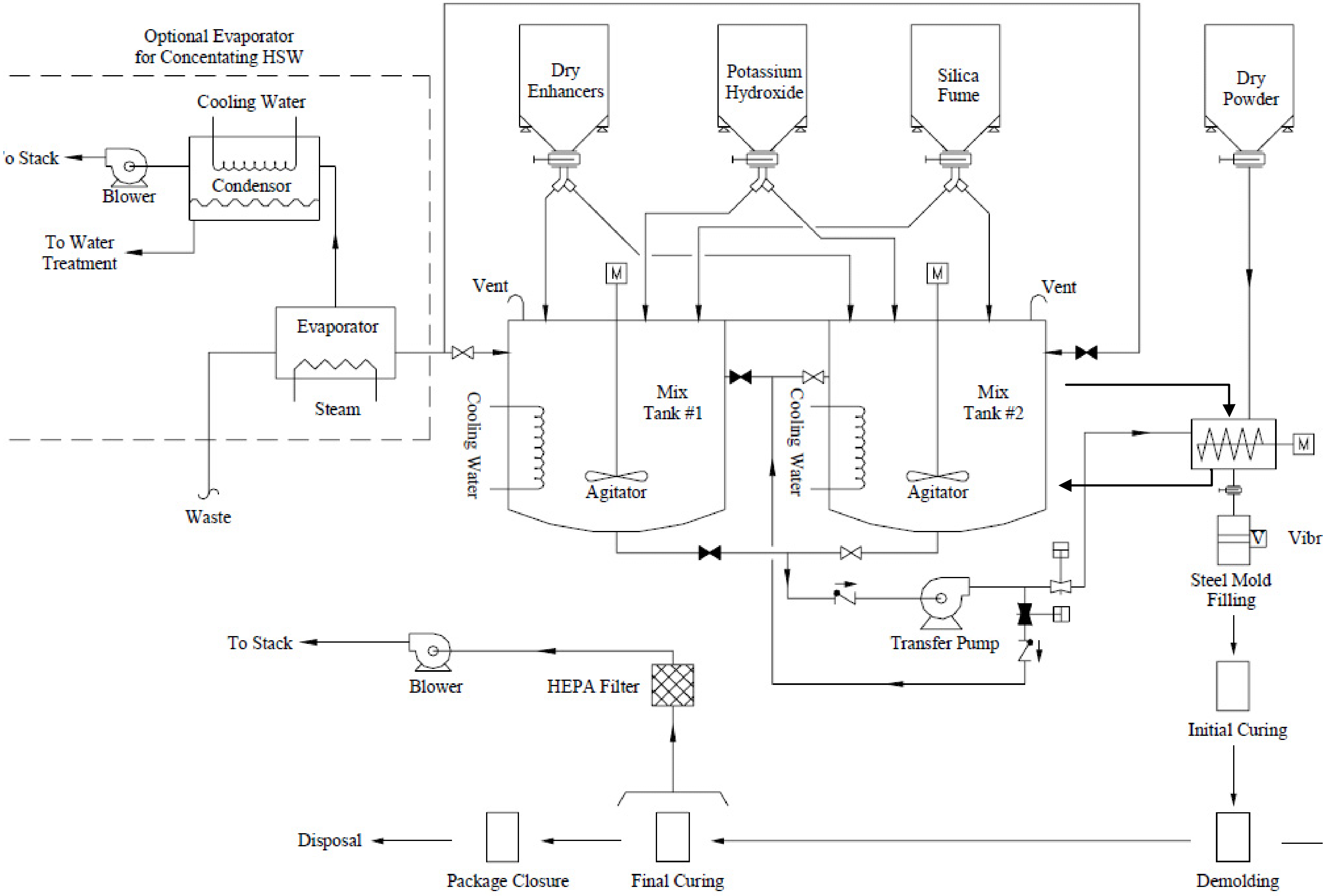


Figure A.2. Hanford Secondary Waste Processing Flow Sheet (Gong et al. 2006)

Appendix B

In-Process Rheology Tests Used During Engineering-Scale Testing

Appendix B

In-Process Rheology Tests Used During Engineering Scale Testing

Cylinder Slumping—the 50-Cent Rheometer

This test uses an open cylindrical sleeve, called the 50-cent rheometer, specified in Pashias et al. (1996). It measures a slumping height once a custom-designed transparent square cylindrical sleeve is filled with slurry simulant and then slipped off as shown in Figure B.1.

A slumping height, a parameter to measure the slumping behavior in this test, is defined by a total height change. A higher slumping tendency is indicated by a greater slumping height, and a slumping height would be governed by a balance between the strength of the slurry (i.e., shear strength) and gravity exerted on the slurry. As an example, Figure B.2 provides illustrations for a 49 wt% kaolin slurry.

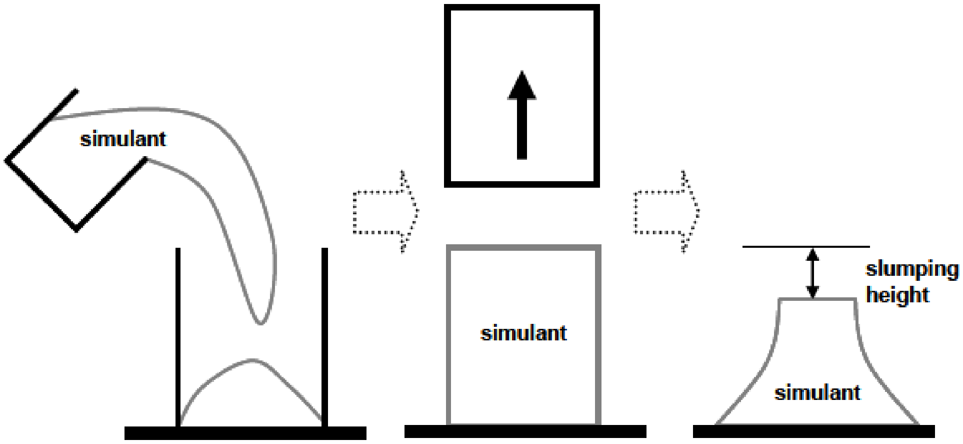


Figure B.1. Schematic Diagram of the Procedure for the 50-Cent Rheometer Test

Figure B.2. Example Pictures for the 50-Cent Rheometer Test with 49-wt% Kaolin Slurry

The following is an abridged description of the ASTM *Consistency, Working Time* and *Initial Setting Time* tests. Exact procedures are copyrighted ASTM methods.

Initial Relative Consistency—This is a timed test. Time zero begins when the slurry is considered homogeneously mixed and the mixer is stopped. Remove sufficient mixed slurry to fill a test cone 40 mm (h) × 60 mm (small d) × 70 mm (large d), ~135cm^3. Place the large diameter of the test cone onto a horizontal non-absorbing surface and scrape the top of the surface flush with the top of the test cone using a sharp flat trowel. Place the 10-mm diameter Vicat test plunger onto surface of the slurry. Thirty seconds after mixing stopped, release the test plunger. Thirty seconds after the test plunger is released, measure the depth the plunger has settled into the slurry. Record this depth for comparison to other formulations.

> **Reference**: ASTM C187—Standard Test Method for Normal Consistency of Hydraulic Cement (ASTM 2011).

Working Time—Remove approximately 25 g of mixed slurry from the container and trowel the slurry onto a horizontal surface of clean, dry freezer paper. Record the time the slurry was removed from the mixture, with zero time being when the mixer is turned off. Repeat the test every five minutes. The *working time* is complete when the material begins to curl behind the spreading trowel. Do not return the tested material to the mixed slurry.

> **Reference**: ASTM C308—Standard Test Methods for Working, Initial Setting, and Service Strength Setting Times of Chemical-Resistant Resin Mortars (ASTM 2005).

Initial Setting Time—Remove sufficient mixed slurry to fill a test cone 40 mm (h) × 60 mm (small d) × 70 mm (large d), ~135cm^3. Place the large diameter of the test cone onto a horizontal non-absorbing surface and scrape the top of the surface flush with the top of the test cone using a sharp flat trowel. As the material sets, periodically drop a Vicat test pin and record the depth the 1-mm pin penetrates into the test material. The initial set time is when the Vicat test pin no longer penetrates deeper than 25 mm. The ASTM method contains the equation to calculate the Initial Setting Time based on the last measurement before the Initial Setting Time (penetration > 25 mm) and the first measurement after the Initial Setting Time (penetration < 25 mm).

> **Reference**: ASTM C191-08—Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle (ASTM 2008).

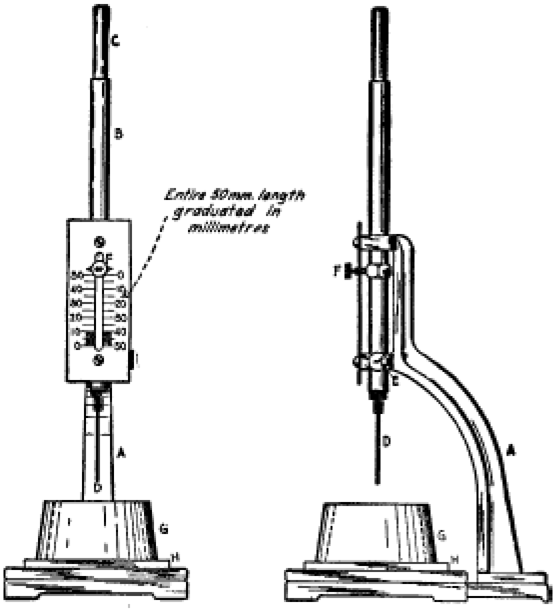


FIG. A1.1 Vicat Apparatus

Figure B.3. Apparatus to Conduct ASTM Consistency and Initial Setting Time Procedures

Appendix C

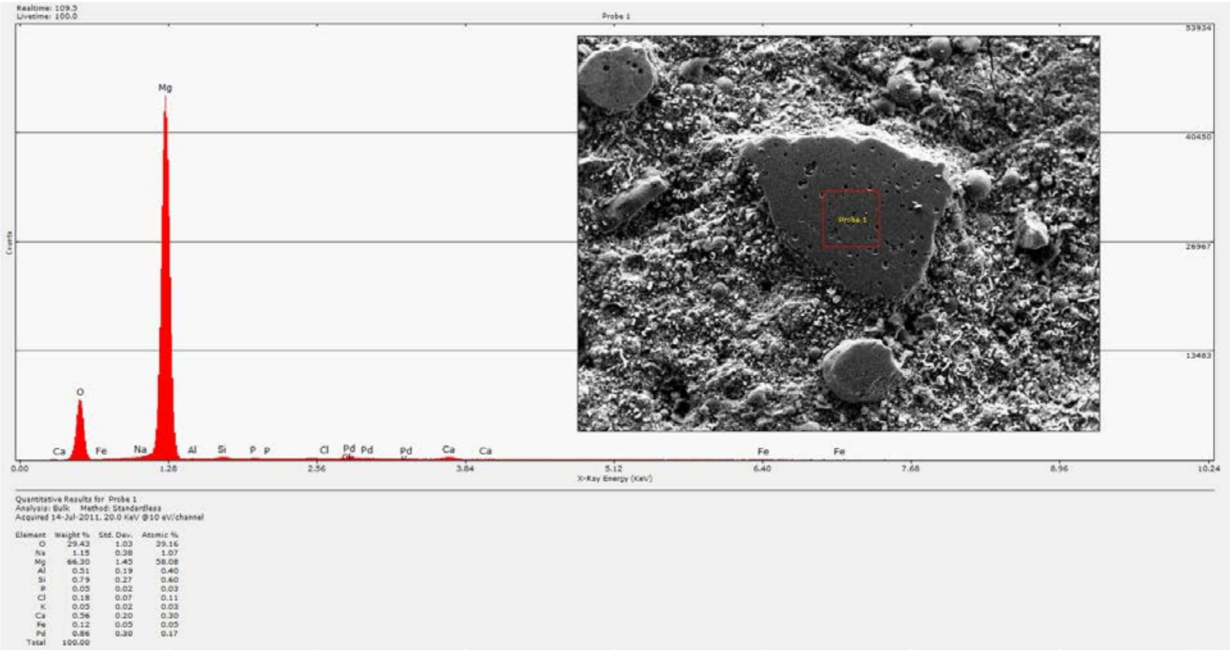
SEM/EDS Analyses of Ceramicrete and DuraLith

Appendix C

SEM EDS Analyses of Ceramicrete and DuraLith

Elemental analysis of Ceramicrete 5-5 was collected using energy dispersive spectroscopy and is given in the figures below. The EDS was collected from SEM views of two different locations. Within each SEM view (location) elemental compositions are determined from spectra collected at small spots with the view (location). Spectra from these smaller spots are called “probes.” At the first location, six different EDS probes were collected. Probe 1 is MgO which confirms the XRD identification of periclase. Probes 2, 4, and 6 shows a high concentration of Si, along with Al, Ca, Na, and Mg. Probe 3 is likely quartz. Probe 5 is an area collection of the matrix that was high in K and Cl.

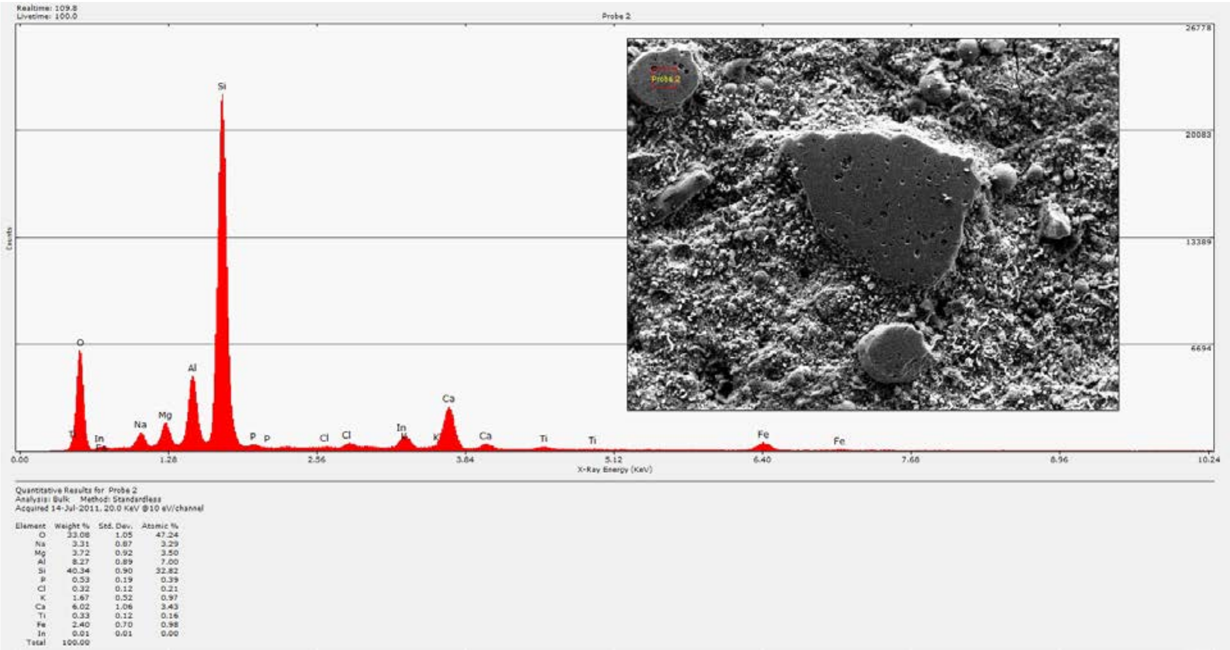
The EDS spectra collected at the second location of Ceramicrete 5-5 are as follows. Probes 1 and 5 were collected on the large particle and show high concentrations of Si, Al, P, K, Ca, and Mg. The particle appears visually to be multiphase and will be further discussed in the next paragraph. Probe 2, 3, and 4 are again high in Si, Al, Ca, and Mg. Probe 6 is an area collection of the matrix which again shows high K and Cl. Probes 7 and 8 are spot collection on the small bright particles in the matrix that are high in K and Cl. The last section of EDS was collected to examine the multiphase appearance of the large particle located in the lower left of EDS Location 2. Several spots in light and dark regions of the particle were examined to look for elemental differences. The light and dark regions both contain the same elements Si, Al, P, K, Ca, and Mg in similar concentrations. The main difference between the two regions appears to be the concentration of P, with the light regions being at ~8 wt% P and the dark regions being ~5 wt% P.



Quantitative Results for Probe 1
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011. 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	29.43	1.03	39.16
Na	1.15	0.38	1.07
Mg	66.30	1.45	58.08
Al	0.51	0.19	0.40
Si	0.79	0.27	0.60
P	0.05	0.02	0.03
Cl	0.18	0.07	0.11
K	0.05	0.02	0.03
Ca	0.56	0.20	0.30
Fe	0.12	0.05	0.05
Pd	0.86	0.30	0.17
Total	100.00		

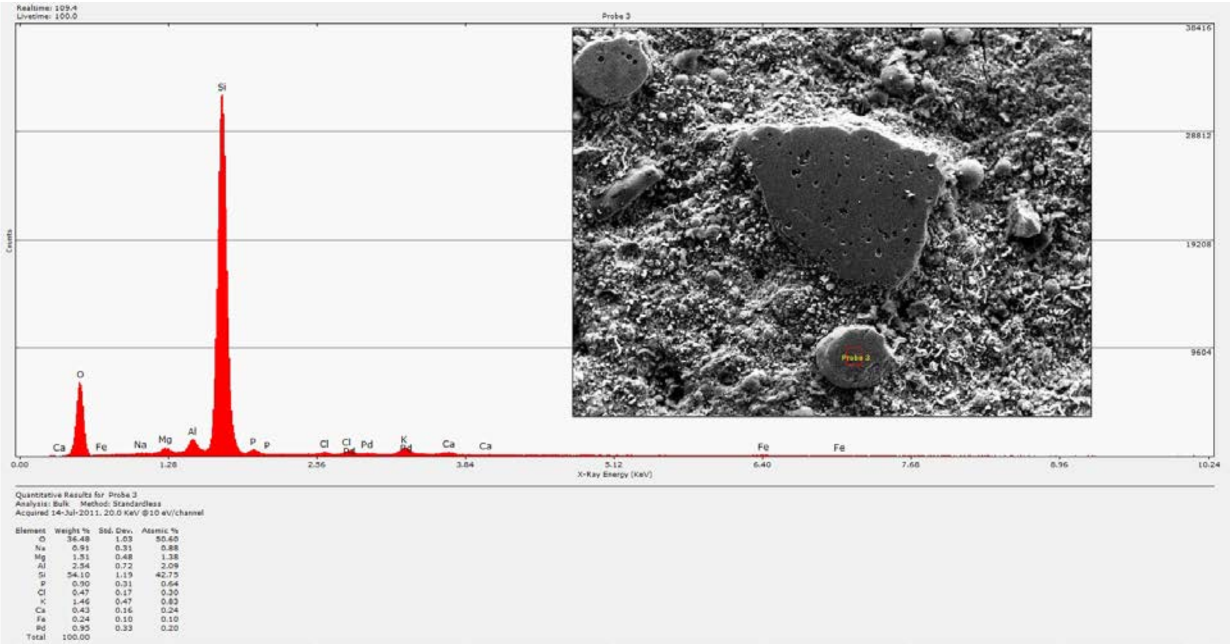
Figure C.1. Ceramicrete 5-5, Location 1, Probe 1



Quantitative Results for Probe 2
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011. 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	33.08	1.05	47.24
Na	3.31	0.87	3.29
Mg	3.72	0.92	3.50
Al	8.27	0.89	7.00
Si	40.34	0.90	32.82
P	0.53	0.19	0.39
Cl	0.32	0.12	0.21
K	1.67	0.52	0.97
Ca	6.02	1.06	3.43
Ti	0.33	0.12	0.16
Fe	2.40	0.70	0.98
In	0.01	0.01	0.00
Total	100.00		

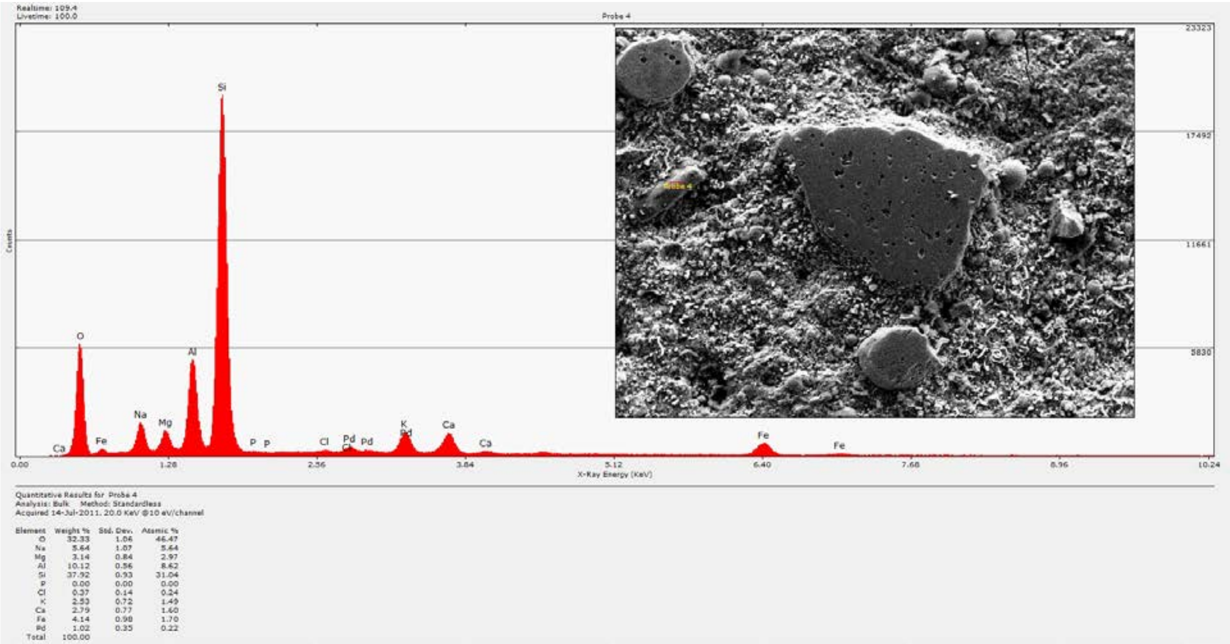
Figure C.2. Ceramicrete 5-5, Location 1, Probe 2



Quantitative Results for Probe 3
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011. 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	36.48	1.03	50.60
Na	0.91	0.31	0.88
Mg	1.51	0.48	1.38
Al	2.54	0.72	2.09
Si	54.10	1.19	42.75
P	0.90	0.31	0.64
Cl	0.47	0.17	0.30
K	1.46	0.47	0.83
Ca	0.43	0.16	0.24
Fe	0.24	0.10	0.10
Pd	0.95	0.33	0.20
Total	100.00		

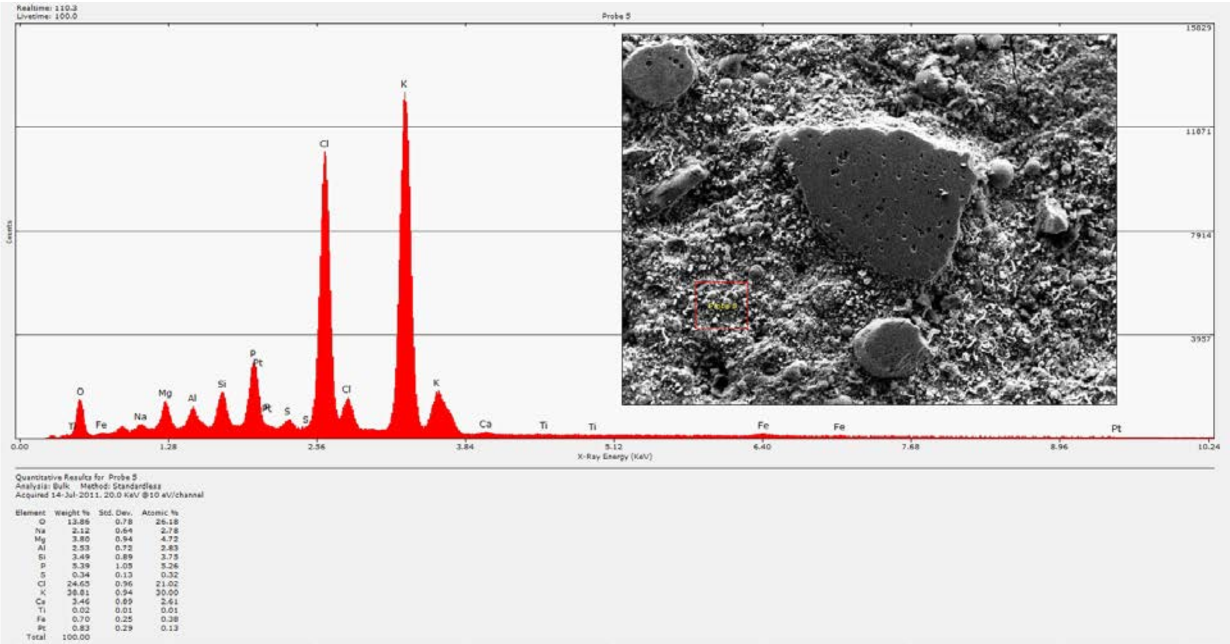
Figure C.3. Ceramicrete 5-5, Location 1, Probe 3



Quantitative Results for Probe 4
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011. 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	32.33	1.06	46.47
Na	5.64	1.07	5.64
Mg	3.14	0.84	2.97
Al	10.12	0.56	8.62
Si	37.92	0.93	31.04
P	0.00	0.00	0.00
Cl	0.37	0.14	0.24
K	2.53	0.72	1.49
Ca	2.79	0.77	1.60
Fe	4.14	0.98	1.70
Pd	1.02	0.35	0.22
Total	100.00		

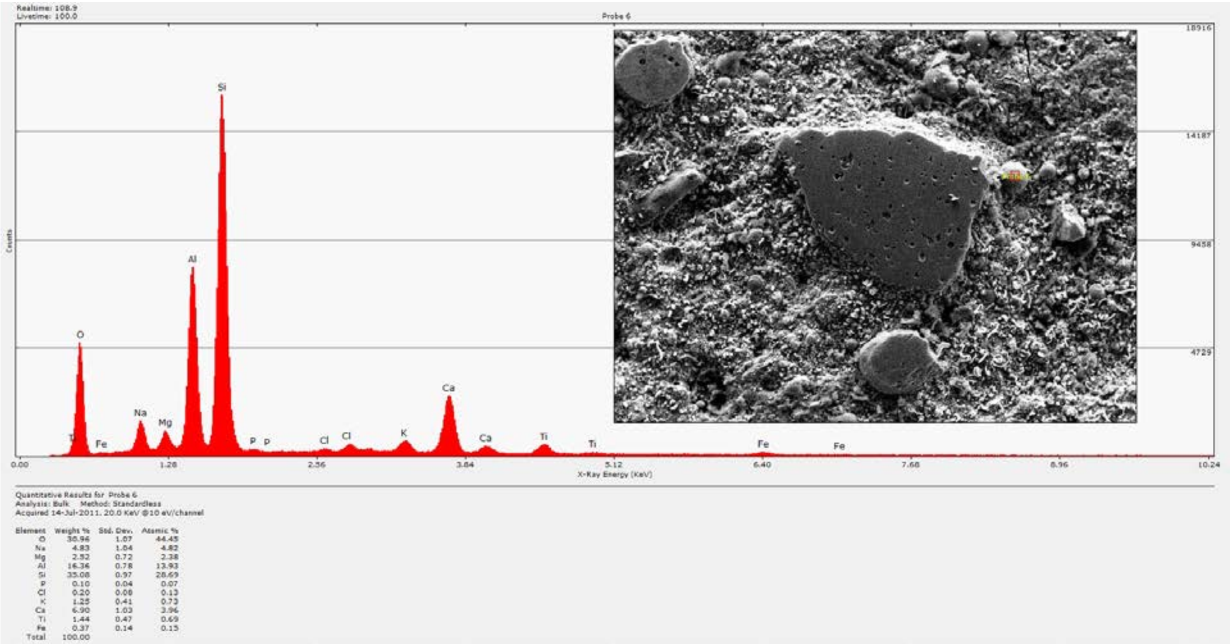
Figure C.4. Ceramicrete 5-5, Location 1, Probe 4



Quantitative Results for Probe 5
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	13.86	0.78	26.18
Na	2.12	0.64	2.78
Mg	3.80	0.94	4.72
Al	2.53	0.72	2.83
Si	3.49	0.89	3.75
P	5.39	1.05	5.26
S	0.34	0.13	0.32
Cl	24.65	0.96	21.02
K	38.81	0.94	30.00
Ca	3.46	0.89	2.61
Ti	0.02	0.01	0.01
Fe	0.70	0.25	0.38
Pt	0.83	0.29	0.13
Total	100.00		

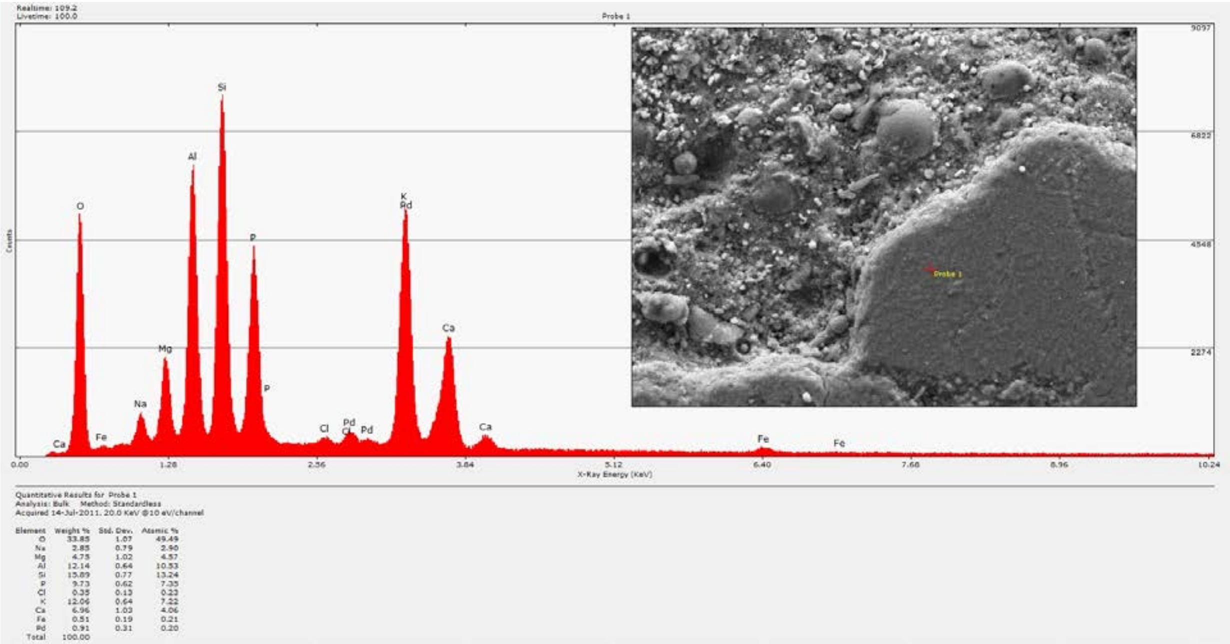
Figure C.5. Ceramicrete 5-5, Location 1, Probe 5



Quantitative Results for Probe 6
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	30.96	1.07	44.45
Na	4.83	1.04	4.82
Mg	2.52	0.72	2.38
Al	16.36	0.78	13.93
Si	35.08	0.97	28.69
P	0.10	0.04	0.07
Cl	0.20	0.08	0.13
K	1.25	0.41	0.73
Ca	6.90	1.03	3.96
Ti	1.44	0.47	0.69
Fe	0.37	0.14	0.15
Total	100.00		

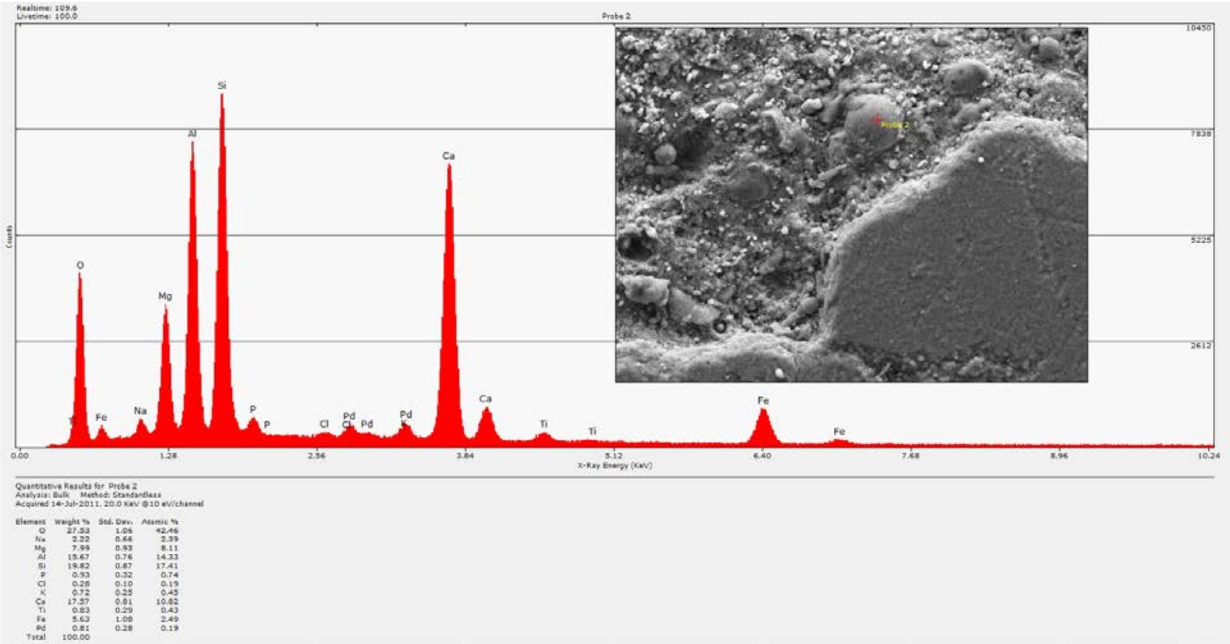
Figure C.6. Ceramicrete 5-5, Location 1, Probe 6



Quantitative Results for Probe 1
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011. 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	33.85	1.07	49.49
Na	2.85	0.79	2.90
Mg	4.75	1.02	4.57
Al	12.14	0.64	10.53
Si	15.89	0.77	13.24
P	9.73	0.62	7.35
Cl	0.35	0.13	0.23
K	12.06	0.64	7.22
Ca	6.96	1.03	4.06
Fe	0.51	0.19	0.21
Pd	0.91	0.31	0.20
Total	100.00		

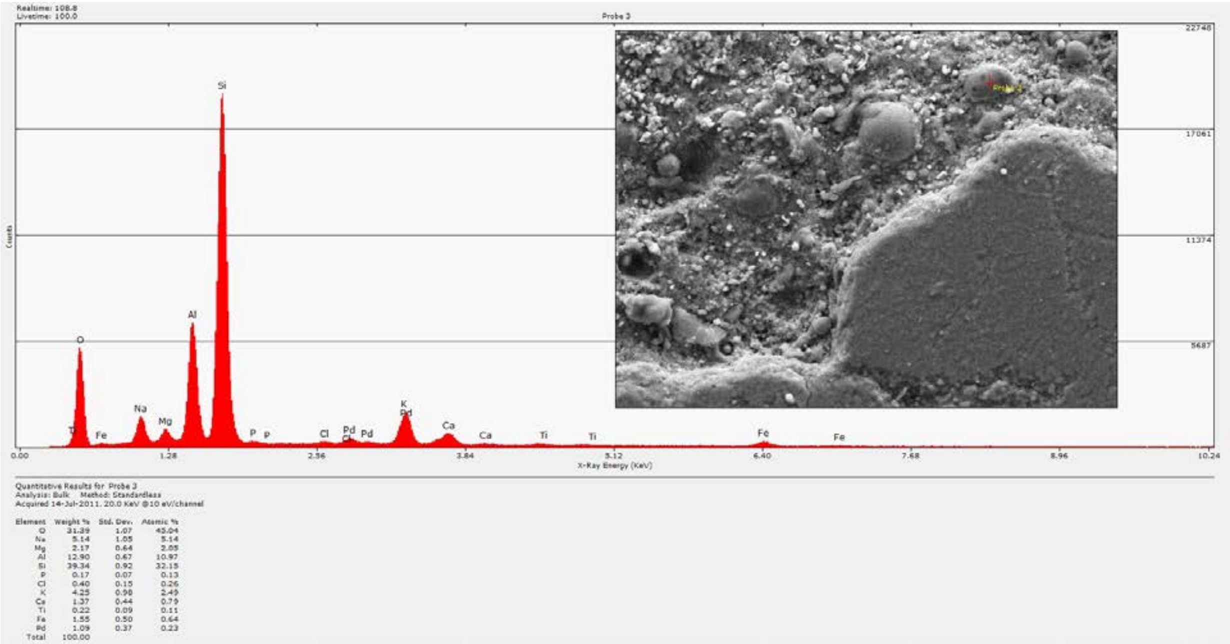
Figure C.7. Ceramicrete 5-5, Location 2, Probe 1



Quantitative Results for Probe 2
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011. 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	27.33	1.06	42.46
Na	2.22	0.66	2.39
Mg	7.99	0.93	8.11
Al	15.67	0.76	14.33
Si	19.82	0.87	17.41
P	0.93	0.32	0.74
Cl	0.28	0.10	0.19
K	0.72	0.25	0.45
Ca	17.57	0.81	10.82
Ti	0.83	0.29	0.43
Fe	5.63	1.08	2.49
Pd	0.81	0.28	0.19
Total	100.00		

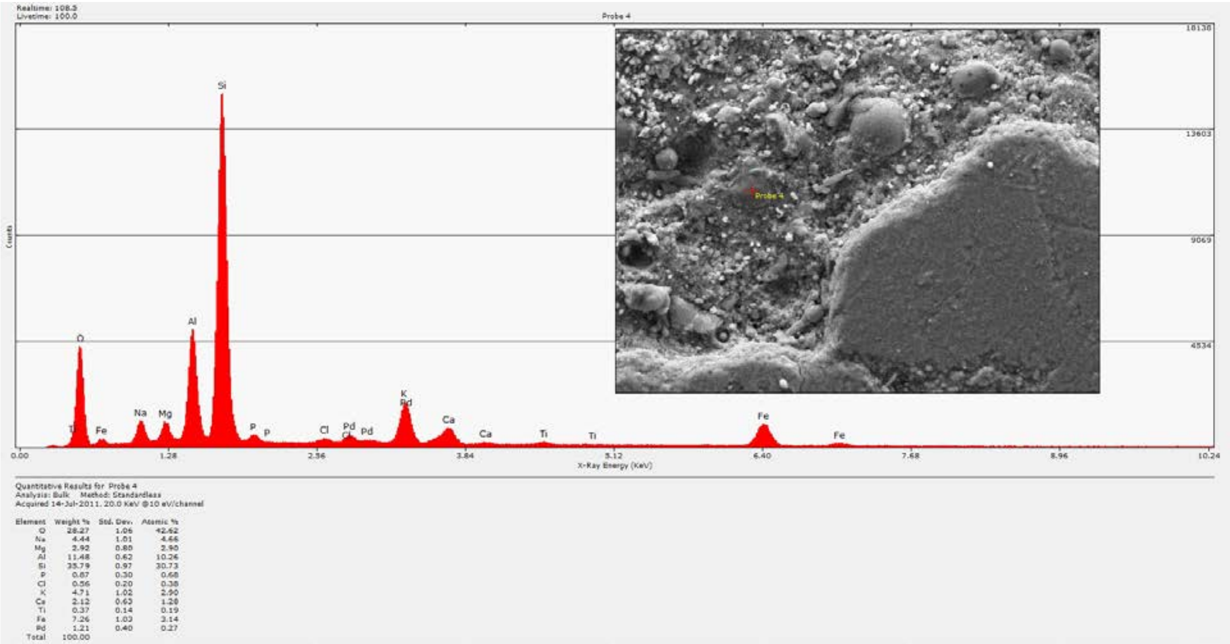
Figure C.8. Ceramicrete 5-5, Location 2, Probe 2



Quantitative Results for Probe 3
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	31.39	1.07	45.04
Na	5.14	1.05	5.14
Mg	2.17	0.64	2.05
Al	12.90	0.67	10.97
Si	39.34	0.92	32.15
P	0.17	0.07	0.13
Cl	0.40	0.15	0.26
K	4.25	0.98	2.49
Ca	1.37	0.44	0.79
Ti	0.22	0.09	0.11
Fe	1.55	0.50	0.64
Pd	1.09	0.37	0.23
Total	100.00		

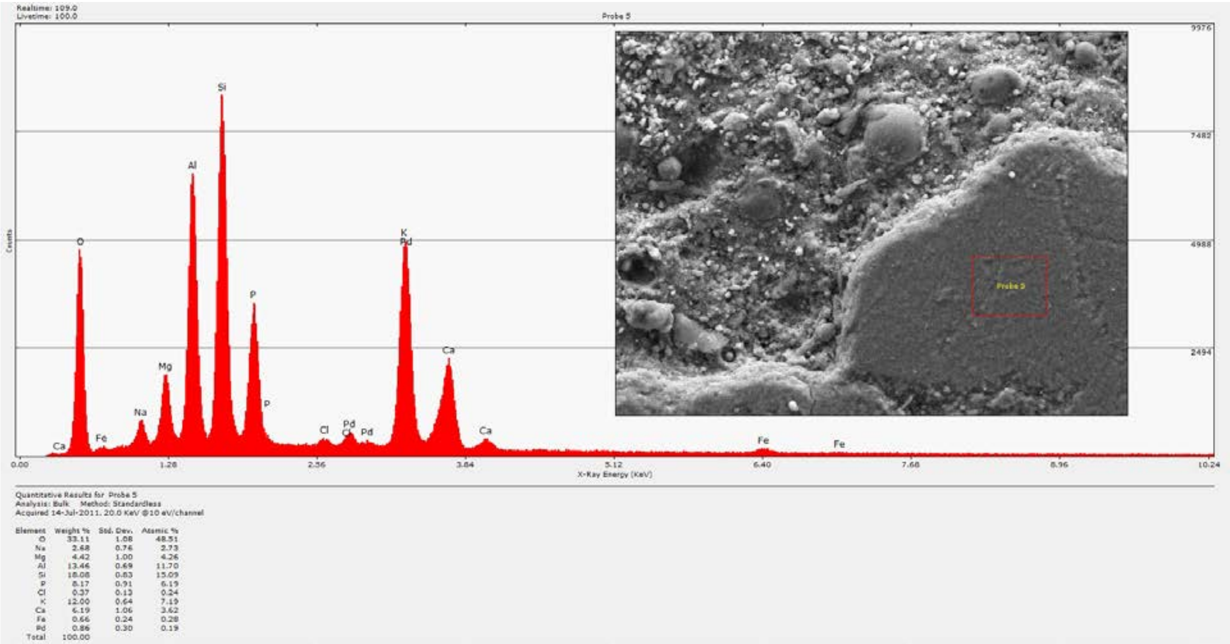
Figure C.9. Ceramicrete 5-5, Location 2, Probe 3



Quantitative Results for Probe 4
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	28.27	1.06	42.62
Na	4.44	1.01	4.66
Mg	2.92	0.80	2.90
Al	11.48	0.62	10.26
Si	35.79	0.97	30.73
P	0.87	0.30	0.68
Cl	0.56	0.20	0.38
K	4.71	1.02	2.90
Ca	2.12	0.63	1.28
Ti	0.37	0.14	0.19
Fe	7.26	1.03	3.14
Pd	1.21	0.40	0.27
Total	100.00		

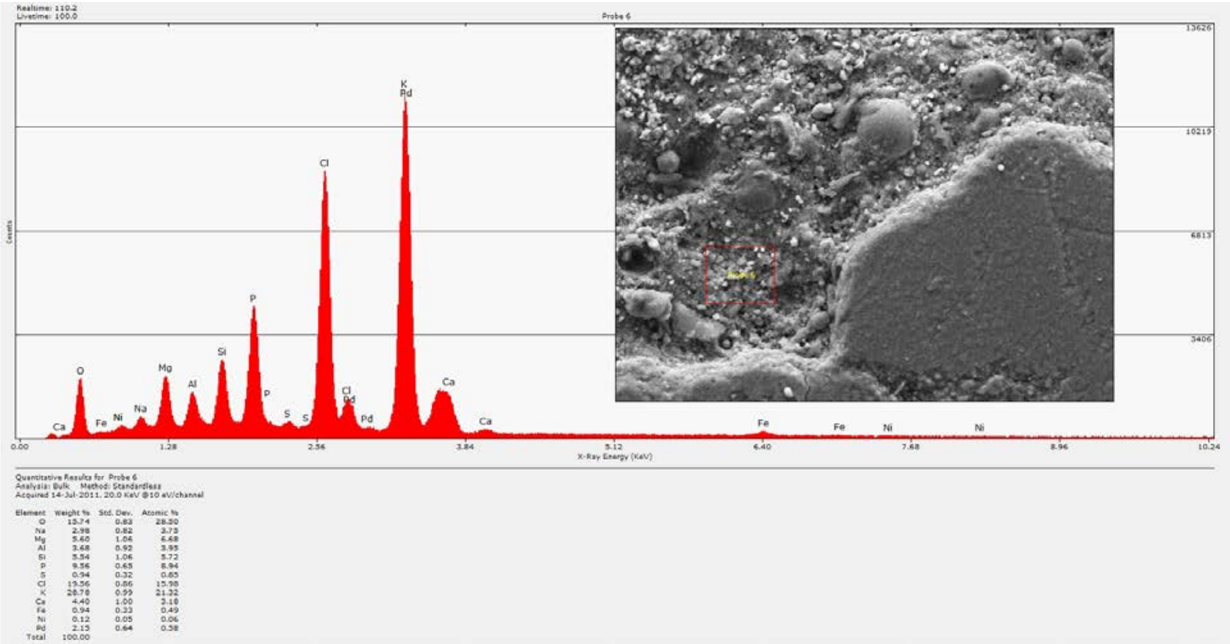
Figure C.10. Ceramicrete 5-5, Location 2, Probe 4



Quantitative Results for Probe 5
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	33.11	1.08	48.51
Na	2.68	0.76	2.73
Mg	4.42	1.00	4.26
Al	13.46	0.69	11.70
Si	18.08	0.83	15.09
P	8.17	0.91	6.19
Cl	0.37	0.13	0.24
K	12.00	0.64	7.19
Ca	6.19	1.06	3.62
Fe	0.66	0.24	0.28
Pd	0.86	0.30	0.19
Total	100.00		

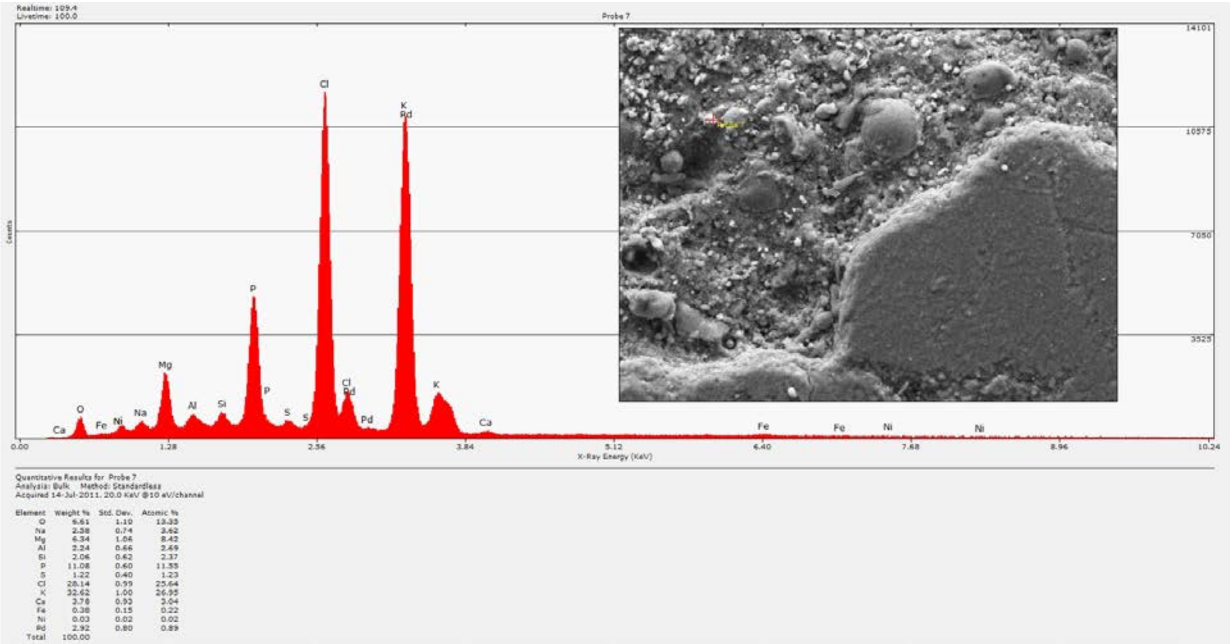
Figure C.11. Ceramicrete 5-5, Location 2, Probe 5



Quantitative Results for Probe 6
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	15.74	0.83	28.30
Na	2.98	0.82	3.73
Mg	5.60	1.06	6.48
Al	3.68	0.92	3.95
Si	5.54	1.06	5.72
P	9.56	0.65	8.94
S	0.94	0.32	0.85
Cl	19.56	0.86	15.98
K	28.78	0.99	21.32
Ca	4.40	1.00	3.18
Fe	0.94	0.33	0.49
Ni	0.12	0.05	0.06
Pd	2.15	0.64	0.58
Total	100.00		

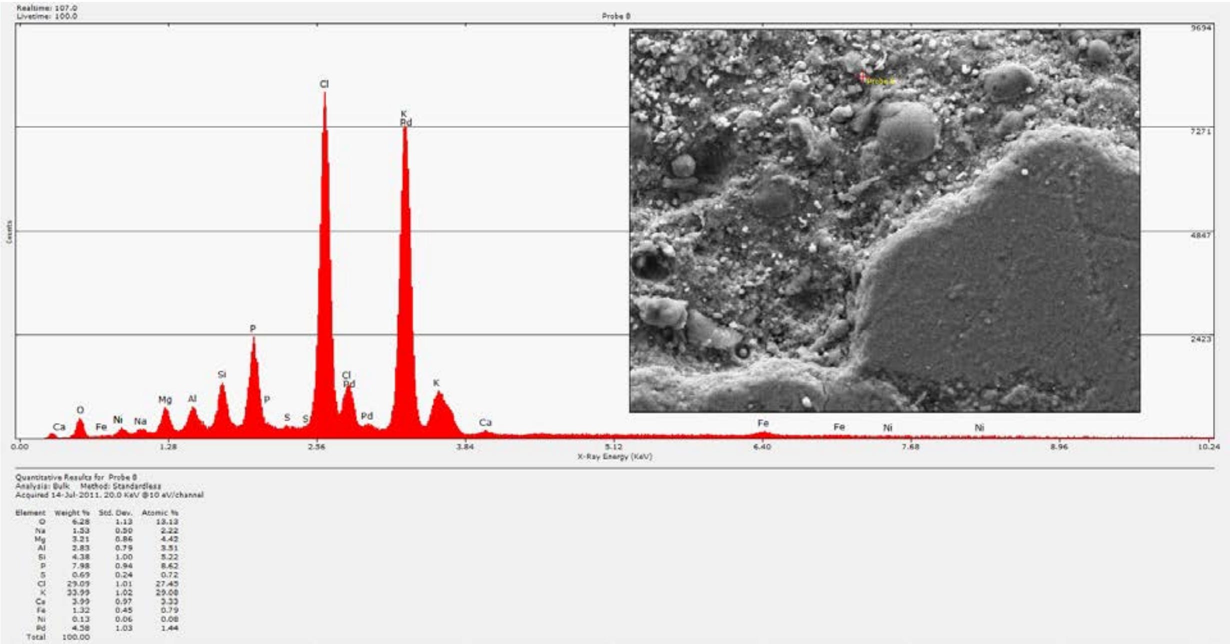
Figure C.12. Ceramicrete 5-5, Location 2, Probe 6



Quantitative Results for Probe 7
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	6.61	1.10	13.33
Na	2.38	0.74	3.62
Mg	6.34	1.06	8.42
Al	2.24	0.66	2.69
Si	2.06	0.62	2.37
P	11.08	0.60	11.55
S	1.22	0.40	1.23
Cl	28.14	0.99	25.64
K	32.62	1.00	26.95
Ca	3.78	0.93	3.04
Fe	0.38	0.15	0.22
Ni	0.03	0.02	0.02
Pd	2.92	0.80	0.89
Total	100.00		

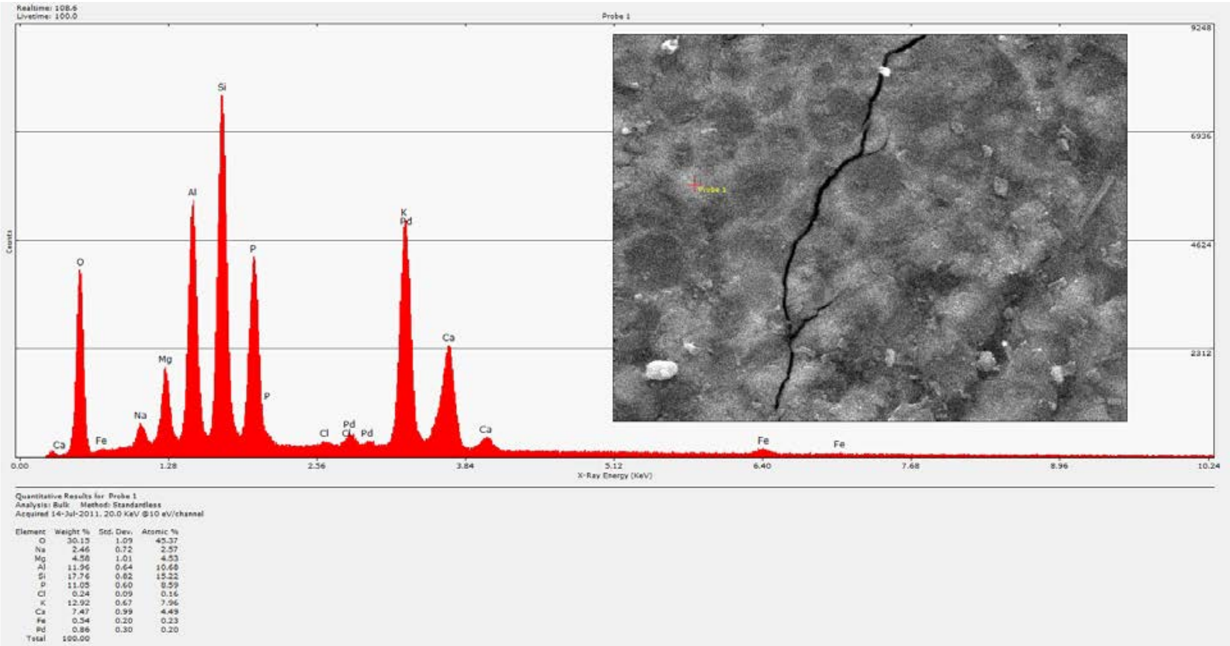
Figure C.13. Ceramicrete 5-5, Location 2, Probe 7



Quantitative Results for Probe 8
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	6.28	1.13	13.13
Na	1.53	0.50	2.22
Mg	3.21	0.86	4.42
Al	2.83	0.79	3.51
Si	4.38	1.00	5.22
P	7.98	0.94	8.62
S	0.69	0.24	0.72
Cl	29.09	1.01	27.45
K	33.99	1.02	29.08
Ca	3.99	0.97	3.33
Fe	1.32	0.45	0.79
Ni	0.13	0.06	0.08
Pd	4.58	1.03	1.44
Total	100.00		

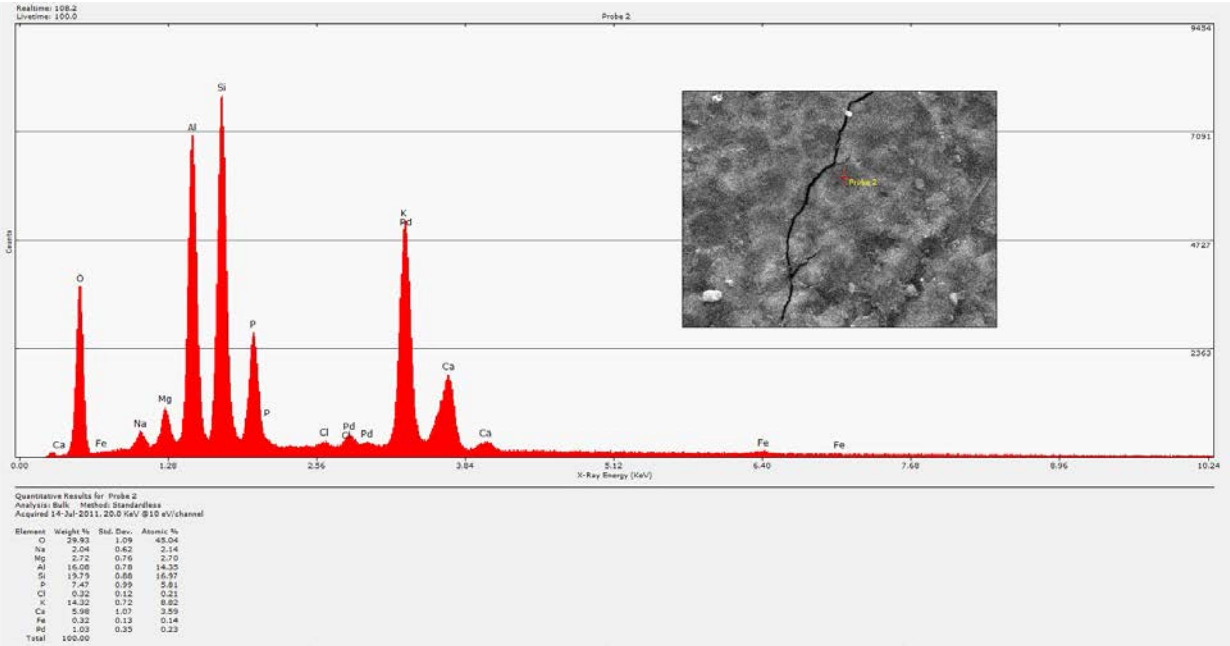
Figure C.14. Ceramicrete 5-5, Location 2, Probe 8



Quantitative Results for Probe 1
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	30.15	1.09	45.37
Na	2.46	0.72	2.57
Mg	4.58	1.01	4.53
Al	11.96	0.64	10.68
Si	17.76	0.82	15.22
P	11.05	0.60	8.59
Cl	0.24	0.09	0.16
K	12.92	0.67	7.96
Ca	7.47	0.99	4.49
Fe	0.34	0.20	0.23
Pd	0.86	0.30	0.20
Total	100.00		

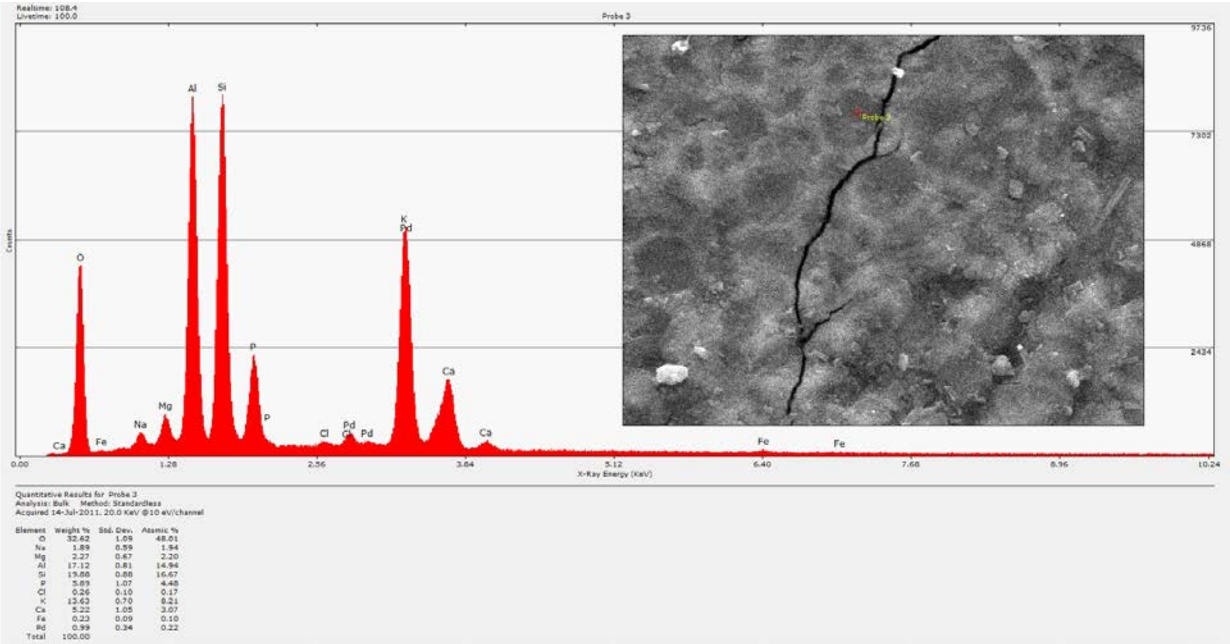
Figure C.15. Ceramicrete 5-5, Location 2(b), Probe 1



Quantitative Results for Probe 2
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	29.93	1.09	45.04
Na	2.04	0.62	2.14
Mg	2.72	0.76	2.70
Al	16.08	0.78	14.35
Si	19.75	0.88	16.97
P	7.47	0.99	5.81
Cl	0.32	0.12	0.21
K	14.32	0.72	8.82
Ca	5.98	1.07	3.59
Fe	0.32	0.13	0.14
Pd	1.03	0.35	0.23
Total	100.00		

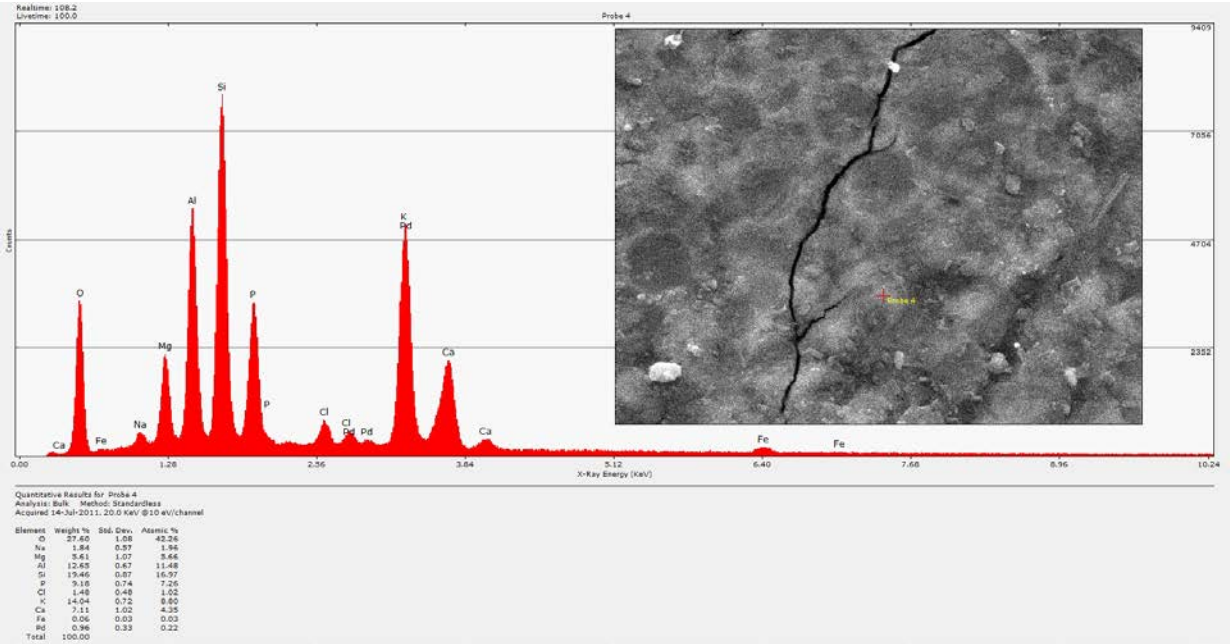
Figure C.16. Ceramicrete 5-5, Location 2(b), Probe 2



Quantitative Results for Probe 3
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	32.62	1.09	48.01
Na	1.89	0.59	1.94
Mg	2.27	0.67	2.20
Al	17.12	0.81	14.94
Si	19.88	0.88	16.67
P	5.89	1.07	4.48
Cl	0.26	0.10	0.17
K	13.63	0.70	8.21
Ca	5.22	1.05	3.07
Fe	0.23	0.09	0.10
Pd	0.99	0.34	0.22
Total	100.00		

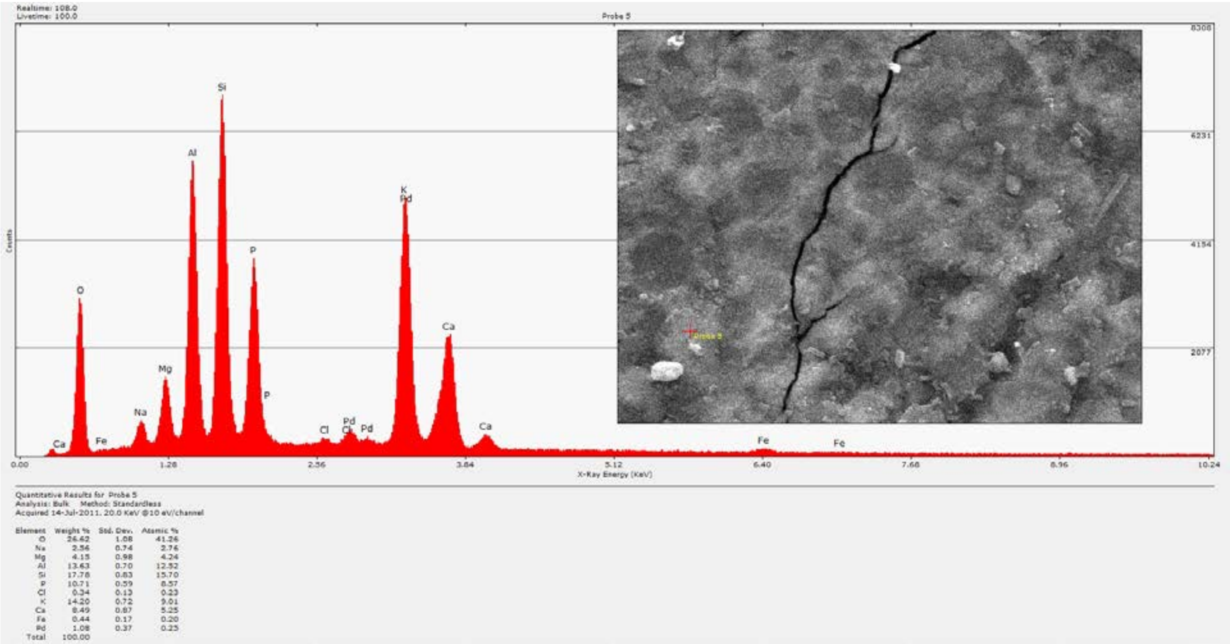
Figure C.17. Ceramicrete 5-5, Location 2(b), Probe 3



Quantitative Results for Probe 4
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	27.60	1.08	42.26
Na	1.84	0.57	1.96
Mg	5.61	1.07	5.66
Al	12.65	0.67	11.48
Si	19.46	0.87	16.97
P	9.18	0.74	7.26
Cl	1.48	0.48	1.02
K	14.04	0.72	8.80
Ca	7.11	1.02	4.35
Fe	0.06	0.03	0.03
Pd	0.96	0.33	0.22
Total	100.00		

Figure C.18. Ceramicrete 5-5, Location 2(b), Probe 4

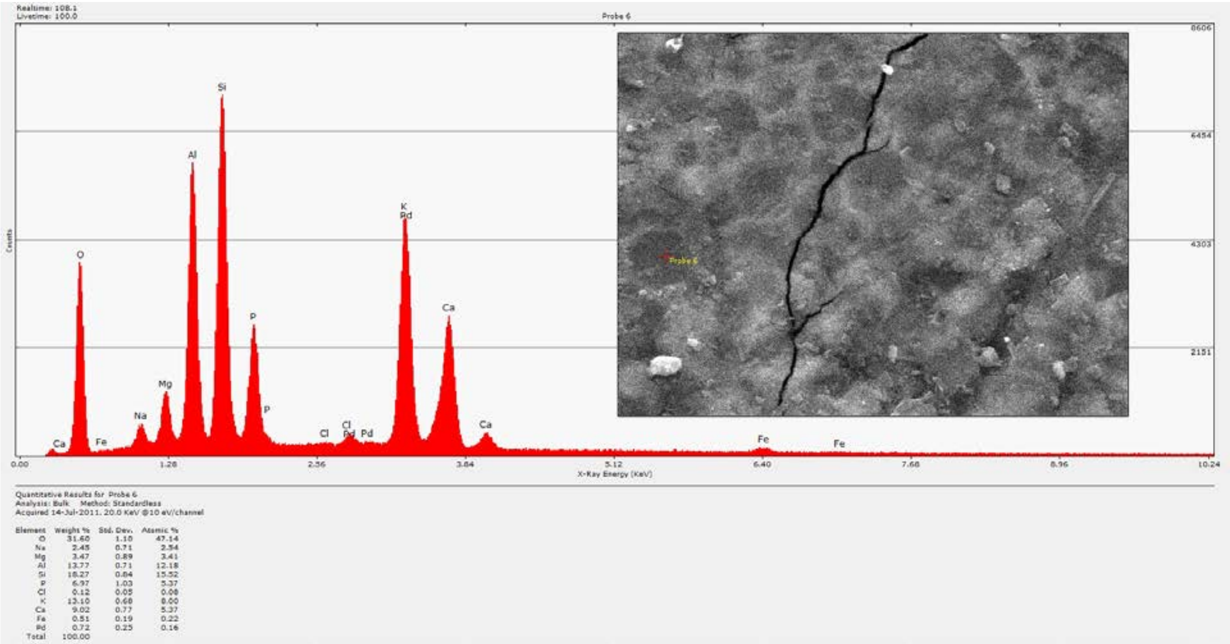


Realtime: 108.0
Livetime: 100.0

Quantitative Results for Probe 5
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011. 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	26.42	1.08	41.26
Na	2.56	0.74	2.76
Mg	4.15	0.98	4.24
Al	13.63	0.70	12.52
Si	17.78	0.83	15.70
P	10.71	0.59	8.57
Cl	0.34	0.13	0.23
K	14.20	0.72	9.01
Ca	8.49	0.87	5.25
Fe	0.44	0.17	0.20
Pd	1.08	0.37	0.25
Total	100.00		

Figure C.19. Ceramicrete 5-5, Location 2(b), Probe 5



Realtime: 108.1
Livetime: 100.0

Quantitative Results for Probe 6
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011. 20.0 KeV @10 eV/channel

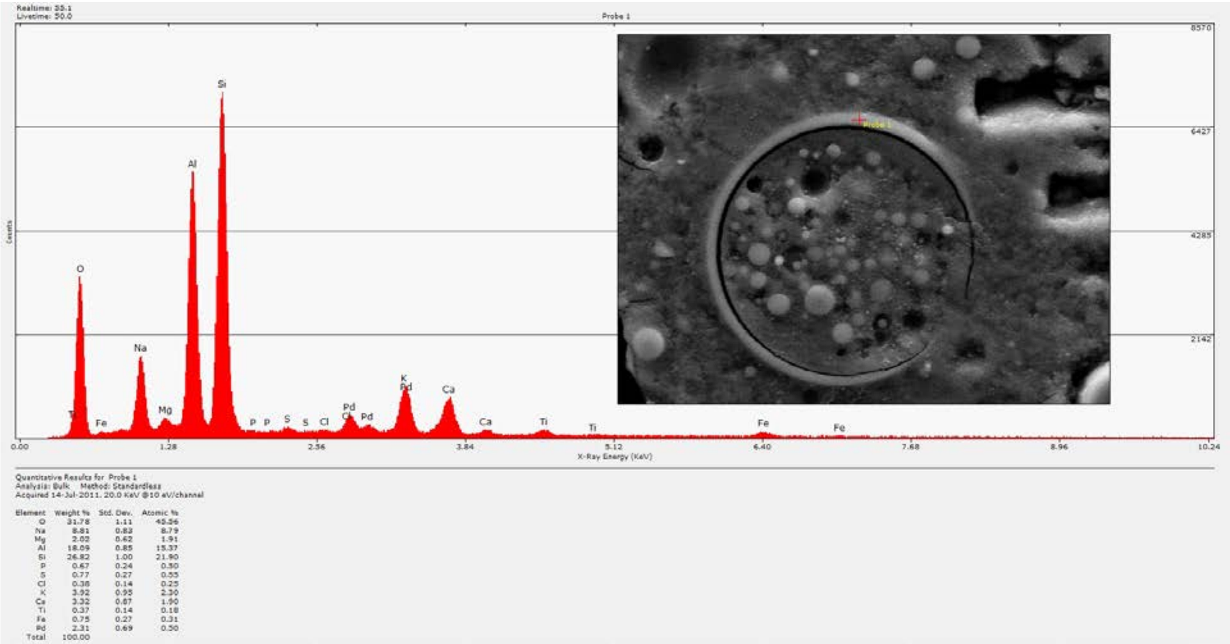
Element	Weight %	Std. Dev.	Atomic %
O	31.60	1.10	47.14
Na	2.45	0.71	2.54
Mg	3.47	0.89	3.41
Al	13.77	0.71	12.18
Si	18.27	0.84	15.52
P	6.97	1.03	5.37
Cl	0.12	0.05	0.08
K	13.10	0.68	8.00
Ca	9.02	0.77	5.37
Fe	0.51	0.19	0.22
Pd	0.72	0.25	0.16
Total	100.00		

Figure C.20. Ceramicrete 5-5, Location 2(b), Probe 6

Elemental analysis of Duralith 17-2 was collected using energy-dispersive spectroscopy in three locations. Oxygen was present in all of the spot analyses although it is not repetitively discussed in the following sentences. Seven different spots were examined in Location 1. Probes 1, 4, and 5 were collected on the cross-sectioned open sphere; they consist of Si, Al, Na, K, and Ca. Probes 2 and 3 are small bright particles inside the sphere. Probe 2 consists of Si, Ca, and Mg whereas Probe 3 consists of Si, Al, and K. Probes 6 and 7 were area collections done inside and outside the sphere on the matrix. Both consist of Si, Al, K, Na, and Ca in very similar concentrations.

At Location 2, nine different spots were probed. Probe 1 is high in Ca, Al, Si, Fe, and Mg. Probe 2 is high in Ca, Al, Si, Mg, and Fe. Probes 3, 8, and 9 were are similar and consist of Si, Al, Na, and K. Probes 4 and 5 consist of Si, Fe, Al, Ca, Mg, and Na. Probes 6 and 7 are area collections of the matrix that consists of Si, Al, K, and Na.

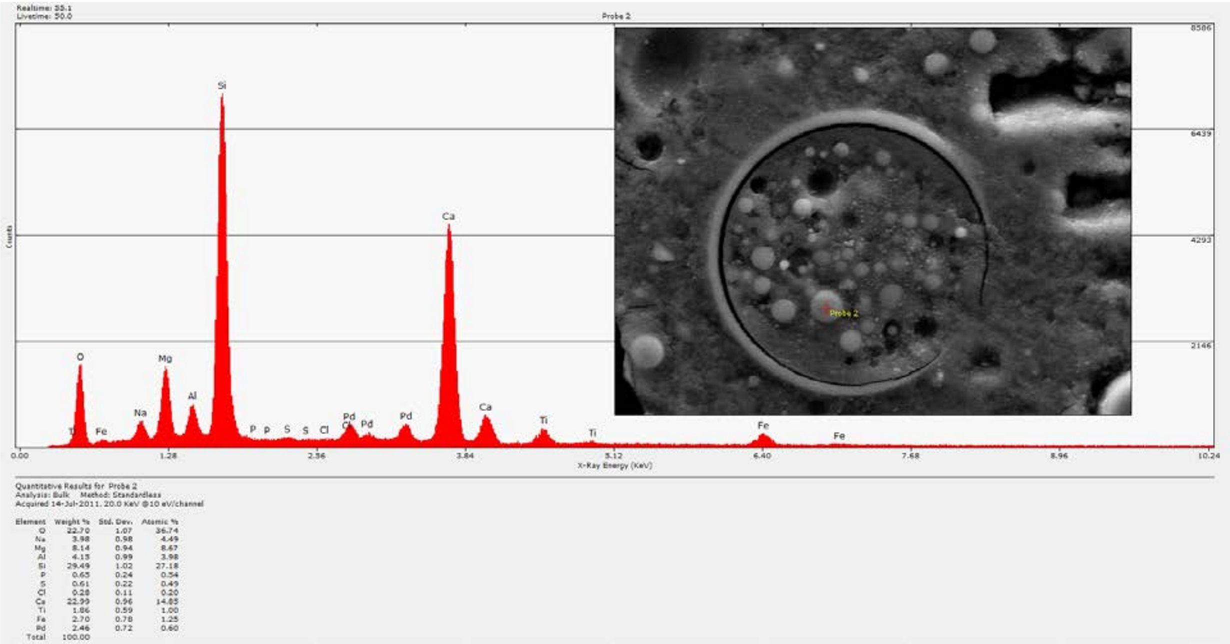
Location 3 was low-magnification examination of the large particles in the Duralith 17-2 sample. The large dark particles (probes 2, 3, 4, 5, 6, 8, 12, and 13) contain only Si and O, which is most likely quartz. Probes 1 and 7 consist of K, Al, and Si which could be a K-feldspar. Probes 9, 11, and 14 contain Ca, Al, and Si, which indicate possibly a Ca-feldspar. Probe 10 is high in Fe and silica. Probe 15 is a mix of Si, Ca, Fe, Al, and Mg. Probe 16 is likely a Ca oxide or hydroxide.


Realtime: 55.1
Livetime: 50.0

Quantitative Results for Probe 1
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011. 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	31.78	1.11	45.26
Na	8.81	0.82	8.79
Mg	2.02	0.62	1.91
Al	18.09	0.85	15.37
Si	26.82	1.00	21.90
P	0.67	0.24	0.50
S	0.77	0.27	0.55
Cl	0.38	0.14	0.25
K	3.92	0.95	2.30
Ca	3.32	0.87	1.90
Ti	0.37	0.14	0.18
Fe	0.75	0.27	0.31
Pd	2.31	0.69	0.50
Total	100.00		

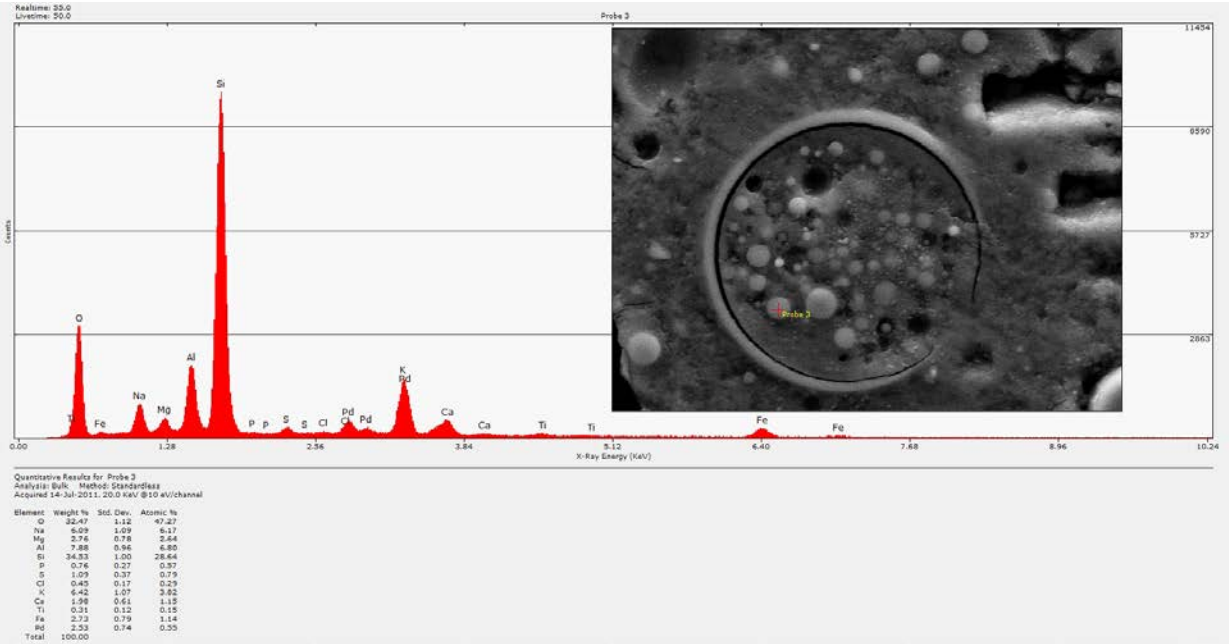
Figure C.21. DuraLith 17-2, Location 1, Probe 1


Realtime: 55.1
Livetime: 50.0

Quantitative Results for Probe 2
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011. 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	22.70	1.07	36.74
Na	3.98	0.98	4.49
Mg	8.14	0.94	8.67
Al	4.15	0.99	3.98
Si	29.49	1.02	27.18
P	0.65	0.24	0.54
S	0.61	0.22	0.49
Cl	0.28	0.11	0.20
Ca	22.99	0.96	14.85
Ti	1.86	0.59	1.00
Fe	2.70	0.78	1.25
Pd	2.46	0.72	0.60
Total	100.00		

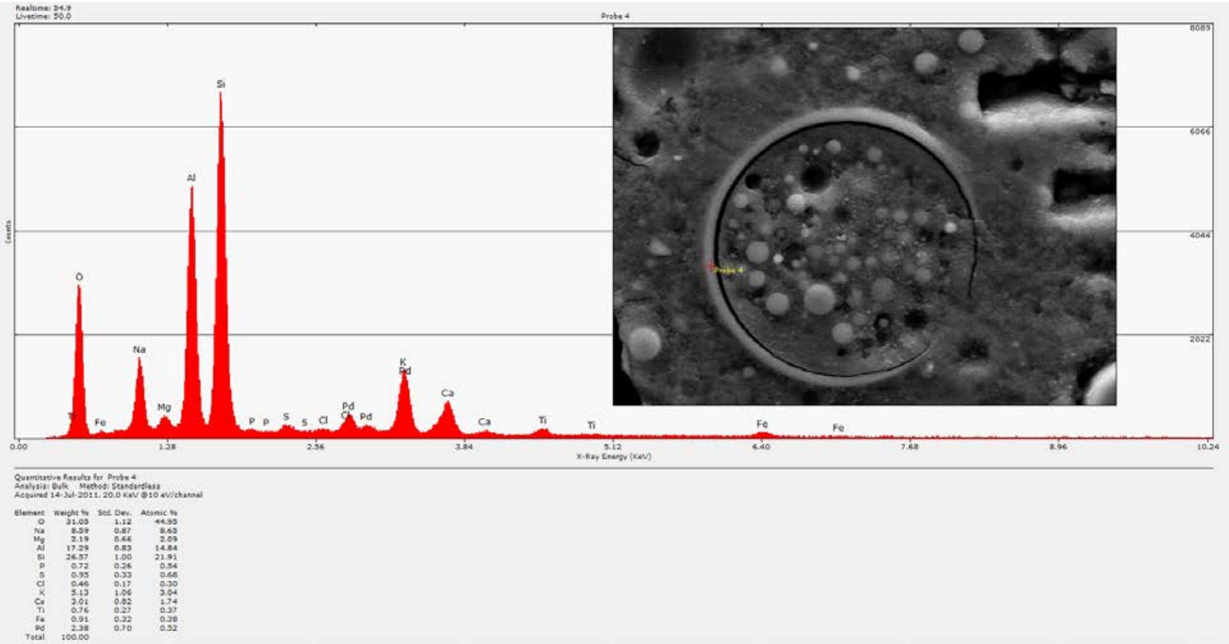
Figure C.22. DuraLith 17-2, Location 1, Probe 2



Quantitative Results for Probe 3
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	32.47	1.12	47.27
Na	6.09	1.09	6.17
Mg	2.76	0.78	2.64
Al	7.88	0.96	6.80
Si	34.53	1.00	28.64
P	0.76	0.27	0.57
S	1.09	0.37	0.79
Cl	0.45	0.17	0.29
K	6.42	1.07	3.82
Ca	1.98	0.61	1.15
Ti	0.31	0.12	0.15
Fe	2.73	0.79	1.14
Pd	2.53	0.74	0.55
Total	100.00		

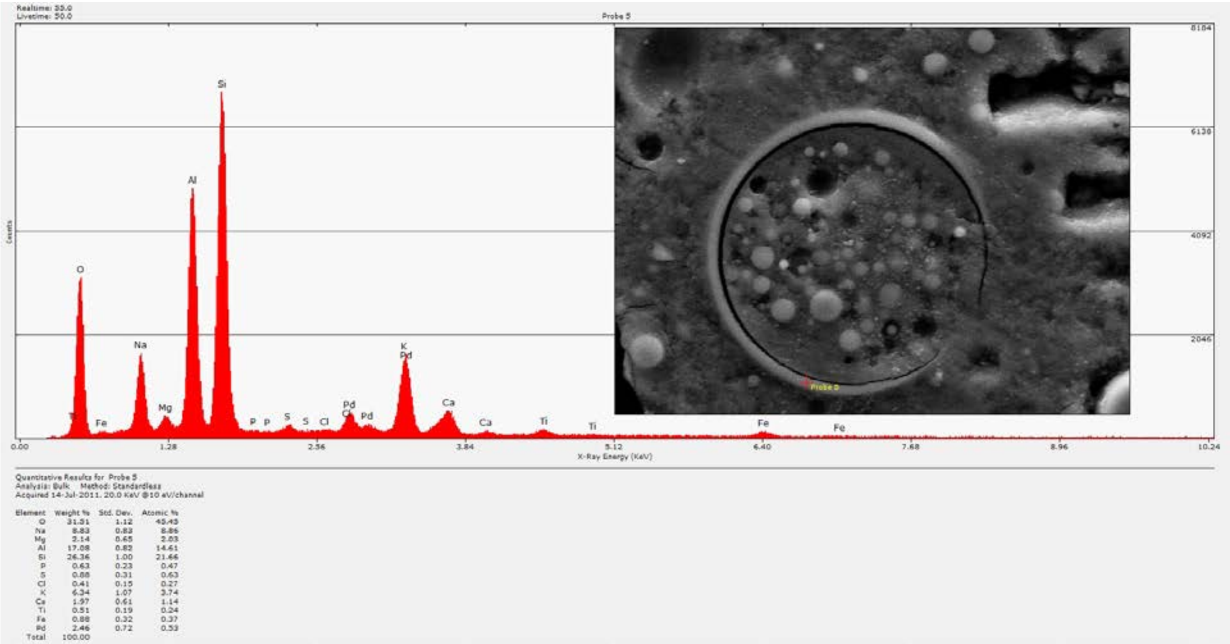
Figure C.23. DuraLith 17-2, Location 1, Probe 3



Quantitative Results for Probe 4
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	31.05	1.12	44.95
Na	8.59	0.87	8.63
Mg	2.19	0.66	2.09
Al	17.29	0.83	14.84
Si	26.57	1.00	21.91
P	0.72	0.26	0.54
S	0.95	0.33	0.68
Cl	0.46	0.17	0.30
K	5.13	1.06	3.04
Ca	3.01	0.82	1.74
Ti	0.76	0.27	0.37
Fe	0.91	0.32	0.38
Pd	2.38	0.70	0.52
Total	100.00		

Figure C.24. DuraLith 17-2, Location 1, Probe 4

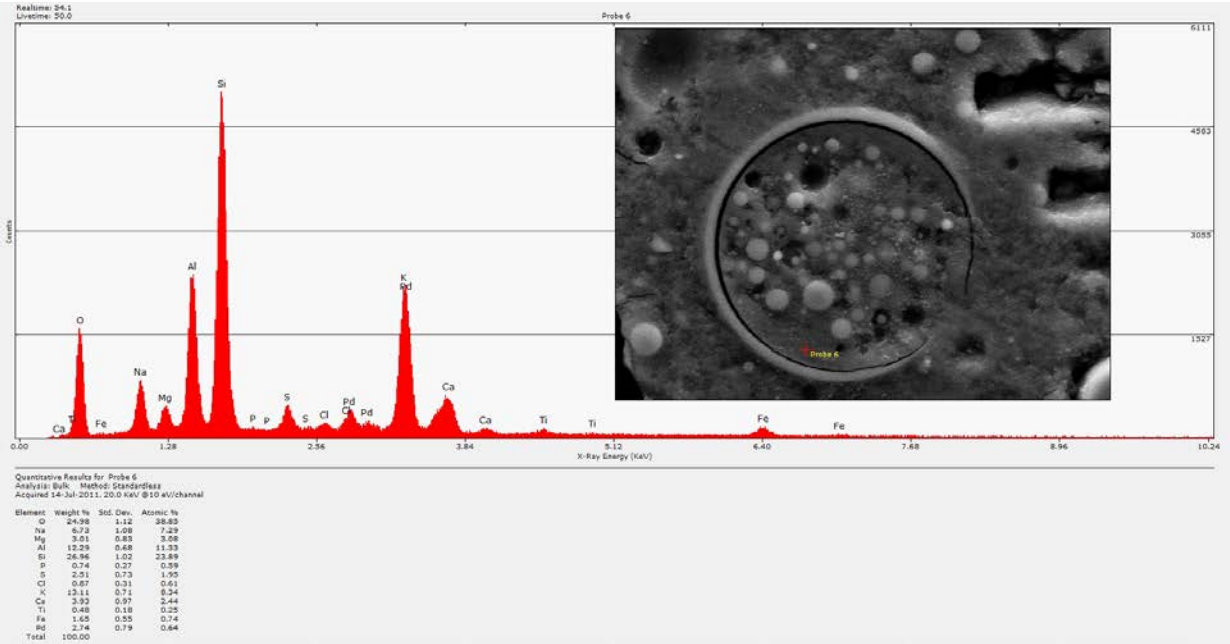


Realtime: 55.0
Livetime: 50.0

Quantitative Results for Probe 5
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	31.51	1.12	45.45
Na	8.83	0.83	8.86
Mg	2.14	0.65	2.03
Al	17.08	0.82	14.61
Si	26.36	1.00	21.46
P	0.63	0.23	0.47
S	0.88	0.31	0.63
Cl	0.41	0.15	0.27
K	6.34	1.07	3.74
Ca	1.97	0.61	1.14
Ti	0.51	0.19	0.24
Fe	0.88	0.32	0.37
Pd	2.46	0.72	0.53
Total	100.00		

Figure C.25. DuraLith 17-2, Location 1, Probe 5

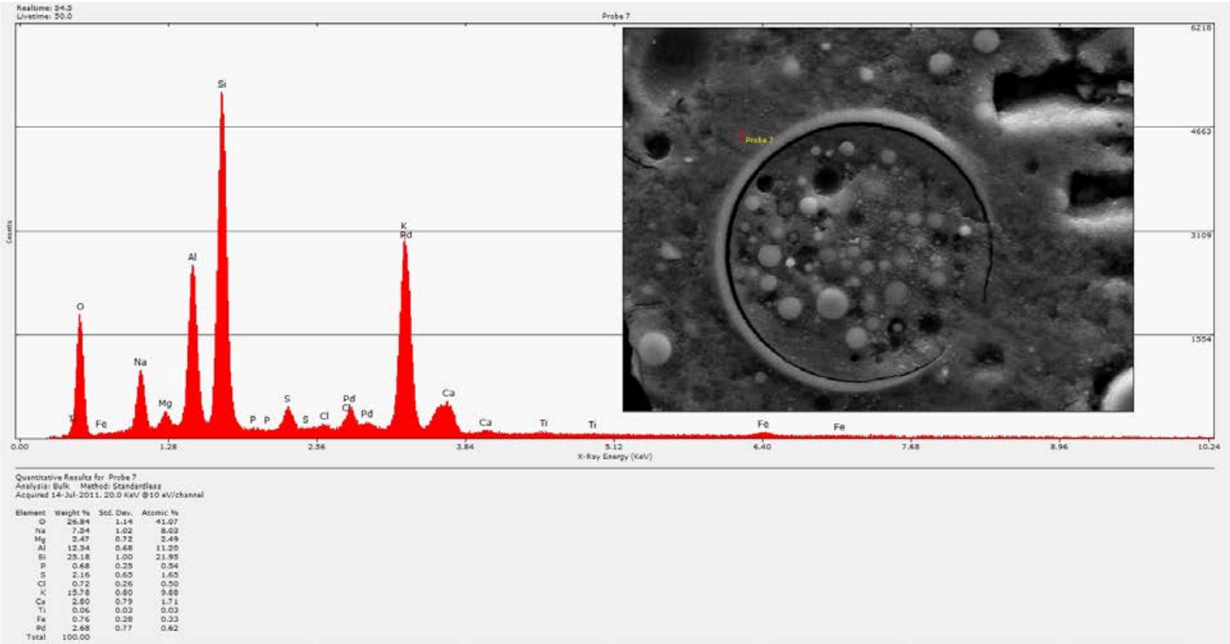


Realtime: 54.1
Livetime: 50.0

Quantitative Results for Probe 6
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	24.98	1.12	38.85
Na	6.73	1.08	7.29
Mg	3.01	0.83	3.08
Al	12.29	0.68	11.33
Si	26.96	1.02	23.89
P	0.74	0.27	0.59
S	2.51	0.73	1.95
Cl	0.87	0.31	0.61
K	13.11	0.71	8.34
Ca	3.93	0.97	2.44
Ti	0.48	0.18	0.25
Fe	1.65	0.55	0.74
Pd	2.74	0.79	0.64
Total	100.00		

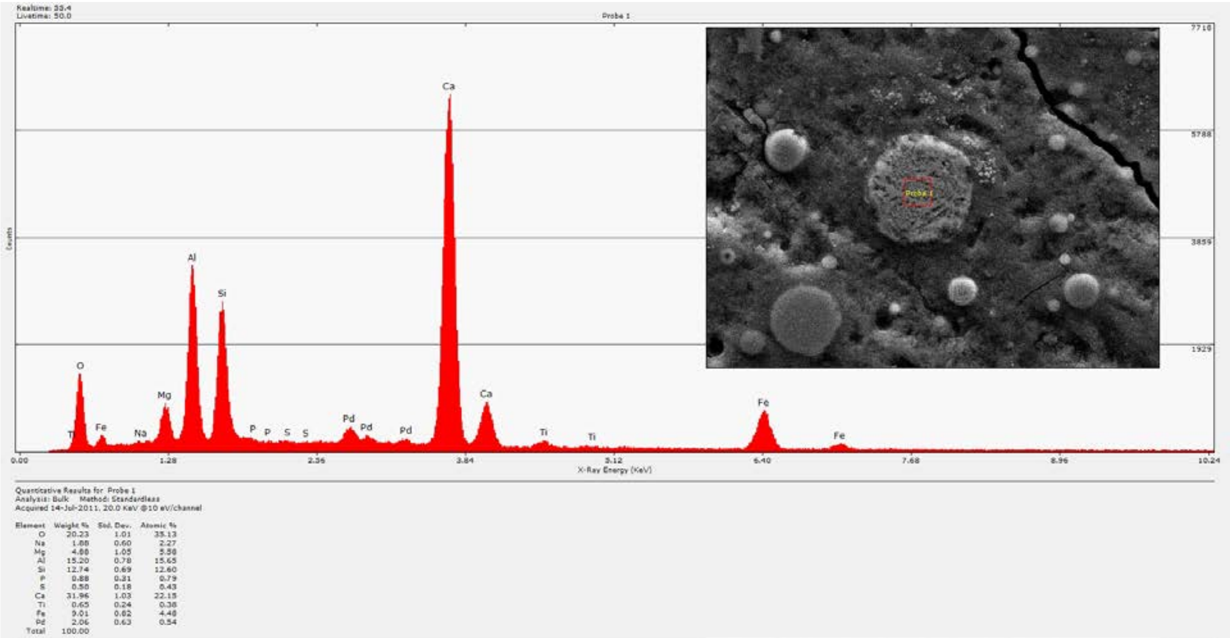
Figure C.26. DuraLith 17-2, Location 1, Probe 6



Quantitative Results for Probe 7
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	26.84	1.14	41.07
Na	7.54	1.02	8.03
Mg	2.47	0.72	2.49
Al	12.34	0.68	11.20
Si	25.18	1.00	21.95
P	0.68	0.25	0.54
S	2.16	0.65	1.65
Cl	0.72	0.26	0.50
K	15.78	0.80	9.88
Ca	2.80	0.79	1.71
Ti	0.06	0.03	0.03
Fe	0.76	0.28	0.33
Pd	2.68	0.77	0.62
Total	100.00		

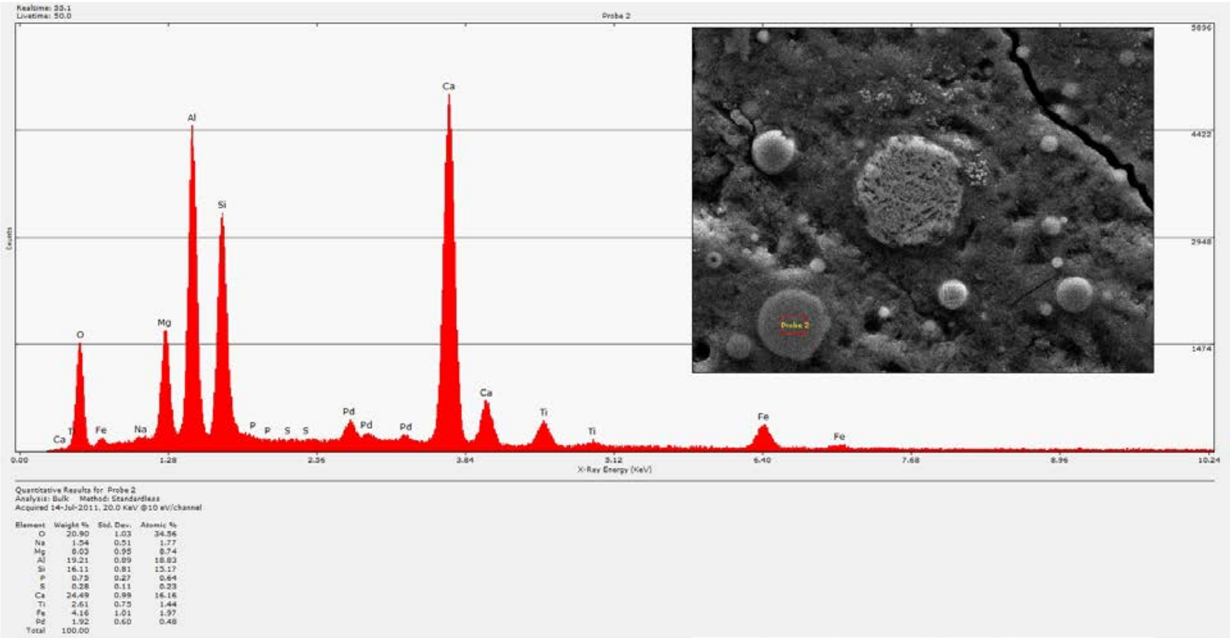
Figure C.27. DuraLith 17-2, Location 1, Probe 7



Quantitative Results for Probe 1
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	20.23	1.01	35.13
Na	1.88	0.60	2.27
Mg	4.88	1.05	5.58
Al	15.20	0.78	15.65
Si	12.74	0.69	12.60
P	0.88	0.21	0.79
S	0.50	0.18	0.43
Ca	31.96	1.03	22.15
Ti	0.65	0.24	0.38
Fe	9.01	0.82	4.48
Pd	2.06	0.63	0.54
Total	100.00		

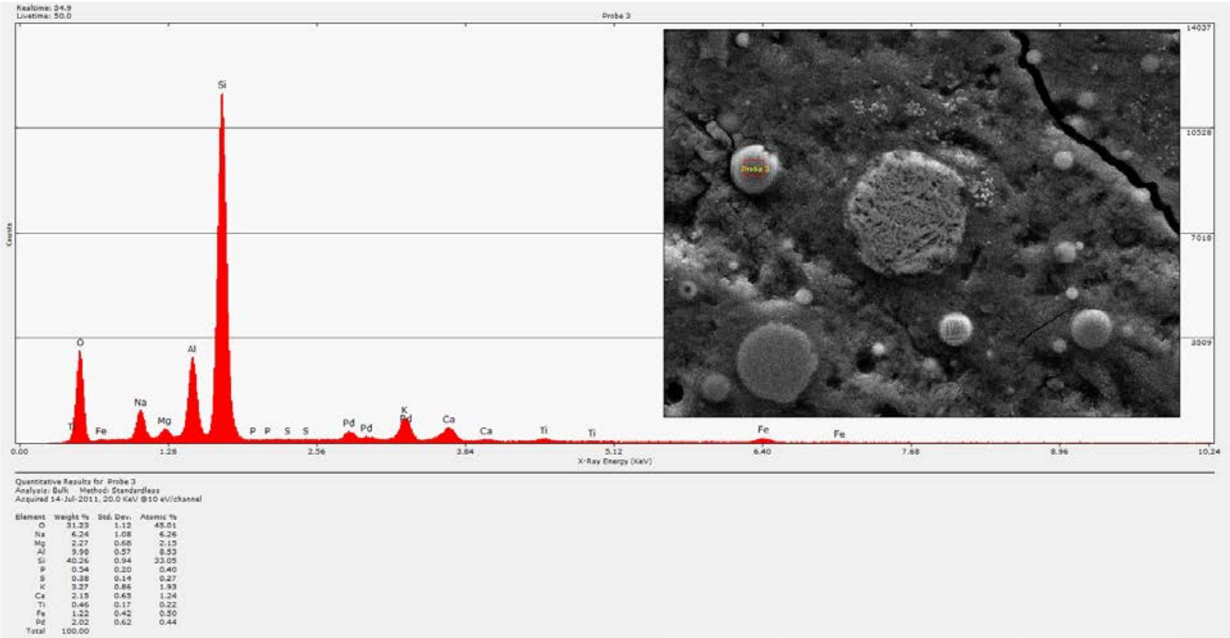
Figure C.28. DuraLith 17-2, Location 2, Probe 1



Quantitative Results for Probe 2
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	20.90	1.03	34.56
Na	1.54	0.51	1.77
Mg	8.03	0.95	8.74
Al	19.21	0.89	18.83
Si	16.11	0.81	15.17
P	0.73	0.27	0.64
S	0.28	0.11	0.23
Ca	24.49	0.99	16.16
Ti	2.61	0.75	1.44
Fe	4.16	1.01	1.97
Pd	1.92	0.60	0.48
Total	100.00		

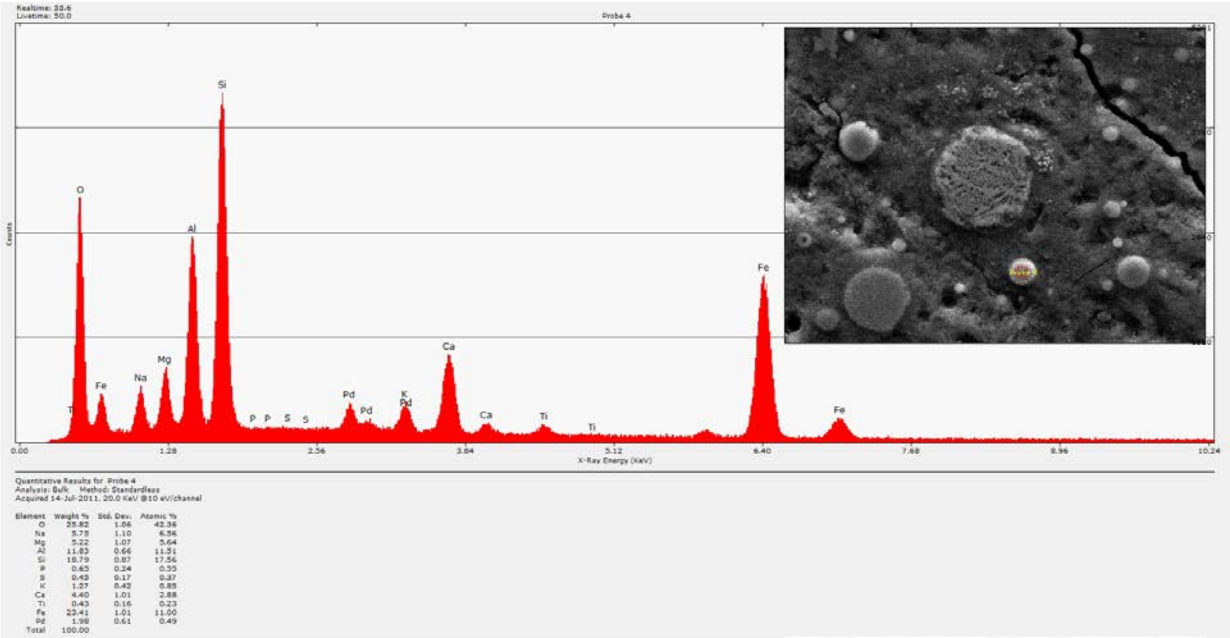
Figure C.29. DuraLith 17-2, Location 2, Probe 2



Quantitative Results for Probe 3
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	31.23	1.12	45.01
Na	6.24	1.08	6.26
Mg	2.27	0.68	2.15
Al	9.98	0.57	8.53
Si	40.26	0.94	33.05
P	0.54	0.20	0.40
S	0.38	0.14	0.27
K	3.27	0.86	1.93
Ca	2.15	0.65	1.24
Ti	0.46	0.17	0.22
Fe	1.22	0.42	0.50
Pd	2.02	0.62	0.44
Total	100.00		

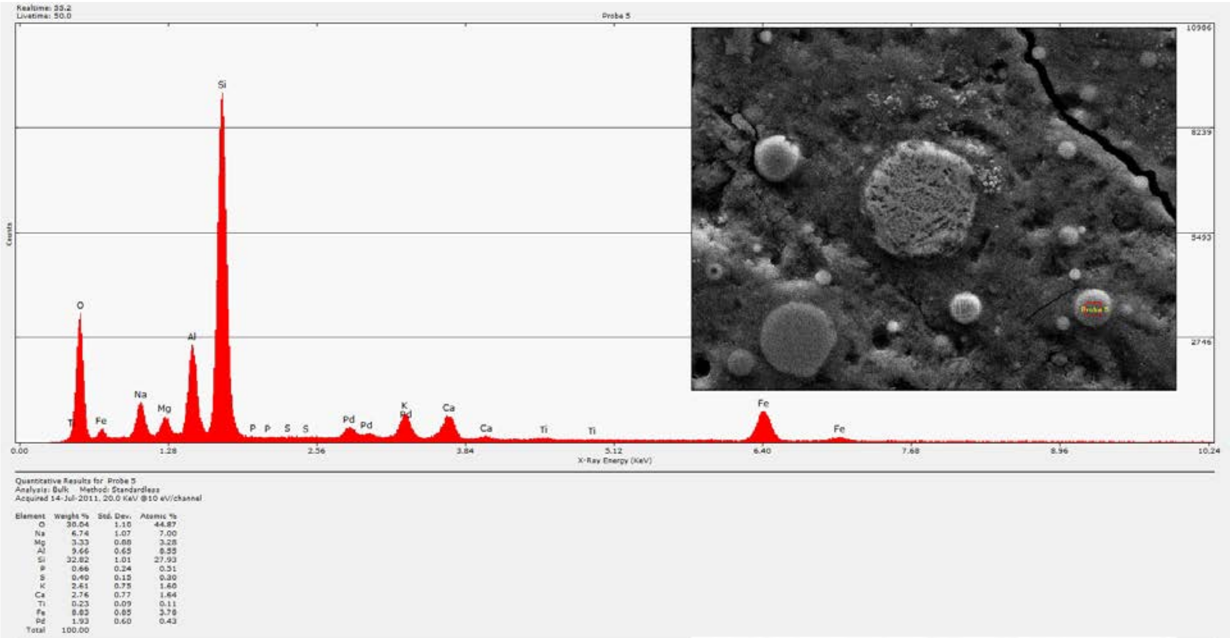
Figure C.30. DuraLith 17-2, Location 2, Probe 3



Quantitative Results for Probe 4
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	25.82	1.06	42.36
Na	5.75	1.10	6.56
Mg	5.22	1.07	5.64
Al	11.83	0.66	11.51
Si	18.79	0.87	17.56
P	0.65	0.24	0.55
S	0.45	0.17	0.37
K	1.27	0.42	0.85
Ca	4.40	1.01	2.88
Ti	0.43	0.16	0.23
Fe	23.41	1.01	11.00
Pd	1.98	0.61	0.49
Total	100.00		

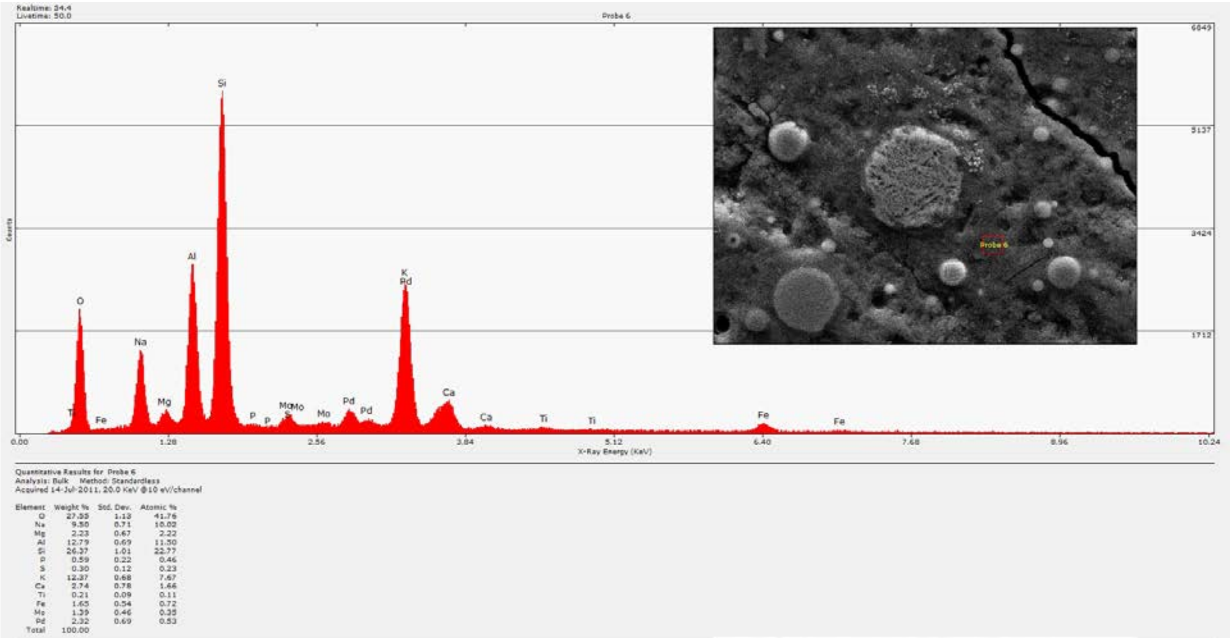
Figure C.31. DuraLith 17-2, Location 2, Probe 4



Quantitative Results for Probe 5
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	38.04	1.10	44.87
Na	6.74	1.07	7.00
Mg	3.33	0.88	3.28
Al	9.66	0.65	8.55
Si	32.82	1.01	27.93
P	0.66	0.24	0.51
S	0.40	0.15	0.30
K	2.61	0.75	1.60
Ca	2.76	0.77	1.64
Ti	0.23	0.09	0.11
Fe	8.83	0.85	3.78
Pd	1.93	0.60	0.43
Total	100.00		

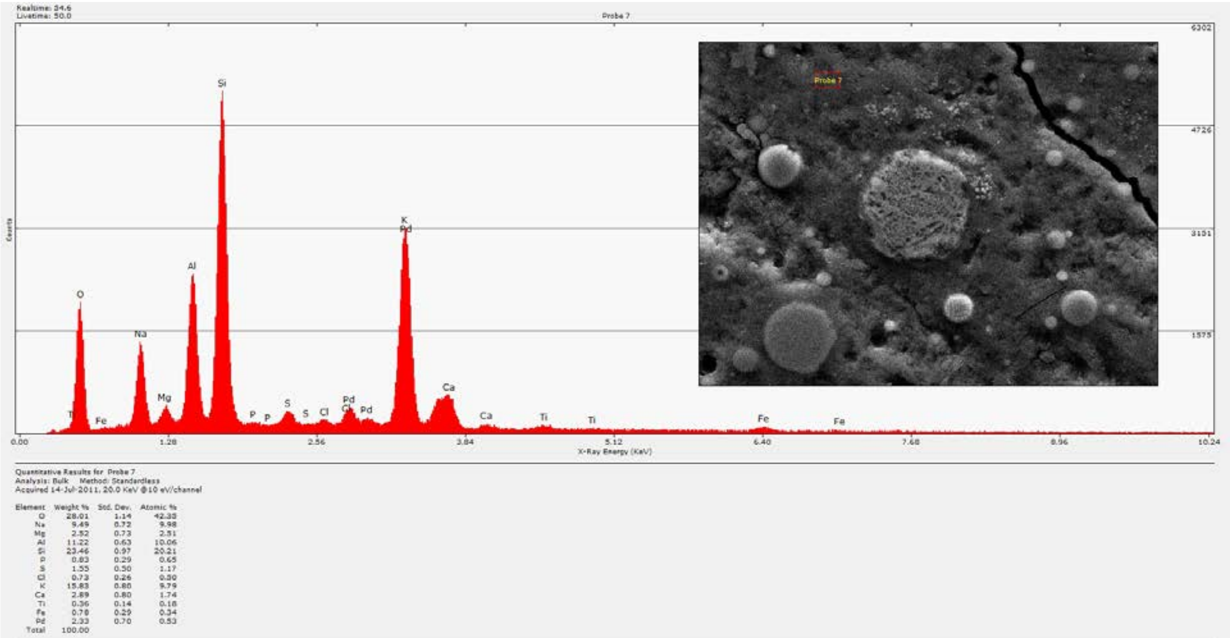
Figure C.32. DuraLith 17-2, Location 2, Probe 5



Quantitative Results for Probe 6
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	27.55	1.13	41.76
Na	9.50	0.71	10.02
Mg	2.23	0.67	2.22
Al	12.79	0.69	11.50
Si	26.37	1.01	22.77
P	0.59	0.22	0.46
S	0.30	0.12	0.23
K	12.37	0.68	7.67
Ca	2.74	0.78	1.66
Ti	0.21	0.09	0.11
Fe	1.65	0.54	0.72
Mo	1.39	0.46	0.35
Pd	2.32	0.69	0.53
Total	100.00		

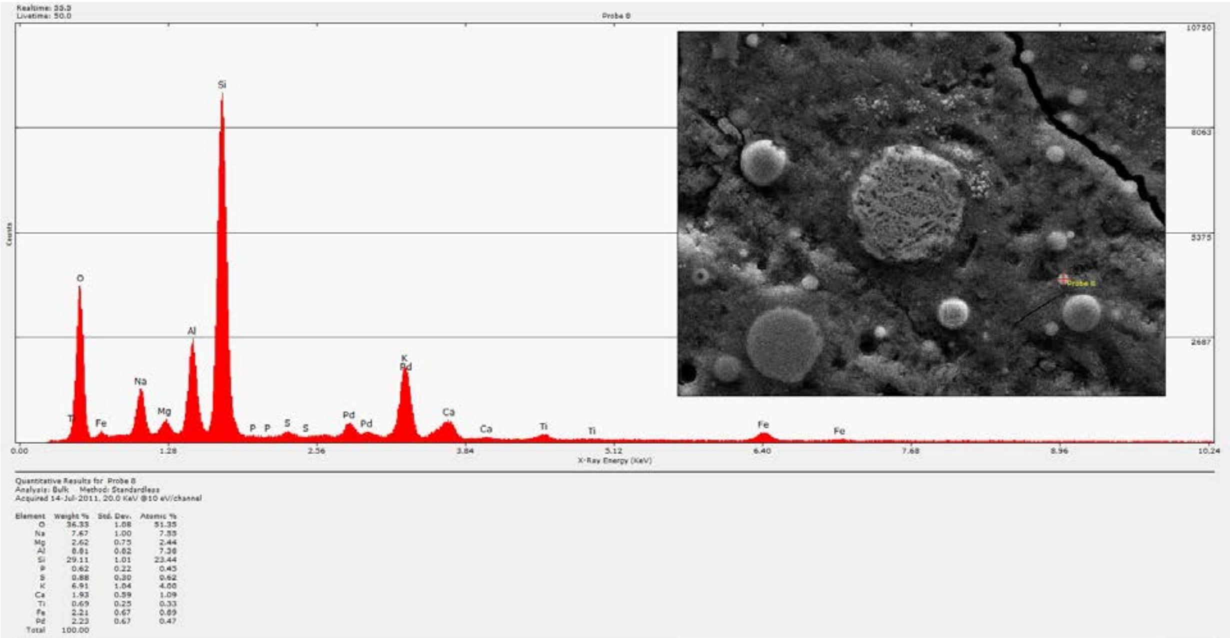
Figure C.33. DuraLith 17-2, Location 2, Probe 6



Quantitative Results for Probe 7
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	28.01	1.14	42.35
Na	9.49	0.72	9.98
Mg	2.52	0.73	2.51
Al	11.22	0.63	10.06
Si	23.46	0.97	20.21
P	0.83	0.29	0.65
S	1.55	0.50	1.17
Cl	0.73	0.26	0.50
K	15.83	0.80	9.79
Ca	2.89	0.80	1.74
Ti	0.36	0.14	0.18
Fe	0.78	0.29	0.34
Pd	2.33	0.70	0.53
Total	100.00		

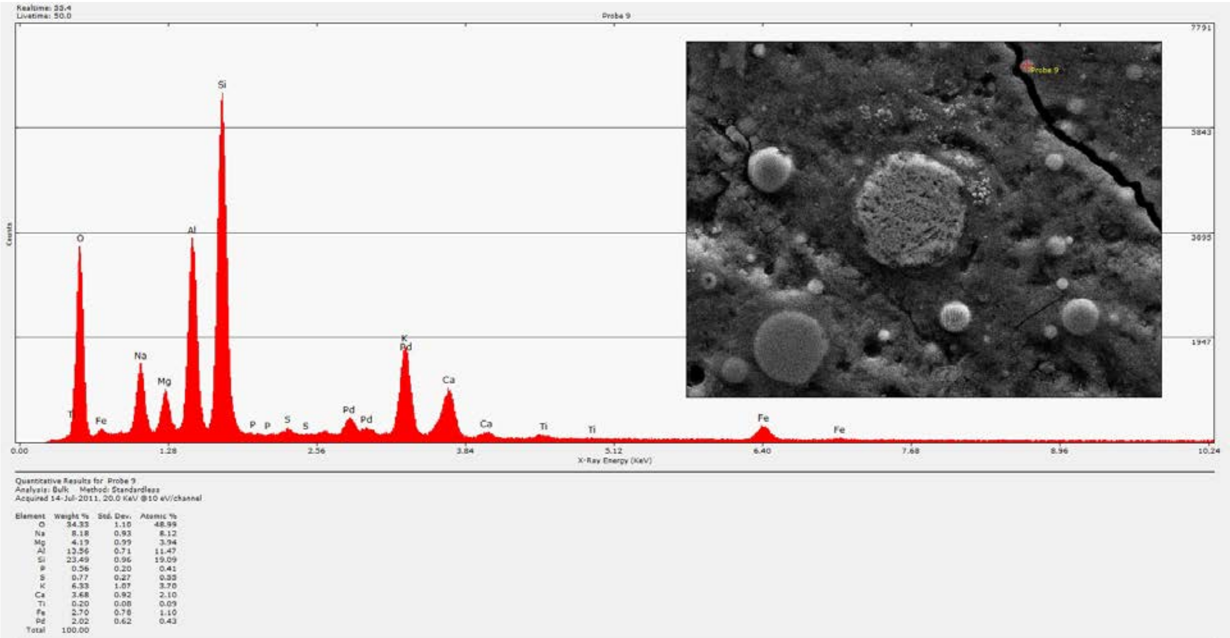
Figure C.34. DuraLith 17-2, Location 2, Probe 7



Quantitative Results for Probe 8
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	36.33	1.08	51.35
Na	7.67	1.00	7.55
Mg	2.62	0.75	2.44
Al	8.81	0.82	7.36
Si	29.11	1.01	23.44
P	0.62	0.22	0.45
S	0.88	0.30	0.62
K	6.91	1.04	4.00
Ca	1.93	0.59	1.09
Ti	0.69	0.25	0.33
Fe	2.21	0.67	0.89
Pd	2.23	0.67	0.47
Total	100.00		

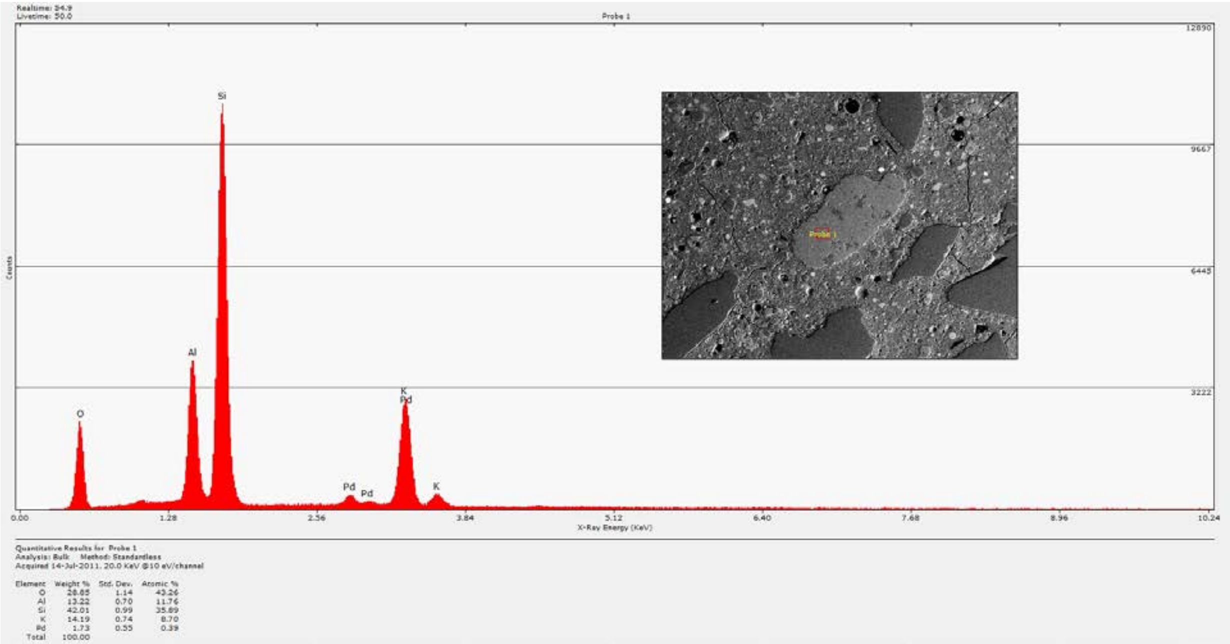
Figure C.35. DuraLith 17-2, Location 2, Probe 8



Quantitative Results for Probe 9
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	34.33	1.10	48.99
Na	8.18	0.93	8.12
Mg	4.19	0.99	3.94
Al	13.56	0.71	11.47
Si	23.49	0.96	19.09
P	0.56	0.20	0.41
S	0.77	0.27	0.55
K	6.33	1.07	3.70
Ca	3.68	0.92	2.10
Ti	0.20	0.08	0.09
Fe	2.70	0.78	1.10
Pd	2.02	0.62	0.43
Total	100.00		

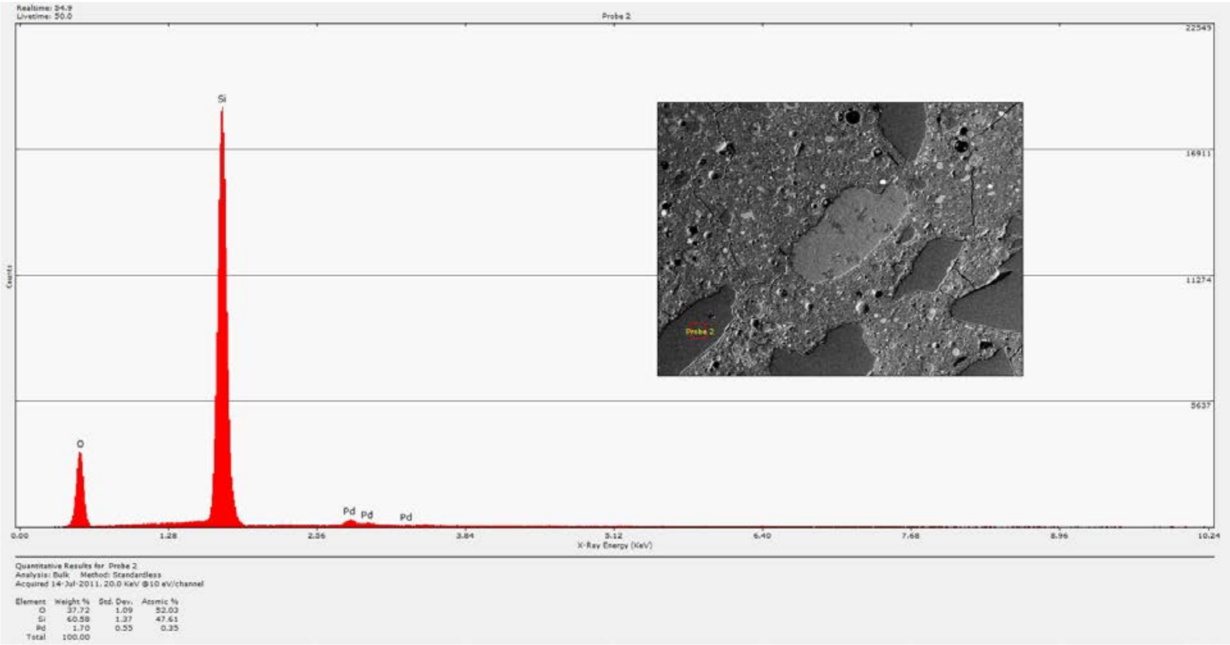
Figure C.36. DuraLith 17-2, Location 2, Probe 9



```
Quantitative Results for  Probe 1
Analysis: Bulk    Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element  Weight %  Std. Dev.  Atomic %
      O     28.65       1.14     43.26
     Al     13.22       0.70     11.76
     Si     42.01       0.99     35.89
      K     14.19       0.74      8.70
     Pd      1.73       0.55      0.39
  Total    100.00
```

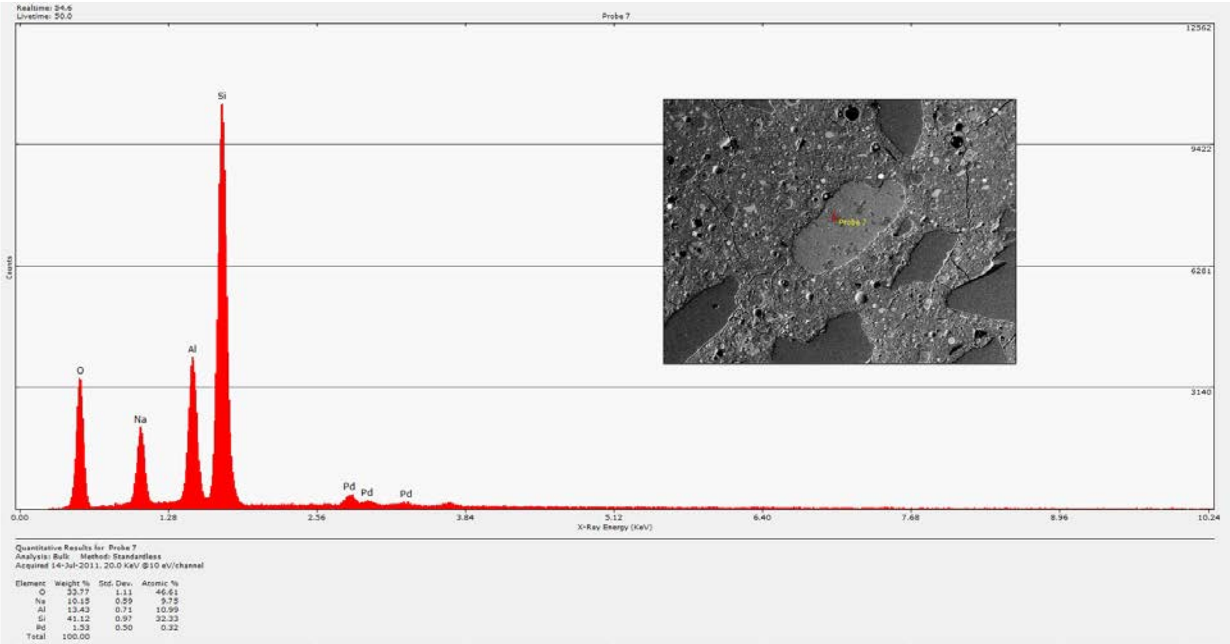
Figure C.37. DuraLith 17-2, Location 3 (low magnification). Probe 1



```
Quantitative Results for  Probe 2
Analysis: Bulk    Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element  Weight %  Std. Dev.  Atomic %
      O     37.72       1.09     52.03
     Si     60.58       1.37     47.61
     Pd      1.70       0.55      0.35
  Total    100.00
```

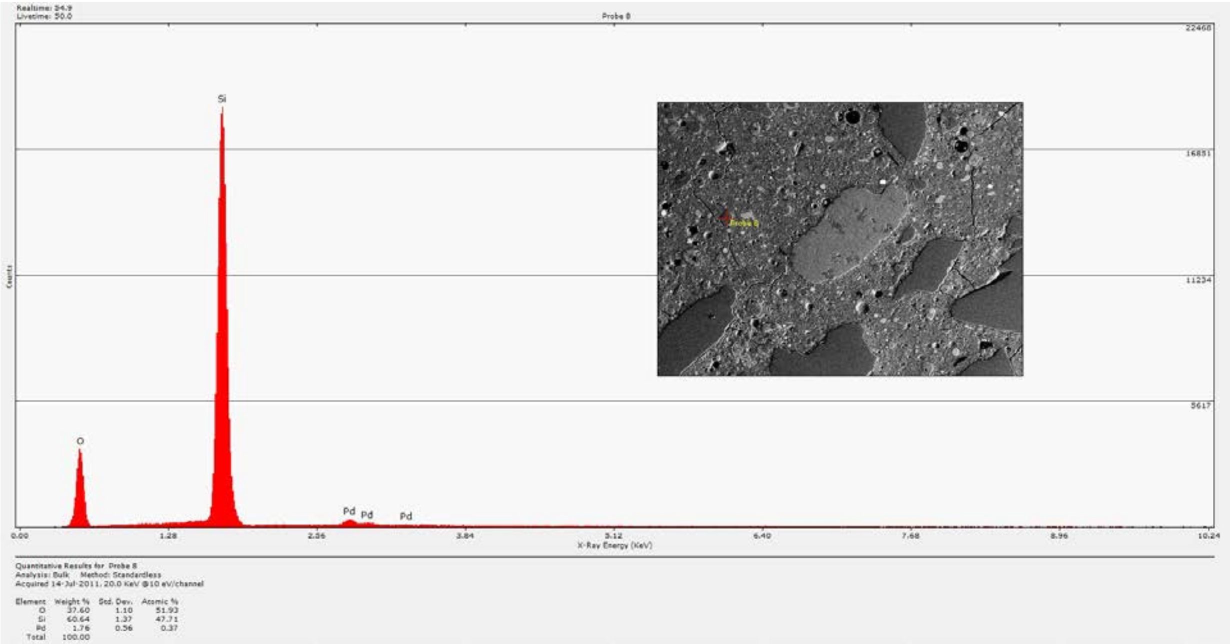
Figure C.38. DuraLith 17-2, Location 3 (low magnification), Probe 2



Quantitative Results for Probe 7
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	33.77	1.11	46.61
Na	10.15	0.59	9.75
Al	13.43	0.71	10.99
Si	41.12	0.97	32.33
Pd	1.53	0.50	0.32
Total	100.00		

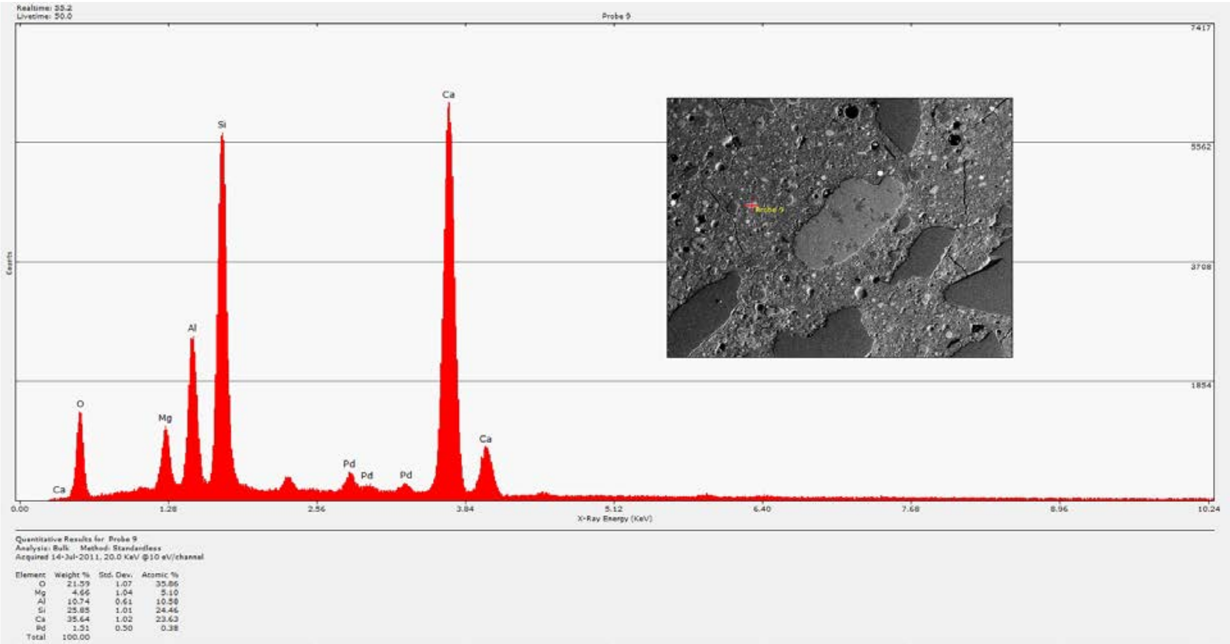
Figure C.39. DuraLith 17-2, Location 3 (low magnification), Probe 7



Quantitative Results for Probe 8
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	37.60	1.10	51.93
Si	60.64	1.37	47.71
Pd	1.76	0.56	0.37
Total	100.00		

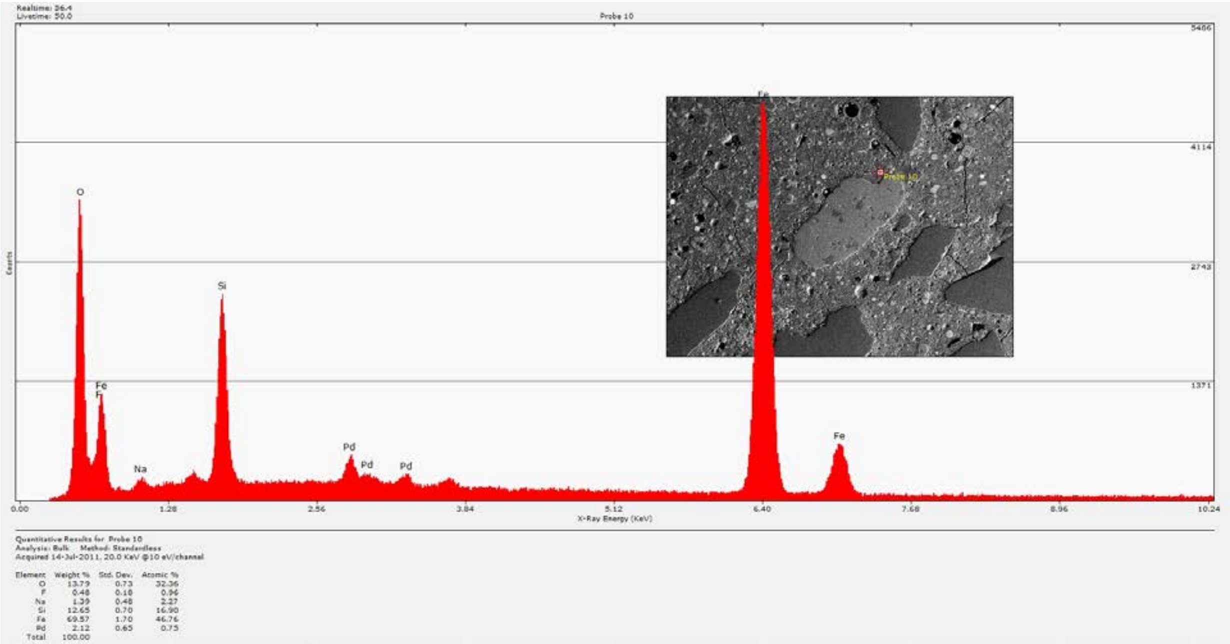
Figure C.40. DuraLith 17-2, Location 3 (low magnification), Probe 8



```
Quantitative Results for  Probe 9
Analysis: Bulk    Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element   Weight %   Std. Dev.   Atomic %
      O      21.59        1.07      35.86
     Mg       4.66        1.04       5.10
     Al      10.74        0.61      10.58
     Si      25.85        1.01      24.46
     Ca      35.64        1.02      23.63
     Pd       1.51        0.50       0.38
  Total     100.00
```

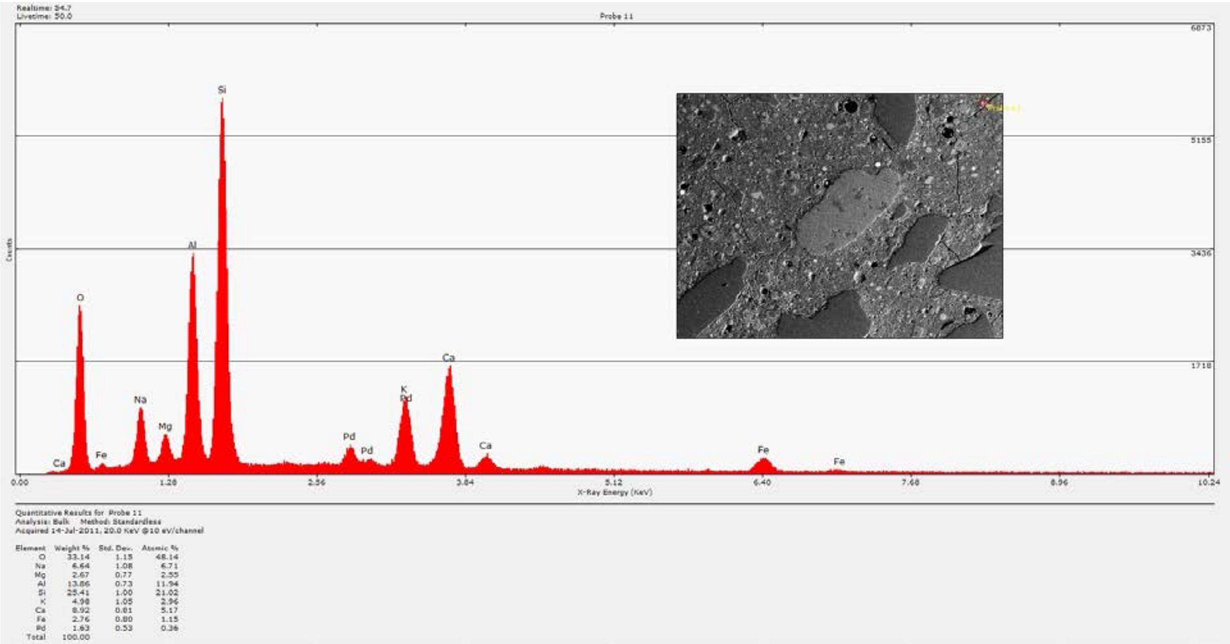
Figure C.41. DuraLith 17-2, Location 3 (low magnification), Probe 9



```
Quantitative Results for  Probe 10
Analysis: Bulk    Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element   Weight %   Std. Dev.   Atomic %
      O      13.79        0.73      32.36
      F       0.48        0.18       0.96
     Na       1.39        0.48       2.27
     Si      12.65        0.70      16.90
     Fe      69.57        1.70      46.76
     Pd       2.12        0.65       0.75
  Total     100.00
```

Figure C.42. DuraLith 17-2, Location 3 (low magnification), Probe 10

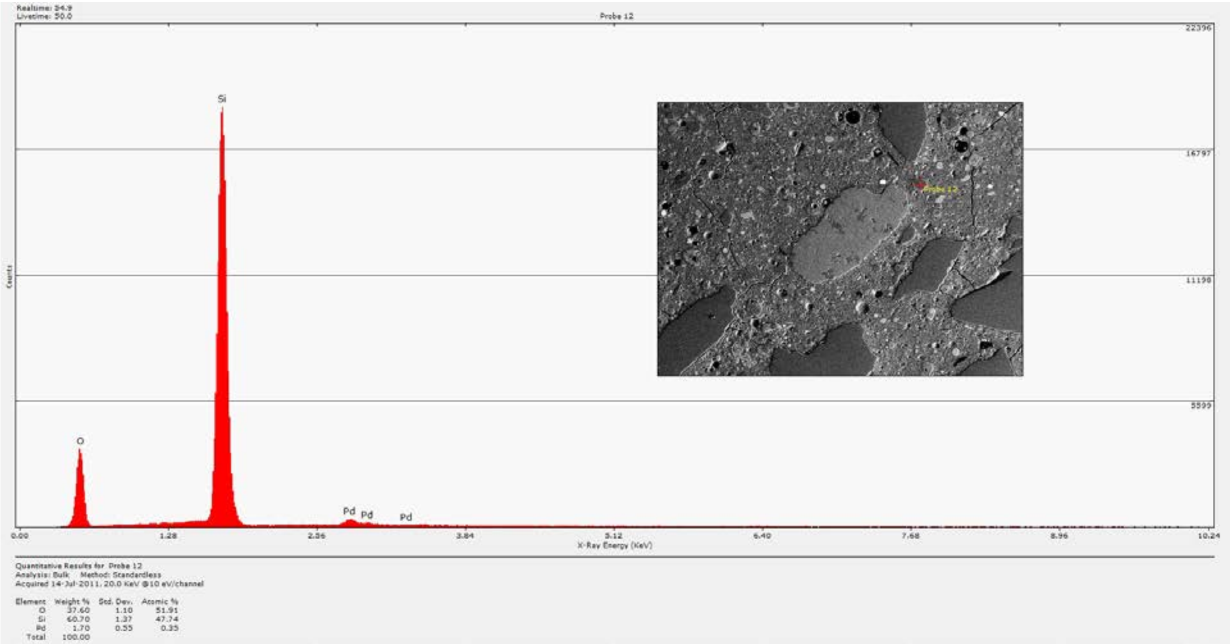


```
Realtime: 54.7
Livetime: 50.0
```

```
Quantitative Results for  Probe 11
Analysis: Bulk    Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element   Weight %   Std. Dev.   Atomic %
      O      33.14        1.15      48.14
     Na       6.64        1.08       6.71
     Mg       2.67        0.77       2.55
     Al      13.86        0.73      11.94
     Si      25.41        1.00      21.02
      K       4.98        1.05       2.96
     Ca       8.92        0.81       5.17
     Fe       2.76        0.80       1.15
     Pd       1.63        0.53       0.36
  Total     100.00
```

Figure C.43. DuraLith 17-2, Location 3 (low magnification), Probe 11

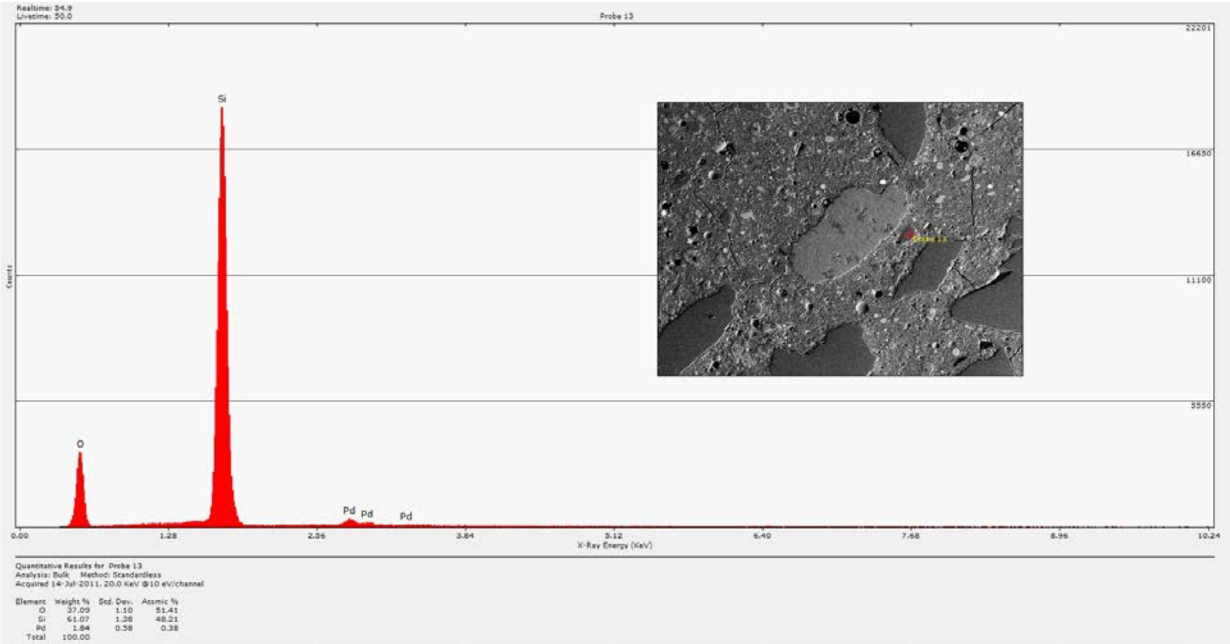


```
Realtime: 54.9
Livetime: 50.0
```

```
Quantitative Results for  Probe 12
Analysis: Bulk    Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element   Weight %   Std. Dev.   Atomic %
      O      37.60        1.10      51.91
     Si      60.70        1.37      47.74
     Pd       1.70        0.55       0.35
  Total     100.00
```

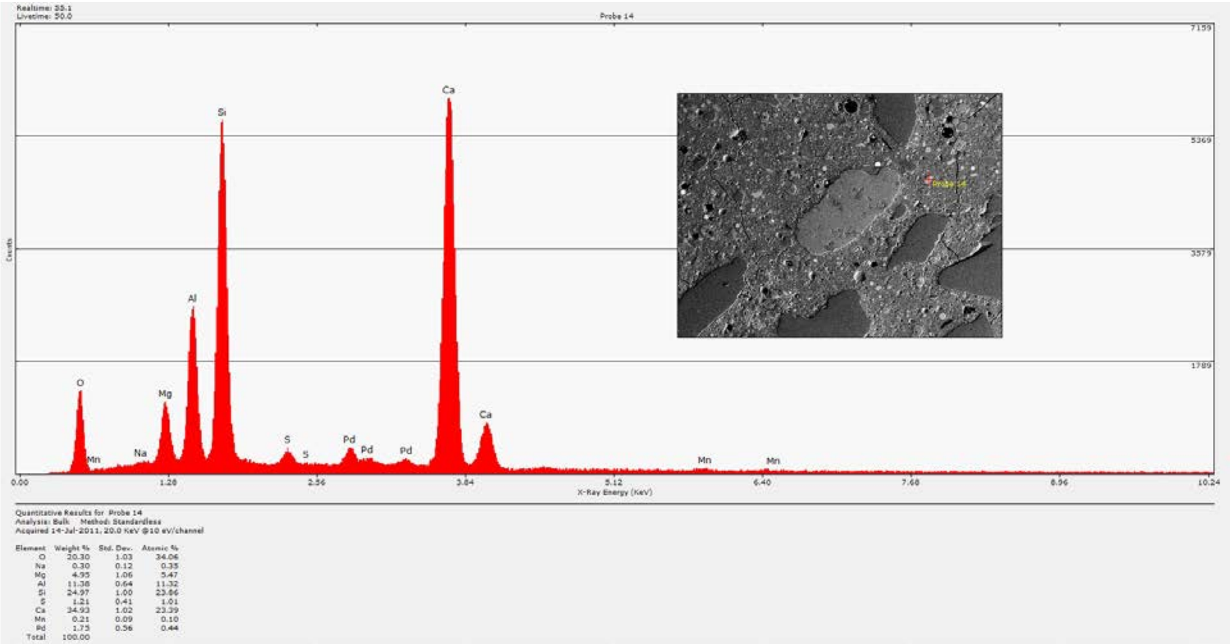
Figure C.44. DuraLith 17-2, Location 3 (low magnification), Probe 12



Quantitative Results for Probe 13
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	37.09	1.10	51.41
Si	61.07	1.38	48.21
Pd	1.84	0.58	0.38
Total	100.00		

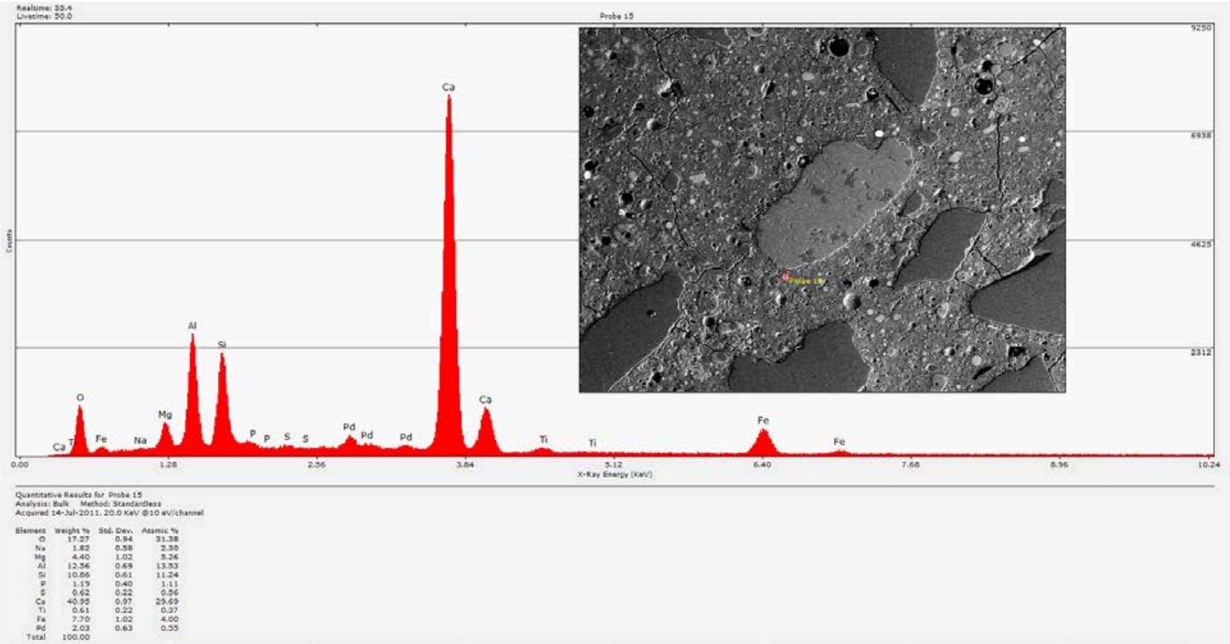
Figure C.45. DuraLith 17-2, Location 3 (low magnification), Probe 13



Quantitative Results for Probe 14
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	20.30	1.03	34.06
Na	0.30	0.12	0.35
Mg	4.95	1.06	5.47
Al	11.38	0.64	11.32
Si	24.97	1.00	23.86
S	1.21	0.41	1.01
Ca	34.93	1.02	23.39
Mn	0.21	0.09	0.10
Pd	1.75	0.56	0.44
Total	100.00		

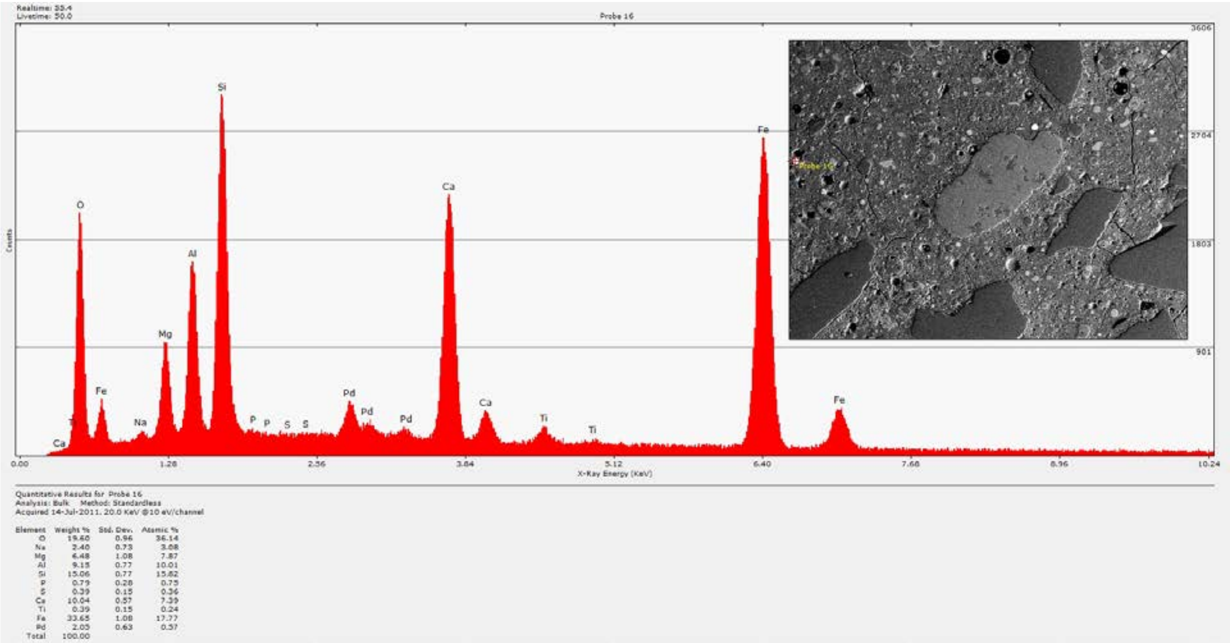
Figure C.46. DuraLith 17-2, Location 3 (low magnification), Probe 14



Quantitative Results for Probe 15
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011. 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	17.27	0.94	31.38
Na	1.82	0.58	2.30
Mg	4.40	1.02	5.26
Al	12.56	0.69	13.53
Si	10.86	0.61	11.24
P	1.19	0.40	1.11
S	0.62	0.22	0.56
Ca	40.95	0.97	29.69
Ti	0.61	0.22	0.37
Fe	7.70	1.02	4.00
Pd	2.03	0.63	0.55
Total	100.00		

Figure C.47. DuraLith 17-2, Location 3 (low magnification), Probe 15



Quantitative Results for Probe 16
Analysis: Bulk Method: Standardless
Acquired 14-Jul-2011. 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	Atomic %
O	19.60	0.96	36.14
Na	2.40	0.73	3.08
Mg	6.48	1.08	7.87
Al	9.15	0.77	10.01
Si	15.06	0.77	15.82
P	0.79	0.28	0.75
S	0.39	0.15	0.36
Ca	10.04	0.57	7.39
Ti	0.39	0.15	0.24
Fe	33.65	1.08	17.77
Pd	2.05	0.63	0.57
Total	100.00		

Figure C.48. DuraLith 17-2, Location 3 (low magnification), Probe 16

Appendix D

Comments from Technology Developers on MSE Engineering Scale Testing Report

Appendix D

Comments from Technology Developers on MSE Engineering Scale Testing Report

Comments on Ceramicrete Engineering-Scale Demonstration

Three specific observations come out of the Ceramicrete engineering-scale demonstration:

1. expansion of the form during curing
2. surface cracking observed on large scale samples
3. formation of "salt" deposits on the waste-form surface

Expansion of waste forms: As discussed in the ANL lab-scale report (Singh et al. 2011), expansion was observed in some of the laboratory-scale samples. This expansion has been attributed to the breakdown of the carbonates/bicarbonates in the waste stream when it comes in contact with an acid phase (potassium phosphate). This reaction will release carbon dioxide which results in the expansion of the waste form during the curing stage. This release of gas and expansion are expected to be more acute for large-scale samples, since the mixing time (20 minutes, the same as the small-scale samples) may not be enough to complete the reaction and purge out all CO_2 before pouring into the mold. One possible solution would be to pre-react the waste stream with an acid or just potassium phosphate to break down the carbonates/bicarbonates before pouring the rest of the binder mix.

Surface cracking observed on large-scale samples: Drying cracks observed on the surface of some of the waste form samples are probably caused by: (a) inadequate water additions and (b) repeated opening of the sample cover during curing.

The amount of water added was not optimized during the engineering-scale tests. As mentioned in the ANL lab-scale report (Singh et al. 2011), additional water was added (350 g water to 2.57 kg waste simulant) in the two-gallon scale-up test. This was because there is some absorption of water by the binder/filler starting powders. This issue will be more critical when large amounts of powders are used, as at the drum scale and engineering scale. Under-addition of water will lead to cracking during the curing process. The report mentions that the covers of waste form molds were opened frequently to observe/make measurements; significant amounts of water may be lost from the surface when the mold is opened, particularly when the waste form is warm, leading to drying cracks.

Formation of a "salt" phase on the waste-form surface: The ribbon mixer probably did not provide enough mixing at large volumes. In the past, ANL has used a double planetary rotary-paddle type mixer, which results in a homogeneous mix. A blade mixer simulates the laboratory-scale mixing using a spatula. Inhomogeneous mixing is the most likely cause of the pockets of amorphous phase and the granular clumps. Inhomogeneous mixing is also resulting in the clumping observed on the blade parts; we did not observe this kind of clumping with the blade mixer. The material separation can also lead to a lower quality product.

Comments on DuraLith Engineering-Scale Demonstration

The DuraLith baseline formulation (Sample #10) proposed by VSL for engineering-scale testing at MSE was developed using the NewCem® slag cement produced by Lafarge, Inc., prior to 2010. In early 2011, we learned from Lafarge that a product specification change had occurred for NewCem slag cement (ground granulated blast-furnace slag) in 2010. The new product has a much smaller grain size, contains significantly more CaO and less MgO, and has a higher activity index. This production specification change was unknown to us when the DuraLith baseline formulation was developed and submitted to PNNL for engineering-scale testing. We had enough 'old' furnace slag to conduct the entire project for PNNL with that material. However, it became clear that the engineering-scale tests had to be conducted with 'new' furnace slag and that adjustments of the recipe had to be made prior to engineering-scale testing.

We gained some experience with the 'new' ground granulated blast-furnace slag in early 2011 in the framework of another DuraLith project at VSL. As an example, just replacing 'old' with 'new' furnace slag in a recipe decreased the setting time from 120 minutes to less than 30 minutes. However, we found that replacement of up to 70 wt% of both furnace slag and metakaolin by low calcium Class F fly ash in DuraLith recipes improved workability, extended set time, and lowered heat release during curing significantly.

This experience and the availability of fly ash on site (a fly ash with less CaO would have been preferred) allowed us to make rapid changes to the baseline formulation at MSE, resulting in Samples #12, 13, and 15 for the 4.5-gal tests and Samples #14, 16, and 17 for the 51-gal tests. Incorporation of Class F fly ash significantly extended workable and set times of the DuraLith products.

On-site adjustments of the recipe made it possible to demonstrate that DuraLith products can be made on an engineering scale. The testing demonstrated the feasibility of mixing the binder and activator ingredients, mixing these two components with each other, and pouring the final mix (the paste) into molds. However, none of the 'modified' recipes can be considered optimal with respect to production-related and final waste-form properties. This is discussed in more detail below. Formulation changes were necessary to accommodate the change in furnace slag and the available equipment used to perform the engineering-scale samples.

The main problem at the time of testing at MSE was to find the best water content for the modified recipe, which we did not. If we consider the modified recipe with 16.45 wt% water to be the new baseline formulation (Samples #15 and 17), then the recipe with 21 wt% water (Samples #14 and 16) contained about 28% more water. This turned out to be too much.

Observations and Comments

- **Set Time**

The paste for Sample #10 (DuraLith baseline formulation) set too quickly, i.e., within less than 10 minutes. Increasing the water content alone was not effective in extending set time (Sample #11). An effective way to extend set time and improve workability is to use less-reactive amorphous aluminosilicate pozzolans. Low-CaO Class F fly ash is the preferred pozzolan. It exhibits lower reactivity in highly alkaline solutions compared to high-CaO fly ash. At MSE, high-CaO Class F fly ash was used due to unavailability of low-CaO fly ash from local suppliers. Incorporation of low-CaO Class F fly ash in DuraLith formulations usually results in lower early strength. However, we can still make DuraLith waste forms with a compressive strength of more than 10,000 psi after 28 days.

Extension of set time may also be achieved by increasing the waste loading above 6-M sodium for the Hanford secondary waste. Nitrate, nitrite, and chloride act as effective set retarders in samples with high waste loading.

In light of the permanent change of the grain size of ground granulated blast furnace slag, a small optimization project at the bench scale is recommended as part of any future work to determine the preferred proportions of metakaolin, furnace slag, and fly ash to achieve desirable processing parameters and product performance.

- **Water Content**

Engineering-scale tests at MSE used DuraLith recipes with water contents as high as 21 wt%. We must point out that excessive water may have undesirable effects:

Bleed water can increase if the water content is too high. Bleed water will vaporize, but may leave precipitates on the sample surface. Minor salt deposition was seen on some sample surfaces (Samples #14, 16, and 17). Most of the water in geopolymer samples escapes by vaporization during curing.

Excess water (i.e., water not needed to make a good product) will increase the volume of pore solution. Figure 4.35 shows pore solution pockets. The pore solution is different in composition from the activator solution. The pore solution contains dissolved silicate and aluminate, alkali and alkali-earth species, and soluble salts from waste. The original activator solution is very reactive and has very little chance to remain unchanged in the presence of binder material. The volume of pore solution will decrease as it is consumed during the dynamic process of curing.

The performance of the material, particularly mechanical strength, can be impaired if excessive water is used.

Correct water content in the recipe would prevent bleeding, salt deposition, and distribution of residual water in micro- or nanopores.

- **Mixing**

Mixing may be insufficient if an inappropriate mixer is used. The ribbon mixer at MSE clearly was not optimal for this purpose. Lumps of undigested raw materials were present during preparation of the DuraLith paste for Sample #14, indicating poor mixing. Some of these lumps may still be digested during geopolymerization (curing). The MSE 20-hp hydraulically driven drum mixer was a better choice (preparation of Samples #16 and 17). However, there are commercially available mixers that are much more appropriate for cementitious materials applications. For example, an Eirich Machines, Inc., intensive mixer uses a rotating mixing pan in conjunction with the dual-purpose bottom/wall scraper to direct the materials into the eccentrically placed, rotating mixing tools. This arrangement produces counter-flowing currents of materials with a high velocity differential (high shear). The mixers can be used for batch modes and continuous processes with useful volumes up to 12,000 liters. Eirich mixers are characterized by very short mixing times and produce highly uniform cementitious products.

Aggregate settling is also common in cementitious formulations with excess water. Therefore, it is not surprising that minor aggregate settling was found in Sample #16 with 21% water (Figure 4.36). Longer mixing definitely helps to alleviate aggregate settling, even in mixtures with a small excess of water. In a cementitious paste, viscosity increases with increasing time and settling tendency decreases. Minor aggregate settling will not affect product performance significantly. A decrease in water content (Sample #17 with 16.45% water) definitely prevented aggregate from settling since the paste was thicker and more viscous.

Appendix E

MSE Hanford Secondary Waste Form Engineering Scale Demonstration Testing Report

Final Report

Engineering-Scale Demonstration of Ceramicrete and DuraLith Waste Forms for the Solidification of Hanford Secondary Wastes

August 2011

MSE-294

Final Report

Engineering-Scale Demonstration of Ceramicrete and DuraLith Waste Forms for the Solidification of Hanford Secondary Wastes

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Washington River Protection Solutions

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August 2011

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LIST OF ACRONYMS

Standard Acronyms

ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials (ASTM International)
BFS	Blast Furnace Slag
CD	Critical Decision
Cfm	cubic feet per minute
DOE	U.S. Department of Energy
EPA	Environmental Protection Agency
ETF	Effluent Treatment Facility
FBSR	Fluidized Bed Steam Reforming
gal	gallon
HLW	high-level waste
IDF	Integrated Disposal Facility
IHLW	immobilized HLW
ILAW	immobilized LAW
LAW	low-activity waste
min	minutes
MSE	MSE Technology Applications, Inc.
ORP	Office of River Protection
PBI	Performance Based Incentive
PF	Power Factor
PNNL	Pacific Northwest National Laboratory
RCRA	Resource Conservation and Recovery Act
RRF	Resource Recovery Facility
sec	seconds
STU	Solidification Treatment Unit
TCLP	toxicity characteristic leaching procedure
wt %	weight percent
WRPS	Washington River Protection Solutions
WTP	Waste Treatment and Immobilization Plant

Component Acronyms

H_20	Water
$Al(OH)_3$	Aluminum Hydroxide
NaCl	Sodium Chloride
Na_2CO_3	Sodium Carbonate
KNO_3	Potassium Nitrate
$NaNO_3$	Sodium Nitrate
$NaNO_2$	Sodium Nitrite
NaOH	Sodium Hydroxide
$NaH_2PO_4 \cdot 2H_20$	Monosodium Phosphate
Na_2SiO_3	Sodium Silicate
Na_2SO_4	Sodium Sulfate
$Na_2C_2O_4$	Sodium Oxalate
$H_2C_2O_4 \cdot 2H_2O$	Oxalic Acid
$NaReO_4$	Sodium Perrhenate
MgO	Magnesium Oxide
KH_2PO_4	Mono Potassium Phosphate
$SnCl_2 \cdot 2H_20$	Stannous Chloride
SnF_2	Tin Fluoride
KOH	Potassium Hydroxide

Background – Section 1

The Hanford Site in southeastern Washington State has 54 million gallons of radioactive and chemically hazardous wastes stored in 177 underground tanks. The U.S. Department of Energy (DOE), Office of River Protection (ORP), through its contractors, is constructing the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to convert the radioactive and hazardous wastes into stable glass waste forms for disposal. Within the WTP, the pretreatment facility will receive the retrieved waste from the tank farms and separate it into two treated process streams. The pretreated high-level waste (HLW) mixture will be sent to the HLW Vitrification Facility, and the pretreated low-activity waste (LAW) stream will be sent to the LAW Vitrification Facility. The two WTP vitrification facilities will convert these process streams into glass, which is poured directly into stainless steel canisters. The immobilized HLW (IHLW) canisters will ultimately be disposed of at an off-site federal repository. The immobilized LAW (ILAW) canisters will be disposed of on site in the Integrated Disposal Facility (IDF).

In addition to the primary IHLW and ILAW glass waste forms, the processing of the tank wastes will generate secondary wastes, including routine solid wastes and liquid process effluents. Liquid wastes may include process condensates and scrubber/off-gas treatment liquids from the thermal waste treatment processes. The liquid-effluent secondary wastes will be sent to the Effluent Treatment Facility (ETF) for further treatment and solidification before disposal at the IDF.

The ETF is a Resource Conservation and Recovery Act (RCRA) permitted, multi-waste treatment and storage unit that can accept dangerous, low-level, and mixed wastewaters for treatment. The ETF receives, treats, and disposes of liquid effluents from cleanup projects on the Hanford Site. Plans are to increase the capacity of the ETF to process the increased volume of secondary wastes when the WTP begins waste treatment and immobilization operations. A Solidification Treatment Unit (STU) will be added to the ETF to provide the needed additional capacity. Washington River Protection Solutions (WRPS) has been chartered to move forward with the design and construction of the STU for ETF. The ETF upgrades need to be operational by 2018 to receive secondary liquid wastes from the WTP. The schedule of activities requires Critical Decision CD0 in February 2011 and submittal of the CD1 package by July 2012. WRPS has a Performance Based Incentive (PBI) to complete the waste form down selection by September 2011. There will be a formal decision on the waste form for the secondary liquid wastes including an agreement with the Washington State Department of Ecology (Ecology) by 2012.

The current baseline calls for solidification of the ETF evaporator concentrate in a cement-based waste form. However, alternative secondary waste forms are being considered. In 2006, Pacific Northwest National Laboratory (PNNL) completed for DOE an evaluation of three low-temperature technologies for the immobilization of mixed radioactive and hazardous waste. That testing program showed that DuraLith® (alkali-aluminosilicate geopolymer) and Ceramicrete® (phosphate bonded ceramic) showed potential as a waste form for the liquid secondary waste stream from WTP based on toxicity characteristic leaching procedure (TCLP), compressive strength, and sodium leachability index requirements.

To support the selection of a waste form for the liquid secondary wastes from WTP, WRPS has initiated secondary waste form testing work at PNNL. In 2009, preliminary screening of waste forms was conducted to assess the viability of each for the solidification of the liquid secondary wastes. Additional testing was undertaken in 2010 to further develop and optimize Cast Stone, DuraLith, and Ceramicrete for the projected liquid secondary waste compositions.

Wastes intended for disposal in IDF must meet requirements of DOE Order 435.1 and permit requirements established by the Washington State Department of Ecology. These requirements are captured in the waste acceptance criteria for IDF. Included are criteria with respect to free liquids, compliance with land disposal restrictions, compressive strength, and leachability. For the purposes of this development and optimization task, the following requirements shall apply:

- Land Disposal Restrictions: The waste form will meet the land disposal requirements in 40 CFR 268 by meeting the universal treatments standards in 40 CFR 268.48 via the TCLP test.
- Free Liquids: The waste form shall contain no detectable free liquids as defined in SW-846 Method 9095
- Leachability Index: The waste form shall have a sodium leachability index greater than 6.0 when tested in deionized water using the ANSI/ANS-16.1 or EPA Method 1315. The waste form shall have a rhenium or technetium leachability index greater than 9.0.
- Compressive Strength: The compressive strength of the waste form shall be at least 3.54E6 Pa (500 psi) when tested in accordance with ASTM C39/C39M.

At the conclusion of this current development and optimization task, PNNL plans on testing each optimized waste form to demonstrate compliance with the IDF criteria to support the final waste form selection. Part of that testing includes engineering-scale demonstrations of the DuraLith and Ceramicrete waste form processes and characterization of the resulting engineering-scale waste form products.

Introduction – Section 2

The Hanford Tank Farm Contractor, WRPS, is scheduled to make a preliminary down select of a secondary waste form to begin conceptual design of the ETF upgrades for a supplemental treatment unit. The candidate waste forms under consideration are:

- Cast Stone
- Fluidized Bed Steam Reforming (FBSR) product
- DuraLith alkali aluminosilicate geopolymer
- Ceramicrete phosphate bonded ceramic

WRPS is sponsoring testing to collect performance data on each of the waste forms to support the down select decision. Laboratory testing was conducted on each of the waste forms to quantify the release of contaminants of concern and understand the fundamental chemistry to support long-term release predictions that are necessary for the performance assessment. Performance of the waste form is a key criterion for the down selection. Additionally, the down selection will consider the operability of the processes that produce each of the waste forms. Among the candidate waste forms, DuraLith and Ceramicrete are less mature and do not have information available to assess their process operability at full-scale. The other two processes are more mature for assessing the operability at full-scale.

The Studsvik treatment facility in Erwin, Tennessee utilizes a fluidized bed steam reforming process to immobilize radioactive waste and provides a basis for assessment of the operability of a full-scale system based on FBSR. Full-scale preliminary designs of the Cast Stone process have been prepared for Hanford and a similar process has been implemented for low-activity waste processing using the similar Saltstone process on the Savannah River site. These activities provide a basis to assess the operability of a full-scale Cast Stone process.

Neither Ceramicrete nor DuraLith have conducted materials testing at larger than laboratory scale. Therefore, PNNL issued a request for proposal late in 2010 for the engineering-scale demonstrations of the DuraLith and Ceramicrete waste forms. MSE Technology Applications, Inc. (MSE) was awarded the contract to perform the DuraLith and Ceramicrete engineering-scale demonstration in January 2011. This test report summarizes the testing conducted at the MSE test facility located on the Mike Mansfield Advanced Technology Center in Butte, Montana. The work was performed to obtain information and collect data to support the waste form down selection and to provide input for the conceptual design of the full-scale process should either the Ceramicrete or DuraLith waste form be selected.

Test Objectives – Section 3

Because the Ceramicrete technology has been demonstrated one time at drum scale and the DuraLith technology has only been demonstrated at bench-scale, the engineering-scale demonstration was conducted to support the final down selection of the secondary waste form product and process. (Ref. 1 & Ref. 2.) The engineering-scale demonstration was conducted to evaluate:

- baseline Ceramicrete and DuraLith formulations.
- the dry materials and liquid wastes blending processes.
- the pourability of the resulting slurries.
- heat generated during curing.
- voids and layering in the waste forms.
- any residual free liquids.
- waste form leachability.
- compressive strength.

Material Descriptions – Section 4

The DuraLith and Ceramicrete technology providers provided MSE with a list of vendors for procurement of the raw materials that were used to generate the simulant liquid secondary waste streams and the solidification materials used for both of the solidification processes.

Simulant Formulation Descriptions – Section 4.1

PNNL provided MSE with the recipe for the secondary liquid waste simulant. Two simulant waste streams were generated for the test sequence, a 1 molar (M) Na^+ solution was used during Ceramicrete sample generation and a 6 M Na^+ solution was used for DuraLith sample generation. Table 4-1 presents the recipe to generate 500 liters (L) of the 1 M Na^+ solution and Table 4-2 presents the recipe to generate 500 L of the 6 M Na^+ solution. The tables also show the actual material amounts used to prepare the simulants.

Table 4-1. 1 M Na^+ solution recipe and actual material amounts to make 500 L.

Component	Chemical Formula	Weight Percent	Calculated Weights	Actual Weights
Water	H_20	93.322	490.55 Kg	490.549 Kg
Aluminum Hydroxide	$AL(OH)_3$	0.697	3.6621 Kg	3.6621 Kg
Sodium Chloride	$NaCl$	0.125	657.450 g	657.45 g
Sodium Carbonate	Na_2CO_3	0.230	1.2083 Kg	1.2085 Kg
Potassium Nitrate	KNO_3	0.006	29.4201 g	29.4200 g
Sodium Nitrate	$NaNO_3$	2.652	13.9384 Kg	13.9384 Kg
Sodium Nitrite	$NaNO_2$	0.079	414.0 g	414.0 g
Sodium Hydroxide	$NaOH$	1.514	7.9600 Kg	7.960 Kg
Monosodium Phosphate	$NaH_2PO_4 \cdot 2H_20$	0.102	535.8256 g	535.826 g
Sodium Silicate	Na_2SiO_3	0.022	114.7364 g	114.7360 g
Sodium Sulfate	Na_2SO_4	0.060	313.1982 g	313.198 g
Sodium Oxalate	$Na_2C_2O_4$	1.114	5.8558 Kg	5.8560 Kg
Oxalic Acid	$H_2C_2O_4 \cdot 2H_2O$	0.078	409.7275 g	409.7280 g
Sodium Perrhenate	$NaReO_4$	0.0004703	2.4724 g	2.4720 g

Table 4-2. 6 M Na^+ solution recipe and actual material amounts to make 500 L.

Component	Chemical Formula	Weight Percent	Calculated Weights	Actual Weights
Water	H_20	67.021	428.0 Kg	428.0 Kg
Aluminum Hydroxide	$AL(OH)_3$	3.441	21.9726 Kg	21.9726 Kg

Sodium Chloride	$NaCl$	0.618	3.9447 Kg	3.9447 Kg
Sodium Carbonate	Na_2CO_3	1.135	7.2497 Kg	7.2497 Kg
Potassium Nitrate	KNO_3	0.028	176.5 g	176.5 g
Sodium Nitrate	$NaNO_3$	13.096	86.6302 Kg	86.6302 Kg
Sodium Nitrite	$NaNO_2$	0.289	2.4840 Kg	2.484 Kg
Sodium Hydroxide	$NaOH$	7.479	47.760 Kg	47.760 Kg
Monosodium Phosphate	$NaH_2PO_4 \cdot 2H_20$	0.503	3.2149 Kg	3.2149 Kg
Sodium Silicate	Na_2SiO_3	0.108	688.4 g	688.4 g
Sodium Sulfate	Na_2SO_4	0.294	1.8792 Kg	1.8792 Kg
Sodium Oxalate	$Na_2C_2O_4$	5.502	35.1248 Kg	35.1348 Kg
Oxalic Acid	$H_2C_2O_4 \cdot 2H_2O$	3.85	2.4583 Kg	2.4583 Kg
Sodium Perrhenate	$NaReO_4$	0.0023299	14.8000 g	14.80 g

The two Hanford secondary simulant wastes were generated several weeks prior to sample generation. Samples were collected from the 1 M Na^+ and the 6 M Na^+ simulant waste streams and specific gravity values were determined for both wastes. The 1 M Na^+ simulant had a specific gravity of 1.05 and the 6 M Na^+ simulant had a specific gravity of 1.27.

Ceramicrete and DuraLith Formulation Descriptions – Section 4.2

Ceramicrete is a phosphate-bonded ceramic cement and DuraLith is an alumino-silicate geopolymer. The Ceramicrete and DuraLith technology providers provided PNNL with the baseline formulations as well as a high and low solids formulation for the waste forms, which were then passed on to the test team at MSE. Table 4-3 shows the three initial baseline recipes for Ceramicrete: one for the 5-gallon (gal) bucket samples, one for the 55-gal drum sample, and another for the engineering-scale box samples. Table 4-4 lists the initial Ceramicrete 5-gal bucket and engineering-scale box high-solids recipes, and Table 4-5 lists the initial 5-gal bucket low solids recipe. The stannous chloride used in the Ceramicrete waste forms during the test sequence was stannous chloride dihydrate not anhydrous stannous chloride that was called for in the Ceramicrete formulations provided by PNNL. The weight percents remained unchanged for the formulations, therefore the stannous chloride quantity increased and the supplemental water quantity decreased since stannous chloride di-hydrate was used. The Ceramicrete formulations were modified during the test sequence and actual sample formulations and weights are presented in Section 7.

Table 4-3. Baseline Ceramicrete grout formulation for each test scale.

Component	Weight Percent	4.5-Gal Component Weight, Kg	51-Gal Component Weight, Kg	11-cubic feet (ft^3) Component Weight, Kg
1 M Na^+ Simulant	19.60	6.68	75.68	122.10
MgO	9.53	3.25	36.80	59.37
KH_2PO_4	32.41	11.04	125.14	201.90
Class C Fly Ash	34.31	11.69	132.47	213.73
$SnCl_2 \cdot 2H_20$	1.26	0.51	5.79	9.34
Ground Zeolite – 5A	1.09	0.37	4.21	6.79
Supplemental H_20	1.81	0.53	6.02	9.72
Totals	**100**	**34.07**	**386.10**	**622.95**

Table 4-4. High solids Ceramicrete grout formulation for 4.5-gal and 11-ft^{3}samples.

Component	Weight Percent	4.5-Gal Component Weight, Kg	11-ft^3 Component Weight, Kg
1 M Na^+ Simulant	18.85	6.42	117.43
MgO	9.63	3.28	59.99
KH_2PO_4	32.74	11.15	203.95
Class C Fly Ash	34.67	11.81	215.98
$SnCl_2 \cdot 2H_20$	1.51	0.51	9.41
Ground Zeolite – 5A	1.10	0.37	6.85
Supplemental H_20	1.50	0.51	9.34
Totals	**100**	**34.07**	**622.96**

Table 4-5. Low solids Ceramicrete grout formulation for a 4.5-gal sample.

Component	Weight Percent	4.5-Gal Component Weight, Kg
1 M Na^+ Simulant	20.36	6.94
MgO	9.43	3.21
KH_2PO_4	32.06	10.92
Class C Fly Ash	33.95	11.57
$SnCl_2 \cdot 2H_20$	1.48	0.50
Ground Zeolite – 5A	1.08	0.37
Supplemental H_20	1.64	0.56
Totals	**100**	**34.07**

The DuraLith samples require that an activator solution be prepared using the 6 M Na^+ simulant and adding sodium and potassium hydroxide and fumed silica. The activator solution was prepared and then mixed continuously before the other dry materials or composite binder materials were added to the activator solution to produce the waste form. Details for activator preparation are included in *Section 8-1*. Table 4-6 lists the initial three baseline recipes for DuraLith: one for the 5-gal bucket samples, one for the 55-gal drum sample, and another for the engineering-scale box samples. Table 4-7 lists the initial DuraLith 5-gal bucket and engineering-scale box high solids recipes, and Table 4-8 lists the initial 5-gal bucket low solids recipe. The DuraLith formulations were modified during the test sequence and the actual formulations and sample weights are provided in Section 8.

Table 4-6. Baseline DuraLith grout formulation for each test scale.

Component	Weight Percent	4.5-Gal Component Weight, Kg	51-Gal Component Weight, Kg	11-ft^3 Component Weight, Kg
Activator Solution				
6 M Na^+ Simulant	23.2	8.19	92.82	149.80
SnF_2	0.17	0.60	0.94	1.52
KOH	6.10	2.17	24.53	39.60
NaOH	0.95	0.33	3.78	6.10
Fumed Silica	7.30	2.56	29.04	46.90
Dry Components				
Blast Furnace Slag	28.10	9.91	112.19	181.0
Copper Slag	2.00	0.70	7.91	12.80
Metakaolin Clay	11.30	4.00	45.29	73.10
Fine Sand	18.80	6.64	75.17	121.30
Ground Zeolite – 5A	0.99	0.35	3.96	6.38
Fumed Silica	0.99	0.35	3.96	6.38
Totals	**100.00**	**35.80**	**399.60**	**644.70**

Table 4-7. High solids DuraLith grout formulation for a 4.5-gal and 11-ft^3 samples.

Component	Weight Percent	4.5-Gal Component Weight, Kg	11-ft^3 Component Weight, Kg
Activator Solution			
6 M Na$^+$ Simulant	22.50	8.19	143.25
SnF_2	0.17	0.060	1.08
KOH	6.00	2.17	38.20
NaOH	0.92	0.33	5.86
Fumed Silica	7.10	2.56	45.20
Dry Components			
Blast Furnace Slag	28.60	10.40	182.08
Copper Slag	2.00	0.73	12.73
Metakaolin Clay	11.50	4.20	73.22
Fine Sand	19.20	6.97	122.24
Ground Zeolite – 5A	1.01	0.37	6.43
Fumed Silica	1.01	0.37	6.43
Totals	**100.00**	**36.35**	**636.72**

Table 4-8. Low solids DuraLith grout formulation for a 4.5-gal sample.

Component	Weight Percent	4.5-Gal Component Weight, Kg
Activator Solution		
6 M Na$^+$ Simulant	24.00	8.60
SnF_2	0.18	0.063
KOH	6.30	2.27
NaOH	0.98	0.35
Fumed Silica	7.50	2.69
Dry Components		
Blast Furnace Slag	27.60	9.91
Copper Slag	1.90	0.70
Metakaolin Clay	11.10	4.00
Fine Sand	18.50	6.64
Ground Zeolite – 5A	0.97	0.35
Fumed Silica	0.97	0.35
Totals	**100.00**	**35.92**

Bench-Scale Rheology Testing Procedures – Section 5

Several rheology tests were performed to determine slumping characteristics, initial relative consistency, working time, and initial setting time for the samples generated during the bench-scale testing.

Initial Relative Consistency - ASTM C187 - Section 5-1

The Vicat test apparatus was used to determine the initial relative consistency of the waste forms by using the 10 millimeter (mm) cylinder plunger per ASTM C187 – *Standard Test Method for Normal Consistency of Hydraulic Cements*. (Ref..1) The test calls for a sample to be collected after mixing, to drop the cylinder plunger 30 seconds (sec) after sample mixing, and to measure the depth the cylinder penetrates the sample's surface after another 30 sec. Then, record measurements for comparison to other samples. Variations to the test method were used during the bench-scale testing. It was problematic to collect a sample within the prescribed 30 sec called for in the test method so Vicat samples were collected at different times for the first 2 bench-scale samples that were generated. The remaining bench-scale and engineering-scale Vicat samples were collected as soon as possible after mixing. The cylinder plunger was never dropped 30 sec after sample collection because the materials did not set-up as quickly as hydraulic cements. The cylinder plunger was routinely dropped several minutes after sample collection to determine the time required for the mixture to cure to a point that the cylinder plunger would not penetrate to the bottom of the Vicat sample, which was 40 mm.

Initial Setting Time - ASTM C191-08 – Section 5-2

The Vicat test apparatus was also used to determine the initial setting time for the samples by using the needle plunger per ASTM C191-08 - *Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle.* (Ref.. 2) The same sample that was used to determine the sample's initial relative consistency was used for the initial setting time test. When the cylinder plunger testing was completed, the cylinder plunger was changed to the needle plunger for the initial setting time tests. The needle plunger was dropped onto the sample's surface and the penetration depth was periodically measured. The initial set time was based on the last penetration measurement that was less than 25 mm and the first measurement that was greater than 25 mm. Subsequently, periodic penetration depth measurements were made until the needle penetrated the surface to a depth of less than 0.5 mm or until the Vicat testing was stopped by test personnel. The formula to determine the initial set time is listed below.

Calculate the Vicat time of setting to the nearest 1 min as follows:

$$\left(\left(\frac{(H-E)}{(C-D)}\right)\times\left(C-25\right)\right)+E$$

Where:
E= time in minutes of last penetration greater than 25 mm,
H= time in minutes of first penetration less than 25 mm,
C= penetration reading at time E, and
D = penetration reading at time H.

50-Cent Rheometer Slump Test – Section 5-3

This test uses an open cylindrical sleeve, called the 50-Cent rheometer. The cylinder sleeve has the same height and diameter measurement of 88 mm and the test was conducted per Pashias et al., 1996. (Ref. 3) The test cylinder mold was filled with the sample and then the cylinder was pulled away from the sample allowing the sample to slump. The change in height of the sample when the cylinder mold was pulled away from the sample is the slump height, which is a parameter used to measure the samples' slumping behavior. This test was modified after the generation of Sample #2 by adding 4 cylinder test molds to the test sequence resulting in a total of 5 cylinders being used per sample to provide a slumping profile for the bench-scale samples. The samples were placed in front of gridded paper with large divisions of 25.4 mm and small divisions of 6.35 mm to help determine slump heights from photos taken periodically through the slumping period.

Working Time – ASTM C308 – Section 5-4

The working time of the sample was determined per ASTM C308 - *Standard Test Method for Working, Initial Setting and Service Strength Times of Chemical Resistant Resin Mortars*. (Ref. 4) Approximately 25 grams of the sample material were placed on clean, dry, freezer paper and then the material was troweled across the paper. The test was to be repeated every 5 minutes (min) until the material began to curl behind the spreading trowel, which indicated the working time of the waste forms. However, this test was eliminated after Sample #2 was generated because the more Ceramicrete is disturbed, the longer it takes for the Ceramicrete waste forms to set-up.

Test Equipment – Section 6

A 10 ft^3 ribbon mixer was purchased for the generation of the drum-scale and engineering-scale waste form samples. Nine different mixers were used during the test sequence: the ribbon mixer for the large-scale samples; the 20 horse power (Hp) hydraulically driven drum-scale mixer for two of the drum-scale samples; three ½ Hp mixers for the generation of the simulant waste streams and large batches of activator solution; three $^{1}/_{15}$ Hp mixers to stir the small batches of activator solution; and the bucket-scale mixer.

The 10ft^3 ribbon mixer was manufactured by Euro Drive, Inc. and had dimensions of 38” tall, 24.5” wide and 87” long with a 6.5” diameter pour spout. The 5 Hp ribbon mixer had a gearbox reduction of approximately 40:1, which reduced the rotation rate of the mixer to approximately 45 rpm. The gear box also gave the ribbon more torque; so whatever increase occurred in the effective viscosity during mixing it did not slow down the mixer or drag on the motor. A picture of the ribbon mixer is shown in Figure 6-1. The 20 Hp drum mixer is pictured in Figure 6-2 with the electric lift that is used to raise and lower the mixing head assembly into the mixing drums. The drum mixer was manufactured by Hepsco Hydraulic Engineered Products and the electric lift was manufactured by Multiton MIC Corporation. The drum mixer is hydraulically driven and has variable speed and Hp, a working pressure of 6000 psi with a reinforced 62.5 inch mixing shaft, and a 15 inch propeller and the electric lift has a 2205 pound capacity and drum holding assembly.

Figure 6-1. 10ft^3 ribbon mixer.

Figure 6-2. 20 Hp hydraulic mixer and electric lift with drum holder assembly.

Three scales were used to weigh out the liquid and dry test materials. A Brookfield viscometer, the Vicat Test apparatus, a data logger, thermocouples, temperature probes, lab timers, a core drill, photo tachometer, power quality analyzer, hydrogen air sampling pump, overhead crane, and walk-in laboratory hood were also used during the test sequence. Appendix A shows all the equipment information as well as pictures of the equipment.

Ceramicrete Solidification Testing – Section 7

The engineering-scale demonstration was performed to help support the final technology down selection to solidify Hanford secondary waste streams by providing waste form processing data including mixing information, pourability and flow characteristics, and to determine if any aggregate settling occurred during the curing process for the Ceramicrete solidification process. Bench-scale testing was conducted prior to the drum-scale and engineering-scale demonstration to observe the mixing process for the baseline solidification formulations provided by the Ceramicrete technology providers and to gather information pertinent to the scale-up formulations that would be used during the drum-scale and engineering-scale demonstrations. The drum-scale demonstration was the first scale-up testing and was conducted to determine if the bench-scale formulations would scale-up, to provide the necessary curing temperature profiles for cylindrical waste form shapes, and to determine mixing characteristics of a sample larger than 4.5 gallons.

PNNL personnel were on site during the bench-scale, drum-scale and engineering-scale sample generation.

Bench-Scale Ceramicrete Testing – Section 7.1

The work plan specified that three Ceramicrete bench-scale samples would be generated during the bench-scale test sequence; one using the baseline formulation, one using the high solids formulation, and one using the low solids formulation. The magnesium oxide, mono potassium phosphate, and the Class C fly ash for each of the three Ceramicrete samples were weighed out and placed into overpack drums the week before PNNL personnel arrived at MSE to prepare for the upcoming test sequence. Both the stannous chloride and ground zeolite were also weighed out and placed into sample bags at that time. Actual component weights used to generate the bench-scale samples are presented in Table 7-1.

Table 7-1. Actual component weights for the Ceramicrete 4.5-gal bench-scale samples.

Component	Sample #1 High-Liquids 4.5-Gal Component Weight, Kg	Sample #2 Baseline 4.5-Gal + 0.5 wt % Boric Acid Component Weight, Kg	Sample #3 Baseline 4.5-Gal Component Weight, Kg	Sample #4 Baseline 4.5-Gal + 0.25 wt % Boric Acid Component Weight, Kg	Sample #7 High-Solids 4.5-Gal + 0.5 wt % Boric Acid Component Weight, Kg
1 M Na^+ Simulant	7.006	6.68	6.68	6.68	6.42
MgO	3.25	3.25	3.25	3.25	3.28
KH_2PO_4	11.04	11.04	11.04	11.04	11.15
Class C Fly Ash	11.69	11.69	11.69	11.69	11.81
$SnCl_2 \cdot 2H_20$	0.5101	0.51	0.51	--	0.5101
Ground Zeolite – 5A	0.370	0.37	0.37	0.37	0.3701
Supplemental H_20	0.53	0.53	0.53	0.53	0.51
Boric Acid	--	0.134	--	0.067	0.135
Totals	**34.3961**	**34.204**	**34.07**	**33.627**	**34.1852**

Sample #1 – High Liquid Ceramicrete Formulation – Section 7.1.1

The baseline Ceramicrete bench-scale sample was to be generated first; however, due to an error when weighing the 2-part lid assembly; more liquid was added to the sample than was called for in the baseline recipe. Therefore, this sample was considered to be the high liquids sample. The three dry components were mixed thoroughly in the overpack drum and then liquid 1 M Na^+ simulant was weighed out into a 6-gal bucket and the supplemental water, stannous chloride, and ground zeolite were added to the liquid simulant waste stream and mixed. Then, the dry components in the overpack drum were added to the bucket and mixed for 20 min. The temperature of the mixture was 19 °C immediately after the dry components were added to the liquid and reached a high temperature of 54 °C approximately 28 min after mixing was stopped.

Approximately 2 min after mixing was stopped, a sample for the Vicat test apparatus was collected and then 1 min later a sample was collected for the 50-Cent slump test. After 12 min, the Vicat cylinder was allowed to drop onto the sample and the cylinder dropped to the bottom of the sample container (40 mm); the Vicat cylinder was dropped 8 min later and again dropped to the bottom of the sample container. No other Vicat cylinder readings were collected during this test. Not enough Vicat needle drop data was collected to obtain the calculated initial setting time.

The 50-Cent slump test mold was removed from the sample approximately 11 min after the sample was collected and the sample slumped from an initial height of 93 mm to 91 mm and is as shown in Figure 7-1. Table 7-2 (at the end of the section) presents the 50-Cent rheometer slump test data for the bench-scale samples.

Figure 7-1. Sample #1 Ceramicrete Slump Test Photo.

A 2-inch diameter by 4-inch tall sample was collected 17 min after mixing was completed that could be used for either leachability or compressive strength testing. A fourth sample was collected to determine the workability of the material approximately 10 min after mixing was completed, and the mixture was workable at that time; at 17.5 min after mixing, the material was still workable, but the sample edges started to pull away from the paper slightly; and 20 min after mixing, the material was no longer workable.

It was noted the next morning that the 2-inch diameter by 4-inch tall sample had a dried salt solution present on the outside of the sample container that had leaked out of the sample container while the lid was closed

Because Sample #1 (the high liquids formulation) only had a slump height of 2 mm approximately 11 min after the mixing process, the team decided that boric acid should be added in an attempt to prolong sample curing. A discussion with the Ceramicrete technology provider determined that 0.5 weight percent (wt %) boric acid was the initial value that should be used to achieve additional working time for the Ceramicrete waste forms.

Sample #2 – Baseline Ceramicrete Formulation with 0.5 wt % Boric Acid – Section 7.1.2
Sample #2 was generated in much the same fashion as Sample #1; three main dry components were mixed in the overpack drum; the 1 M Na^+ stimulant was weighed out into the 6-gal bucket and the supplemental water, stannous chloride, ground zeolite, and boric acid were added to the bucket and mixed. The main dry components were then added to the bucket and mixed for approximately 20 min. The initial sample temperature was 18 °C and reached a high temperature of 53 °C approximately 70 min after mixing was stopped.

Several samples were collected at different times for the Vicat and 50-Cent rheometer tests to try and better understand the workability and curing nature of the Ceramicrete mixtures. One sample was collected for the 2-inch diameter by 4-inch tall sample container when mixing was stopped and another sample was collected for workability testing approximately 21 min after mixing was complete. The sample was workable at 21 min but started to lift off the paper at the sample edges. However, it was observed that the more the waste form was disturbed, the more workable the material became. Once the sample was disturbed, the sample's matrix seemed to change and this prolonged the workability of the sample and delayed the set-up time.

The 50-Cent slump data presented in Table 7-2 (at the end of this section) for Sample #2 shows the times that the samples were collected after mixing was completed, not the times that the slump molds were removed from the samples as is the case with the other samples denoted in the table. Slump molds were removed 30 to 90 sec after the samples were collected. Because there were only 2 sample molds, one was cleaned when the other was in use.

Sample #2 for the 50-Cent slump test was collected approximately 11 min after mixing and was still flowable enough to fill the sample container and did slump from 93 mm to 49 mm when the container was removed 15 sec later. Sample #2a was collected 20 min after mixing and the slump mold was removed 30 sec later, showing there was a void in the sample. This indicated that the Ceramicrete mixture was no longer flowable when it was placed into the sample container. The initial height for Sample #2a was 93 mm and it slumped to a height of 72 mm after the container was removed from the sample. Sample #2b was collected 27 min after the completion of mixing and the sample mold was removed 30 sec later resulting in a slump from the initial height of 94 mm to 83 mm. Sample #2c was collected 41 min after mixing was stopped and the mixture was not flowable resulting in a sample with many voids when it was placed into the sample mold. The sample had a high point on the left hand side of the sample of about 90 mm – an 8 mm slump. Figure 7-2 shows the four samples after the sample molds were removed.

Four samples were collected for Vicat testing: the first at 11 min; the second at 20 min; the third at 28 min; and the fourth at 36 min after mixing. The Vicat cylinder was dropped one time onto the first three Vicat samples with the cylinder penetrating to the bottom of the sample mold. The Vicat cylinder was dropped onto the fourth sample 5 min, 20 min, and 30 min after mixing. The first two drops resulted in the cylinder penetrating to the bottom of the sample mold while the third drop resulted in the Vicat cylinder penetrating only 3 mm into the sample. The Vicat cylinder was then replaced with the Vicat needle and it was dropped approximately 33 min and 88 min after mixing, with the needle penetrating to the bottom of the sample each time. The fourth sample did start to set-up during testing after the sample was left undisturbed in the sample mold, but a needle drop penetration depth of less than 40 mm was not collected therefore an initial setting time could not be calculated for Sample #2.

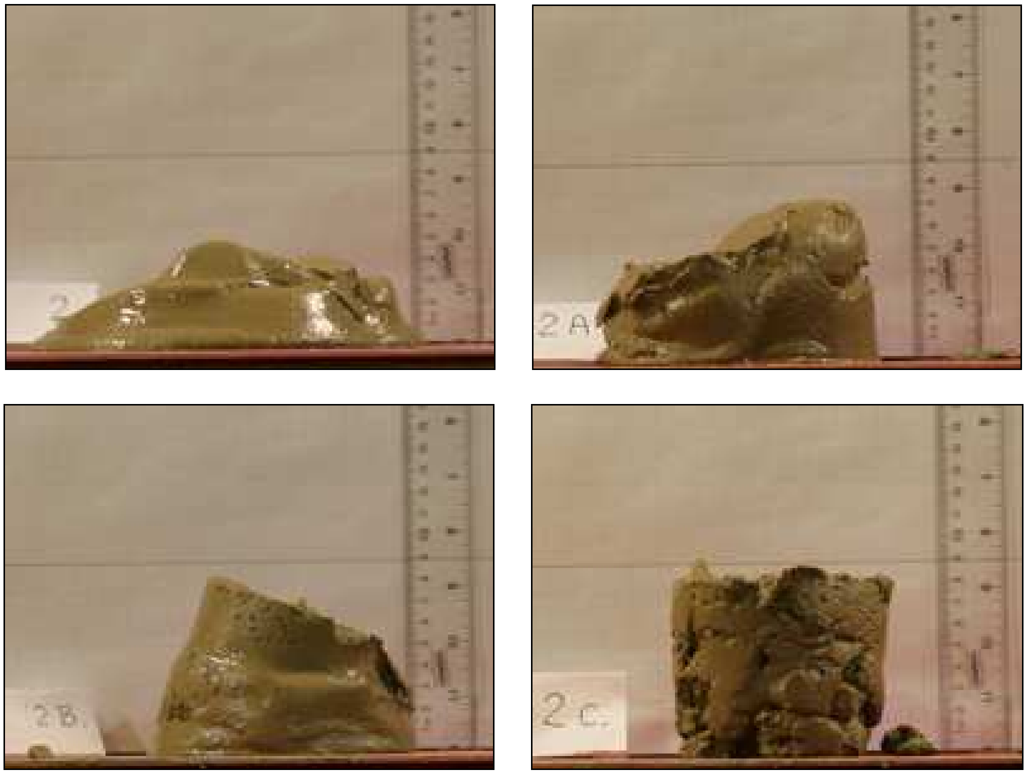


Figure 7-2. Sample #2 Ceramicrete Slump Test Photos.

Rheology Test Modifications – Section 7.1.2.1

Because the rheology tests were developed for hydraulic cements and resin motars and not ceramic cements or geopolymers that have such different curing properties, the team modified the testing methods to provide more compatible data for the materials being tested. It was decided to collect 5 samples instead of 1 for the 50-Cent slump tests after mixing. Then each 4.5-gal sample was monitored in the bucket to determine when the sample started to set-up. That information was used as an indication for the start time to remove the slump test molds. Several additional 50-Cent slump molds were then cut to use for future tests. The workability test was basically eliminated because the more the Ceramicrete material was disturbed during the curing process the longer the workability of the material was prolonged. Also, the team decided to collect only 1 sample for the Vicat cylinder and needle test so the curing process could remain as undisturbed as possible for that test even though each cylinder and needle drop test slightly disturbed the sample. The Vicat sample was rotated during the testing to avoid sample areas that previously penetrated by the cylinder or plunger to obtain data from the undisturbed sample sections.

Sample #3 – Baseline Ceramicrete Formulation – Section 7.1.3

The third sample generated during the Ceramicrete bench-scale testing was the Ceramicrete baseline formulation. This sample was generated to determine how quickly the sample would remain workable without the addition of boric acid, which prolongs the samples curing time. The third sample was generated much like the first two samples: the 1 M Na^+ simulant was weighed into the 6-gal bucket and the major dry materials were thoroughly mixed in the overpack drum. The supplemental water, stannous chloride, and ground zeolite were added to the simulant while mixing and then the major dry components were added to the simulant mixture and mixed for 14 min instead of 20 min since the first two samples started to set-up relatively quickly. The initial sample temperature was 20 °C and a maximum temperature of 69 °C was reached 46 min after mixing stopped.

The Vicat sample was collected 2 min after mixing and the 5 slump samples were all collected within 4 min after mixing, however no 2-inch by 4-in sample was collected. The mixture was already starting to set-up when the 50-Cent slump samples were collected resulting in slump samples that were actually mounded above the slump molds. The samples were not vibrated, shaken, or scraped off to obtain level samples to minimize waste form disturbance. The mold was removed from Sample #3a approximately 110 sec after collection and had a slump of only 4 mm. The second sample mold was pulled 20 sec after the first and showed no slump. The third, fourth, and fifth sample molds were pulled at 40 sec, 60 sec, and 75 sec after the first sample and none of these samples exhibited any slumping as shown in Figure 7-3. Notice the voids in each of the 5 slump samples that indicate the mixture was not fluid within 4 min after mixing. The quick set-up times for the baseline Ceramicrete formulation indicated that boric acid must be used in the formulations to delay the set-up time to ensure enough working time for the solidification process.

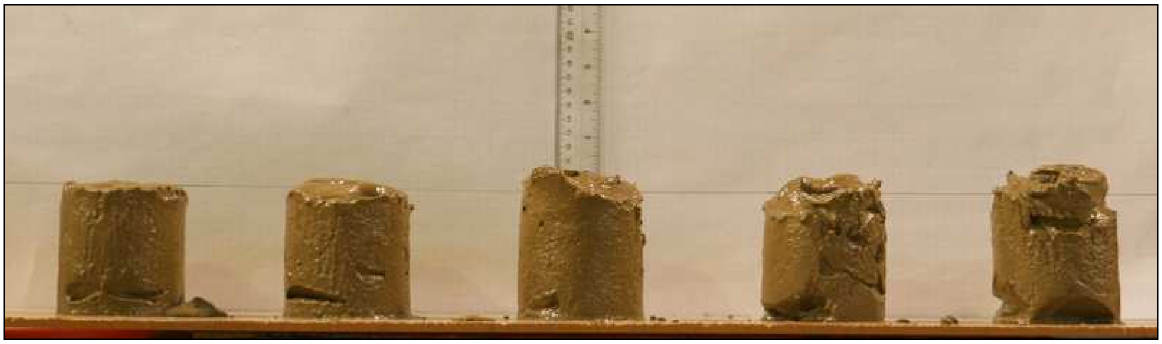


Figure 7-3. Sample #3 Ceramicrete Slump Test Photo.

The Vicat cylinder test was dropped onto the sample 10 min after mixing was stopped, and resulted in a penetration depth of only 3 mm indicating the sample's initial relative consistency was achieved early in the curing process. The cylinder plunger was then replaced by the needle and testing was initiated for the initial setting time. The first two times that the needle plunger was dropped onto the sample, it penetrated to the bottom of the sample mold, a depth of 40 mm at 15 and 23 min after mixing, respectively. The needle drop test continued until 104 min when there was no penetration made by the needle plunger. The Vicat cylinder drop and needle drop data for Samples #3, #4, and #7 are presented in Table 7-3, which is located at the end of this section. The initial setting time calculated for Sample #3 was 28 min.

Since Sample #3 did not produce a mixture with a long enough working time, it was decided to add boric acid to Sample #4 to prolong the working time for the sample.

Sample #4 – Baseline Ceramicrete Formulation with 0.25 wt % Boric Acid – Section 7.1.4

The fourth sample was generated much like the first three samples: the 1 M Na^+ simulant was weighed into the 6-gal bucket and the major dry materials were thoroughly mixed in the overpack drum. The supplemental water, boric acid, and ground zeolite were added to the simulant while mixing and then the major dry components were added to the simulant mixture and mixed for 14 min. No stannous chloride was added to this sample as only 3 bench-scale bucket tests were called for in the test plan and a limited quantity of the material was ordered. The initial sample temperature was 18 °C and a maximum temperature of 71.8 °C was reached 62 min after mixing stopped.

The 50-Cent slump mold samples were obtained within 3 min after mixing was stopped, the Vicat sample was collected seconds later and no 2-inch diameter by 4-inch tall sample was collected for this sample. The slump mold for Sample 4a was pulled away from the sample 5.58 min after mixing and the sample tilted a little to the right but the left hand side of the sample maintained full sample height, therefore no slump was recorded. A picture of the 5 samples after the molds were removed is shown in Figure 7-4. The remaining 4 slump samples had their slump molds removed at 6.25 min, 6.75 min, 7.17 min, and 7.75 min after mixing and none of the samples exhibited any slumping. This indicated that the samples were setting up very quickly and that additional amounts of boric acid should be used when generating the next baseline sample to prolong the working times for the waste forms.

Figure 7-4. Sample #4 Ceramicrete Slump Test Photo.

The first Vicat cylinder drop test was performed 9 min after mixing with a penetration depth of 12.5 mm. Vicat cylinder tests were performed until 15 min after mixing when the penetration depth was 1 mm. At that point, the cylinder plunger was replaced with the needle plunger and the needle drop testing was initiated 20 min after mixing was stopped with a penetration depth of 40 mm – the bottom of the test mold. Vicat needle drop testing continued until 122 min after mixing when the needle no longer penetrated the sample's surface. An initial setting time of 24 min was calculated for Sample #7. All the Vicat data for test #4 is presented in Table 7-3 at the end of this report section.

Sample #7 – High Solids Ceramicrete Formulation with 0.5 wt % Boric Acid – Section 7.1.5

The seventh sample was generated much like the first four samples: the 1 M Na^+ simulant was weighed into the 6-gal bucket and the major dry materials were thoroughly mixed in the overpack drum. The supplemental water, stannous chloride, boric acid, and ground zeolite were added to the simulant while mixing and then the major dry components were added to the simulant mixture and mixed for 20 min. Stannous chloride was added to this sample because smaller volumes were used to generate one of the first engineering-scale samples. The initial sample temperature was 18 °C and a maximum temperature of 55 °C was reached 76.5 min after mixing was stopped.

Three 2-inch diameter by 4-inch tall samples were collected immediately after mixing. A Vicat sample was then collected approximately 1.5 min after mixing, and the five 50-Cent slump samples were all collected in less than 3.5 min after mixing.

The slump mold was removed from Sample #7a, 7 min after mixing, resulting in a sample slump of approximately 68 mm. Sample #7b's mold was removed 9.5 min after mixing and the sample slumped approximately 50 mm. Sample #7c's mold was removed 12 min after mixing and the sample slumped 10 mm. Sample #7d's mold was removed 13 min after mixing and slumped 10 mm. Sample #7e's mold was removed 15 min after mixing and the sample slumped 3 mm. Table 7-2 (at the end of this section) shows the bench-scale slump data and Figure 7-5 shows a picture of the slump test samples.

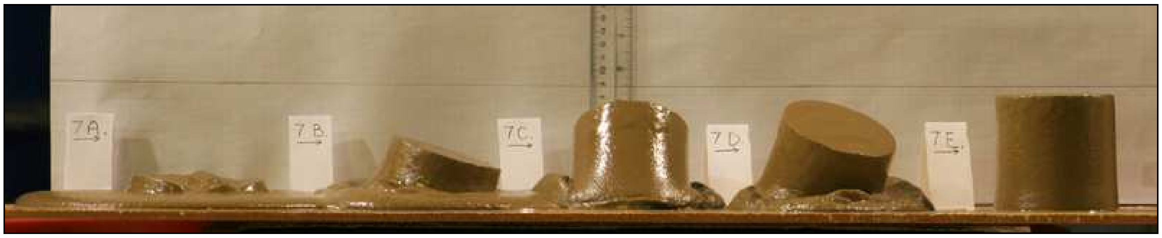


Figure 7-5. Sample #7 Ceramicrete Slump Test Photo.

The Vicat cylinder test was initiated 37 min after mixing was completed with the cylinder plunger dropping to the bottom of the sample mold within 2 sec. Cylinder drop tests were performed until 94 min after mixing when a penetration depth of 4 mm was observed. The Vicat needle drop testing was initiated at 104 min after mixing and continued until 200 min after mixing with all of the needle plunger tests penetrating the full sample depth of 40 mm. Since not enough Vicat needle penetration depth data were obtained that were less than 25 mm, the initial setting time was estimated to be > 200 min. All the Vicat cylinder and needle drop test data appear in Table 7-3.

It was noted the next morning that the 2-inch diameter by 4-inch tall samples had a dried salt solution present on the outside of the sample containers that had leaked out of the sample containers while the lids were closed. Refer to Figure 7-6. The 2-inch diameter by 4-inch tall samples collected for Samples #1 and #2 also had a dried salt solution on the outside of the sample containers the morning after sample generation.

Figure 7-6. Ceramicrete Sample #7 showing salt solution that leaked out of the sample containers.

Table 7-2. Ceramicrete bench-scale 50-Cent rheometer slump test data.

Sample Number	50-Cent Slump Tests			Sample Molds Removed - Time after mixing, min
	Initial Slump Height, mm	Final Slump Height, mm	Slumping Height, mm	
1	93	91	2	14.25
2	93	49	34	11 *
2a	93	72	21	20 *
2b	94	83	11	27 *
2c	98	90	8	41 *
3a	94	90	4	5.83
3b	100	100	0	6.17
3c	105	105	0	6.50
3d	102	102	0	6.83
3e	110	110	0	7.08
4a	89	89	0	5.58
4b	89	89	0	6.25
4c	89	89	0	6.75
4d	89	89	0	7.17
4e	89	89	0	7.75

7a	88	~ 20	68	7
7b	88	~ 50	38	9.50
7c	88	78	10	12
7d	88	78	10	13
7e	88	85	3	15
* Times that samples were collected after mixing, not time when the sample molds were removed.				

When comparing the 50-Cent slump data presented in Table 7-2, Sample #7 seems to provide the best Ceramicrete formulation slump results. The samples did have some slumping after 15 min, showing a longer cure time than the rest of the formulations. Sample #3 and #4 had already set between 5 and 6 min after mixing was completed and Sample #2 was remixed to obtain slump samples that were more liquefied. Therefore, the sample matrix was compromised and the data cannot be compared to the other data sets.

When comparing the Vicat cylinder and needle drop test data, Sample #7 also has longer set times when compared to Sample #3 and #4. Again, Sample #2 will not be used in the comparison because several samples were collected during that test and the sample matrix was disturbed and Sample #1 did not have enough Vicat data for comparison. The cylinder drop data for Sample #3 show a 3-mm penetration depth 10 min after mixing; Sample #4 had a cylinder penetration depth of 2 mm 13 min after mixing; while Sample #7 had a cylinder penetration depth of 4 mm 94 min after mixing was stopped. The needle drop data for Sample #3 and Sample #4 show no penetration 104 min and 122 min, respectively, after mixing, while Sample #7 data show full sample penetration of 40 mm 200 min after mixing was completed.

Both the 50-Cent rheometer test data and the Vicat test data indicate that Sample #7 has the longest set or cure time for the formulations tested during the Ceramicrete bench-scale test sequence and the initial setting time was calculated to be greater than 200.

Table 7-3. Ceramicrete bench-scale Vicat cylinder drop and needle drop test data.

Sample Number	**Vicat Tests**				
	Cylinder Drop		**Needle Drop**		**Initial Setting Time**
	Penetration Depth, mm	**Time, min**	**Penetration Depth, mm**	**Time, min**	**Time, min**
3	3	10	--	--	28
3	--	--	40	15	
3	--	--	40	23	
3	--	--	7.5	33	
3	--	--	7.0	36	
3	--	--	4.0	39	
3	--	--	2.78	42	
3	--	--	3.0	45	
3	--	--	1.75	48	
3	--	--	1.75	51	
3	--	--	2.0	57	
3	--	--	1.75	62	
3	--	--	5.50	73	
3	--	--	0.50	74	
3	--	--	0.50	84	
3	--	--	0.50	94	
3	--	--	0	104	
4	12.5	9	--	--	24
4	5.0	11	--	--	
4	2.0	13	--	--	
4	1.0	15	--	--	
4	--	--	40	20	

4	--	--	21.0	25	
4	--	--	17.50	28	
4	--	--	8.50	31	
4	--	--	3.50	34	
4	--	--	2.50	37	
4	--	--	0.50	42	
4	--	--	0.50	52	
4	--	--	0.50	62	
4	--	--	0	122	
7	40	32.5	--	--	>200
7	40	42	--	--	
7	40	53	--	--	
7	30	73.5	--	--	
7	4	94	--	--	
7	--	--	40	104	
7	--	--	40	134	
7	--	--	40	153	
7	--	--	40	200	
Vicat Test Apparatus used either cylinder or needle component for individual drop tests – not both.					

Drum-Scale Ceramicrete Testing – Section 7.2

As stated previously, the drum-scale test was performed to validate bench-scale Ceramicrete formulations and to provide a curing temperature profile for a large cylindrical waste form. Power requirements were also monitored for the ribbon mixer during mixing.

After Sample #4 was generated, team discussions were held to determine the mixing time for the 55-gal drum sample. It was agreed that the drum sample would be mixed until the slurry temperature reached approximately 40 °C. Therefore, 2 temperature probes were installed on the outside of the ribbon mixer to monitor the slurry temperature through the walls of the ribbon mixer during the mixing process.

One 55-gal sample was generated using the Ceramicrete baseline formulation with the addition of 0.5% boric acid to prolong the cure time for the sample and ensure adequate mixing time. Table 7-4 lists the actual component weights used to generate the drum-scale sample. Fifty-five gallons of the waste form were generated for the 55-gal sample so that there would be enough extra sample to collect for post generation sampling and account for any waste form hold up in the ribbon mixer.

Table 7-4. 55-gal Ceramicrete baseline formulation with 0.5 wt % boric acid.

Component	Baseline 55-Gal + 0.5 wt % Boric Acid Component Weight, Kg
1 M Na^+ Simulant	81.61
MgO	39.68
KH_2PO_4	134.95
Class C Fly Ash	142.86
$SnCl_2 \cdot 2H_20$	6.24
Ground Zeolite – 5A	4.54
Supplemental H_20	6.50
Boric Acid	1.641
Totals	**418.021**

Sample #5 - Drum-Scale Ceramicrete Sample Generation – Section 7.2.1

The major dry components (magnesium oxide, mono potassium phosphate, and Class C fly ash) were weighed out and delivered to the 10 ft^3 ribbon mixer by a conveyor belt and mixed for approximately 30 min. The boric acid was then added to the mixer and the dry solids were mixed for an additional 5 min. The dry materials were then dropped from the ribbon mixer into two 55-gal storage drums. The 1 M Na^+

simulant was weighed into six 5-gal buckets and manually poured into the ribbon mixer. A picture of the Ceramicrete simulant waste and the engineering-scale mixing and delivery system are shown in Figure 7-7. Finally, the stannous chloride, supplemental water, and ground zeolite were added to the liquid simulant while mixing. The major dry components were then placed on the conveyor belt manually from 5-gal buckets and the belt fed the materials into the ribbon mixer while the mixer was mixing. The sample was mixed for 24 min total after the addition of the major dry components.

Figure 7-7. 1 M Na^+ Simulant and the large-scale mixing and delivery system.

Mixing was stopped occasionally to monitor slurry temperature and compare it to the temperature data acquired from the two temperature probes attached to the outside of the ribbon mixer. The outside temperature probes measured approximately 2 °C to 5 °C lower than the actual slurry temperature. When the inside slurry temperature reached 37.5 °C at 22 min into the mixing, the two temperature probes had temperatures of 34.3 °C and 32.7 °C; at the 24-min mixing mark, the temperature probes measured temperatures of 35.2 °C and 33.7 °C. At this point, the decision was made to stop mixing because the slurry temperature was at or near 40 °C.

The power and power factor (PF) were monitored for the ribbon mixer during the mixing process as well as the probe temperatures. Appendix B contains the power and temperature probe data collected during the mixing process.

After the sample was mixed, it was poured out of the ribbon mixer into a 55-gal drum container. The sample poured easily into the drum, and was very flowable and self-leveling. The temperature was monitored and a temperature of 54 °C was measured 40 min after mixing. A Plexiglas sheet with 7 thermocouples attached to collect a curing temperature profile was inserted into the 55-gal drum approximately 3.5 min after the pour, and the drum was covered in shrink wrap 57 min later. The top thermocouple was moved so the thermocouple was on the top of the sample instead of 6 inches below the sample's surface. Some of the sample remained in the ribbon mixer and it was collected in a 5-gal bucket and used for three 2-inch diameter by 4-inch tall sample molds, the Vicat sample, and the 50-Cent slump test samples.

The 50-Cent slump samples were collected between 3 and 5 min after mixing was stopped and the Vicat sample was collected 6 min after mixing was stopped. The slump mold for Sample #5a was pulled 5.5 min after mixing; Sample #5b mold was pulled 8.75 min after mixing; Sample #5c mold was pulled at 8.75 min after mixing; Sample #5d mold was pulled 13 min after mixing; and Sample #5e mold was pulled 18 min after mixing. The slump samples are shown in Figure 7-8 after the sample molds were removed. The Vicat cylinder plunger was dropped at 18 min, 28 min, 43 min, and 53 min with the cylinder penetration depth of 40 mm, which is the complete sample depth. The Vicat cylinder was dropped again at 75 min and 91 min with penetration depths of 18.5 mm and 11.5 mm, respectively, and Vicat testing was stopped at that point in time since the first engineering-scale test sample was then generated, therefore an initial setting time could not be calculated for Sample #5.

Figure 7-8. Sample #5 Ceramicrete Slump Sample Photo.

The 2-inch diameter by 4-inch tall sample molds were not collected until 29 min after mixing was stopped, and the sample in the bucket had to be remixed by hand to liquefy the sample so the 2-inch diameter by 4-inch tall samples could be collected. The sample matrix was disturbed while obtaining those samples and it was noted the following morning that the samples inside the 2-inch diameter by 4-inch tall sample molds had expanded and popped the top off the sample molds. The material had swelled from 0.375 inches to 0.75 inches above the top of the sample container. The material was very friable and was easily flaked off the top of the sample. Figure 7-9 shows a picture of the samples.

Figure 7-9. Ceramicrete Sample #5 – 2-inch diameter by 4-inch tall sample molds the next morning.

The 55-gal drum Ceramicrete sample was also checked the following morning approximately 18 hours into the cure time. Condensate had formed on top of the sample and a white precipitate had formed where the condensate pooled on top of the sample as shown in Figure 7-10. Figure 7-11 shows Sample #5 where the sample had swelled and cracked the top sample surface.

Figure 7-10. Ceramicrete Sample #5 the following morning.

Figure 7-11. Ceramicrete Sample #5 the following morning showing sample surface.

Engineering-Scale Ceramicrete Sample Generation – Section 7.3

Three box samples were generated during the engineering-scale demonstration: two were poured into 2-ft by 2-ft by 3-ft boxes and one was poured into a 2-ft by 2-ft by 6-ft box. The samples were generated to provide waste form processing data including mixing information, pourability and flow characteristics, and to determine if any aggregate settling occurred during the curing process for the Ceramicrete solidification process.

Sample #6 was generated using 11-ft^3 volume, which was the maximum that could be accommodated by the 10-ft^3 ribbon mixer. Samples #8 and #9 were generated using a 9-ft^3 volume because the 11-ft^3 volume was too large for the ribbon mixer to mix efficiently. The actual component weights for the three engineering-scale samples are listed in Table 7-5.

Table 7-5. Actual component weights for the Ceramicrete engineering-scale samples.

Component	Sample #6 11-ft^3 Baseline + 0.5 wt % Boric Acid Component Weight, Kg	Sample #8 9-ft^3 Baseline + 0.5 wt % Boric Acid Component Weight, Kg	Sample #9 9-ft^3 High Solids + 0.5 wt % Boric Acid Component Weight, Kg
1 M Na^+ Simulant	122.1	99.90	96.08
MgO	59.37	48.57	49.08
KH_2PO_4	201.90	165.19	166.87
Class C Fly Ash	213.73	174.87	176.71
$SnCl_2 \cdot 2H_20$	9.34	7.64	7.70
Ground Zeolite – 5A	6.79	5.56	5.61
Supplemental H_20	9.72	7.95	7.65
Boric Acid	2.46	1.94	2.03
Totals	**625.41**	**511.62**	**511.73**

Sample #6 – 2-ft by 2-ft by 3-ft Box Ceramicrete Baseline Formulation with 0.5 wt % Boric Acid – Section 7.3.1

The major dry components and the boric acid were weighed and fed into the ribbon mixer by the conveyor belt and mixed until the dry components were completely blended. The dry blend was dropped into 55-gal storage drums and staged for delivery. The box was placed under the ribbon mixer so that the sample would be poured into the center of the box. The 1 M Na^+ simulant was weighed into eight 5-gal buckets and manually placed into the ribbon mixer. The supplemental water, stannous chloride, and ground zeolite were then manually `added to the simulant and mixed for approximately 12 min. The dry components were then fed to the ribbon mixer by the conveyor belt and mixed for 22 min. The mixer was stopped several times during the mixing process to manually work the dry components into the Ceramicrete slurry and to monitor slurry temperature. Appendix B contains the outside temperature probe data and mixer power data.

The slurry pour was initiated into the 2-ft by 2-ft by 3-ft box and the pour was stopped approximately 1 min later to collect a bucket of the material for the 2-inch diameter by 4-inch tall sample molds and then the remaining sample was poured into the box. The slurry was very liquid and self-leveling in the box as shown in Figure 7-12 and the box was not vibrated. Lumps were noticed in the bottom of the ribbon mixer after the slurry was poured into the box, and material hold-up had collected at the top edges of the mixer and around the middle of the mixing shaft as shown in Figure 7-13 when the mixer was being cleaned. There were also lumps of the dry material in the bucket collected for samples. The lumps were broken up by hand and examined. The material in the lumps was damp, but not incorporated into the slurry. A picture of one of the lumps is shown in Figure 7-14.

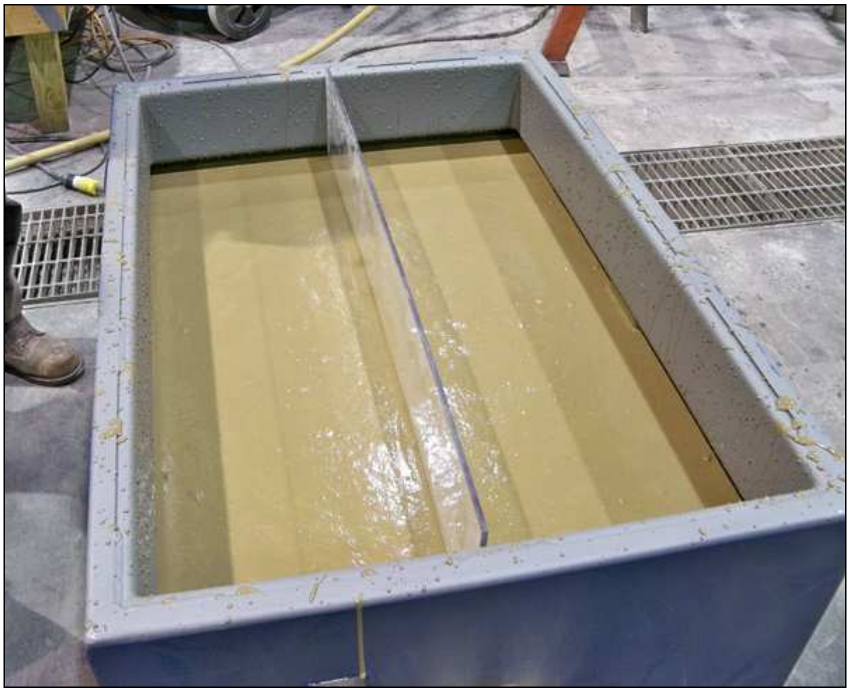


Figure 7-12. Ceramicrete Sample #6 after being placed into the 2 ft by 2 ft by 3 ft box.

Figure 7-13. Ribbon mixer shaft after Sample #6 was generated.

Figure 7-14. Lumps in Ceramicrete Sample #6.

The 2-inch diameter by 4-inch tall samples were collected immediately after collecting the slurry for sampling and then the box sample was moved and a Plexiglas divider was inserted down the centerline of the sample. Approximately 1 hour after pouring the box sample, the slurry temperature was 57 °C, small amounts of liquid were observed on the sample's surface, and liquid was collecting at the Plexiglas divider and at the interface of the box walls. The lid was not placed on the sample and the next morning white precipitation growths were observed on the sample surface as shown in Figures 7-15 and 7-16. The sample appeared to have swelled or expanded slightly at the surface.

Figure 7-15. Ceramicrete Sample #6 the morning after the sample pour.

Figure 7-16. Ceramicrete Sample #6 showing the white precipitation growths on the sample surface.

The 2-inch diameter by 4-inch tall samples were checked and the samples had again expanded out of the top of the containers and all of the sample lids were popped off. The material expanded from 0.25 to 0.5 inches out of the sample molds as shown in Figure 7-17. The material was friable and cracked and easily flaked off with a light touch or by tapping the sample containers – the same as the 55-gal molded samples.

Figure 7-17. Ceramicrete Sample #6, 2-inch diameter by 4-inch tall samples.

Sample #8 - 2-ft by 2-ft by 6-ft Box Ceramicrete Baseline Formulation with 0.5 wt % Boric Acid – Section 7.3.2

The major dry components and the boric acid were weighed and fed into the ribbon mixer by the conveyor belt and mixed until the dry components were completely blended for Sample #8 and then for Sample #9. The dry blend for each sample was dropped into 55-gal storage drums and staged for delivery. The 2-ft by 2-ft by 6-ft box was oriented directly above a point such that the delivery chute of the ribbon mixer was 12 inches from the end of the box at the centerline of the box as shown in Figure 7-18 during the addition of the simulant. The 1 M Na^+ simulant for Sample #8 was weighed into seven 5-gal buckets and manually placed into the ribbon mixer. The mixer leaked approximately 20 mL of the simulant into the box below the ribbon mixer before it was stopped by tightly closing the valve. The mixer was turned on and the supplemental water, stannous chloride, and ground zeolite were then added to the simulant and mixed for approximately 9 min. The dry components were then added to the conveyor belt using the overhead crane as shown in Figure 7-19 and fed to the ribbon mixer over an extended period of approximately 10 min in hopes of eliminating the dry blend material from collecting in the middle of the mixing shaft. The slurry was mixed for a little over 27 min. The mixer was stopped several times during the mixing process to observe the mixing blades, which extended about 1.5 inches above the slurry level, and to monitor slurry temperature. Appendix B contains the outside temperature probe data and mixer power data that was collected during the mixing process.

Figure 7-18. Orientation of the 2-ft by 2-ft by 6-ft box for Ceramicrete Sample #8.

Figure 7-19. Dry material fed using the overhead crane.

It was observed that the dry blend had settled approximately 2.75 inches in the storage drums and over a period of 10 to 15 min indicating that the ribbon mixer incorporated air during the dry blend mixing. A picture of the settled material is shown in Figure 7-20 by the faint line above the materials in the storage drum.

At the 27-min mixing mark, the slurry temperature was 39 °C and mixing was stopped and the pour into the 2-ft by 2-ft by 6-ft box was initiated. A bucket sample was collected before the sample was poured into the box. The slurry was again self-leveling in the box and extended into all corners of the large box as shown in Figure 7-21. The sample was not vibrated.

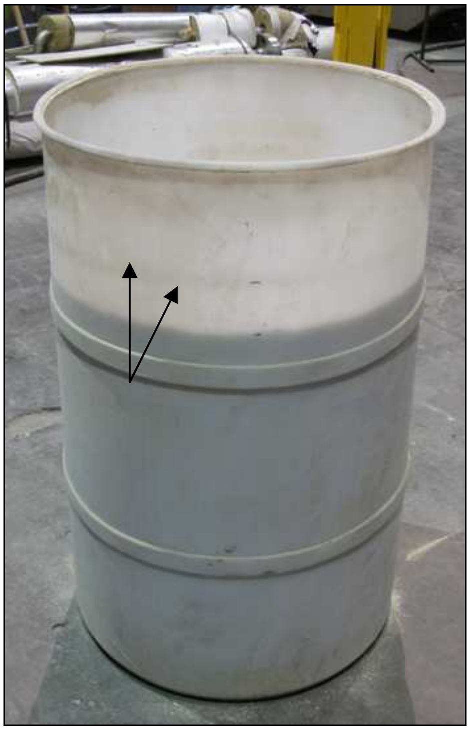


Figure 7-20. Dry material settling in the material storage drum.

Figure 7-21. Ceramicrete Sample #8 after the pour.

The 2-inch diameter by 4-inch tall samples were collected immediately and lumps were noticed in the slurry, but there were not as many and they were smaller than the lumps observed in the 11-ft^3 sample. The box was moved and the Plexiglas divider was placed at the centerline of the 2-ft by 2-ft by 6-ft box. Approximately 57 min after mixing was stopped, the slurry temperature was 57 °C and the lid was placed on the sample box before leaving for the night.

The next morning, Sample #8 and the 2-inch diameter by 4-inch tall samples were checked and the small samples had expanded out of the sample containers again even though the samples were not disturbed during collection (shown in Figure 7-22). When the lid was removed from Sample #8, quite a bit of condensation was poured onto the floor as shown in Figure 7-23. The sample had minimal amounts of white precipitation on top of the sample and at the divider and at the interface of the sample and the box as shown in Figure 7-24. The sample height within the box was checked and the sample was 8 inches high – the same sample height as after the pour the previous day.

Figure 7-22. Ceramicrete Sample #8 – 2-inch diameter by 4-inch samples the next morning.

Figure 7-23. Ceramicrete Sample #8 condensation.

Figure 7-24. Ceramicrete Sample #8 the morning after sample generation.

Sample #9 - 2-ft by 2-ft by 3-ft Box Ceramicrete High Solids Formulation with 0.5 wt % Boric Acid – Section 7.3.3

Because the dry components had been blended previously and staged for delivery, the 1 M Na+ simulant for Sample #9 was placed into the ribbon manually using seven 5-gal buckets. Then the mixer was turned on and the stannous chloride, supplemental water, and ground zeolite were added and mixed for 7 min before adding the blended dry solids. The blended solids were fed to the conveyor belt using the overhead crane and the conveyor belt fed the dry materials into the ribbon mixer in approximately 15 min and the slurry was mixed for 25 min when the slurry temperature reached 40.5 °C. The mixer was stopped several times during the mixing process to observe the mixing blades for material hold-up, incorporate dry materials, and monitor slurry temperature. Appendix B contains the outside temperature probe data and mixer power data that was collected during the mixing process.

The box had been placed under the ribbon mixer so the sample would be poured approximately in the center of the box. Figure 7-25 shows a picture of Sample #9 being poured. The slurry was again self-leveling with slurry easily flowing into the corners of the box. The pour was stopped after approximately 1 min, a bucket sample was collected, and the pour was then completed. The 2-inch diameter by 4-inch tall samples were collected immediately and lumps were identified in the bucket sample that seemed larger than those for Sample #8 but smaller than those from Sample #6. A picture of the sample being collected is shown in Figure 7-26. The blended dry solid material again collected around the center of the mixing shaft as shown in Figure 7-27.

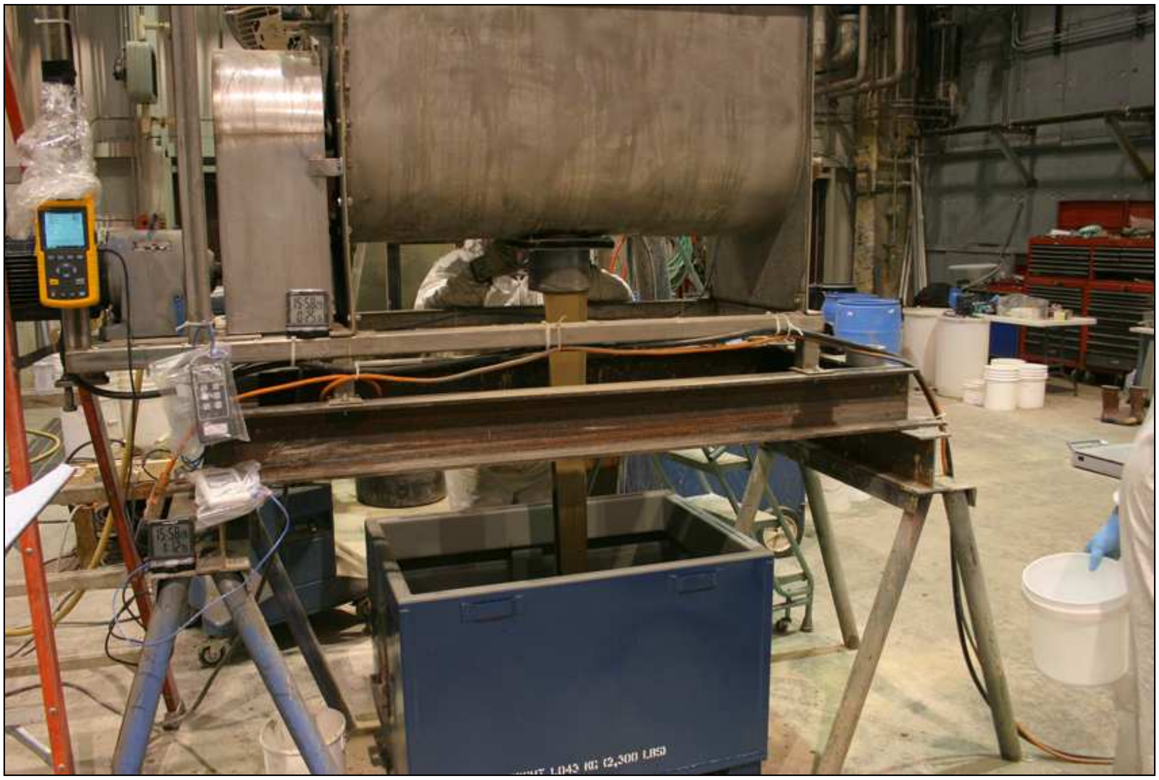


Figure 7-25. Ceramicrete Sample #9 during the pour.

Figure 7-26. 2-inch diameter by 4-inch tall sample collection for Ceramicrete Sample #9.

Figure 7-27. Ceramicrete dry material build-up around the mixing shaft.

The box was moved and the Plexiglas divider was inserted along the centerline of the box. The height of the slurry was measured to determine whether the sample swelled overnight. The slurry temperature was 57 °C approximately 44 min after the pour and the lid was not placed on the box since the divider extended out of the top of the sample box.

The next morning Sample #9 and the 2-inch diameter by 4-in tall samples were checked for expansion and the small samples had again expanded out of the top of the sample containers as shown in Figure 7-28. Figure 7-29 shows the sample level with the box the next morning and shows that the sample had swelled approximately one inch within the sample box.

Figure 7-28. Ceramicrete Sample #9 - 2-inch diameter by 4-inch tall samples the next morning.

Figure 7-29. Ceramicrete Sample #9 the morning after sample generation.

DuraLith Solidification Testing – Section 8

Bench-scale testing was conducted prior to the drum-scale and engineering-scale demonstrations to observe the mixing process for the baseline solidification formulations provided by the DuraLith technology providers and to gather information pertaining to the scale-up formulations that were used during the drum-scale and engineering-scale demonstrations. The drum-scale demonstration was the first scale-up testing and it was conducted to determine if the bench-scale formulations would scale-up and to provide the necessary curing temperature profile for a large cylindrical waste form. The engineering-scale demonstration was not performed because the first 55-gal drum sample that was mixed in the ribbon mixer was not adequately mixed. The engineering-scale demonstration consisted of generating two 51-gal drum samples in 80-gal drums using the 20 Hp drum mixer to help support the final technology down selection to solidify Hanford secondary waste streams. The tests were able to provide waste form processing data including mixing and curing information and to determine if any aggregate settling occurred during the curing period of the DuraLith solidification process.

PNNL and WRPS personnel and the DuraLith technology provider were on site during the DuraLith bench-scale and engineering-scale demonstration to observe testing and provide formulation development for the bench-scale and engineering-scale samples.

DuraLith Activator Solution Make-up – Section 8-1

DuraLith activator solution for three 4.5-gal samples, one 51-gal sample, and 4 extra gal was prepared the week before testing began. The calculated and actual weights for the first batch of DuraLith activator solution are listed in Table 8-1. The 6 M Na^+ simulant was weighed out in buckets and manually poured into an 80-gal drum; the tin fluoride, potassium hydroxide, and sodium hydroxide were added and mixed until well blended. The fumed silica was then added in 6 batches with constant mixing. The first 4 batches of the fumed silica wetted well using the mixer, but the last 2 batches floated on top of the surface until manually incorporated into the solution. Once the silica was wetted it did easily incorporate into the solution. The maximum temperature of the solution reached 56 °C at 5:00 pm (initiation was ~ 3:30 pm) and the temperature dropped to 51 °C by 5:15 pm and bubbles were noticeably coming to the surface of the solution. At that point in time the hydrogen generation was measured and the value was 0.05% by volume.

The solution was checked again that evening at 10:45 pm and 6 gal of make-up water was added to bring the solution back up to original volume level and the temperature of the solution had dropped to 40°C. There were no longer bubbles coming to the surface of the solution and the solution was less viscous. The solution was checked again Saturday morning at 8:15 and 3.5 gal of make-up water was added to bring it back to the original volume. The mixture was even less viscous with a viscosity resembling water and had a temperature of 26 °C. The solution was checked again that afternoon at 4:10 pm and had a temperature of 20 °C. No make-up water was needed to bring the solution to the original volume, and again no bubbles were observed. At 9:25 pm, the solution was checked and had a temperature of 20 °C and no make-up water was added. It appeared that the fumed silica had completely dissolved after more than 24 hours of mixing.

Table 8-1. DuraLith activator solution calculated and actual weights for batch 1.

Component	Weight %	Batch #1 Calculated Weight, Kg	Batch #1 Actual Weight, Kg
6 M Na^+ Simulant	61.38	132.9	132.9
Tin Fluoride	0.61	1.27	1.27
Potassium Hydroxide	16.30	35.13	35.13
Sodium Hydroxide	2.49	5.41	5.41
Fumed Silica	19.23	41.6	41.60
Totals	**100.00**	**213.61**	**213.61**

When the mixture was checked on Sunday morning at 9:05 am, the mixer had stopped mixing. The solution temperature was 18 °C and no bubbles were coming to the top of the sample but the sample had a crusty layer on top of the liquid surface and solids in the bottom of the 80-gal tank. An operator and another engineer were called in to replace the mixer and mixing was reestablished by 10:20 am. After 9 min of mixing there were no solids on the tank bottom or crust on the surface and 1 gal of make-up water was added. The solution was checked again at 4:15 pm and at 10:00 pm that evening. No make-up water was required and the solution had a temperature of 18 °C. The solution was checked again Monday morning and no make-up water was necessary. 41 Kg of the activator solution was weighed out and brought to the Resource Recovery Facility (RRF) for the bench-scale tests. The activator solution was placed into three 5-gal buckets and continually mixed until sample make-up. A picture of the activator solution is shown in Figure 8-1. A specific gravity measurement was made for the DuraLith activator solution, which yielded a value of 1.509 g/mL.

Figure 8-1. Activator solution for three 4.5 gal samples continuously mixing.

Two additional batches of activator solution were generated during the DuraLith test sequence. The second batch generated was for a 51-gal sample plus ~ 2 additional gal and the last batch was made for a 51-gal waste form in the container used to generate Sample #17. Table 8-2 presents the calculated component weights and the actual component weights used to make the last two batches of activator solution.

Table 8-2. DuraLith activator solution calculated and actual weights for batches 2, 3, and 4.

Component	Weight %	Batch #2 Calculated Weight, Kg	Batch #2 Actual Weight, Kg	Batch #3 Calculated Weight, Kg	Batch #3 Actual Weight, Kg
6 M Na^+ Simulant	61.38	106.108	106.108	92.82	92.82
Tin Fluoride	0.61	1.015	1.015	0.940	0.940
Potassium Hydroxide	16.30	28.033	28.033	24.53	24.53
Sodium Hydroxide	2.49	4.315	4.315	3.78	3.78
Fumed Silica	19.23	33.169	33.169	29.04	29.04
Totals	**100.00**	**172.64**	**172.64**	**151.11**	**151.11**

The same procedure was used to generate the second and third batches of activator solution that was used to generate the first batch. The simulant and the other dry materials except the fumed silica were thoroughly mixed and then the fumed silica was added in 6 separate batches. The slurry heated up after the sodium hydroxide was added and gas bubbles were generated by the slurry after the fumed silica was added to the mixture. Make-up water was added over a 24 hour mixing period. Hydrogen generation values were checked after the fumed silica was added to the second batch of activator solution. The first measurement was made after the fumed silica was incorporated into the liquid at 12:03 pm and a value of 0.15% was obtained. The next measurement was made 8 min later and the hydrogen generation value was 0.05% by volume. The third measurement was made 4.25 hours later and a value of 0.00% was obtained. It appears that hydrogen is generated initially after the fumed silica is added when the solution temperature is elevated and subsides within approximately 4 hours.

DuraLith Bench-Scale Solidification Testing - Section 8.2

The work plan specified that 3 DuraLith bench-scale samples would be generated during the bench-scale test sequence: one using the baseline formulation, one using the high solids formulation, and one using the low solids formulation.

The DuraLith baseline, high liquids and high solids formulation dry components or binder materials were weighed out and placed into overpack drums the week before PNNL, WRPS, and DuraLith personnel arrived at MSE to prepare for the upcoming test sequence. The calculated and actual component weights that were used to generate the samples are presented in Table 8-3 for the baseline and high liquids formulations. The DuraLith bench-scale samples were generated in much the same fashion as the Ceramicrete samples: the dry binder materials were thoroughly mixed in the overpack drums; the activator solution was weighed out into a 6-gal bucket and the supplemental water was added and mixed; then the binder materials were added and the entire quantity was mixed.

Table 8-3. Actual component weights for the initial DuraLith baseline samples.

Component	Weight %	4.5 Gal Baseline Calculated Component Weight, Kg	Sample #10 Baseline Actual Component Weight, Kg	Sample #11 High Liquids Actual Component Weight, Kg
Activator Solution		13.31	13.31	13.31
Binder Materials				
Blast Furnace Slag	45.15	9.91	9.91	9.91
Copper Slag	3.19	0.70	0.70	0.70
Metakaolin Clay	18.22	4.00	4.00	4.00

Fine Sand	30.25	6.64	6.64	6.64
Ground Zeolite – 5A	1.59	0.35	0.35	0.35
Fumed Silica	1.59	0.35	0.35	0.35
Totals	**100.00**	**21.95**	**21.95**	**21.95**
Total Additional Water	**0**		16.45 wt % (164 g)	20 wt % (1689 g)

Sample #10 – DuraLith Baseline Formulation with 16.45 wt % Water– Section 8-2.1

The dry binder materials (Blast Furnace Slag (BFS), copper slag, metakaolin clay, zeolite, and fumed silica) were thoroughly mixed in the overpack drum; the activator solution was weighed out into a 6-gallon bucket and the supplemental water was added and mixed; then the binder materials were added while mixing. The supplemental water was added to make up for the lower water content of the sand located at the MSE test site compared to the sand used by the technology provider. The sample was mixed for approximately 3.25 min and moved to the sampling location. Figure 8-2 shows Sample #10 during the mixing process.

Figure 8-2. DuraLith Sample #10 during the mixing process.

Within 1.5 min after mixing the Vicat sample was collected; at the 2 min mark after mixing the only 50-Cent slump sample was collected; and approximately 2 min later a 2-inch diameter by 4-inch tall sample was collected. Two min later, the sample divider could not be inserted into the sample in the 6-gal bucket due to the quick rate of curing resulting in a very hard material. At 5.08 min after mixing, the Vicat cylinder plunger was dropped on the sample and had a penetration depth of 6 mm; however, the cylinder did not cut into the sample. The entire sample's surface deformed to accommodate the cylinder as shown in Figure 8-3. At 6 min after mixing, personnel attempted to remove the slump mold from the sample, however the sample would not release from the mold as shown in Figure 8-4.

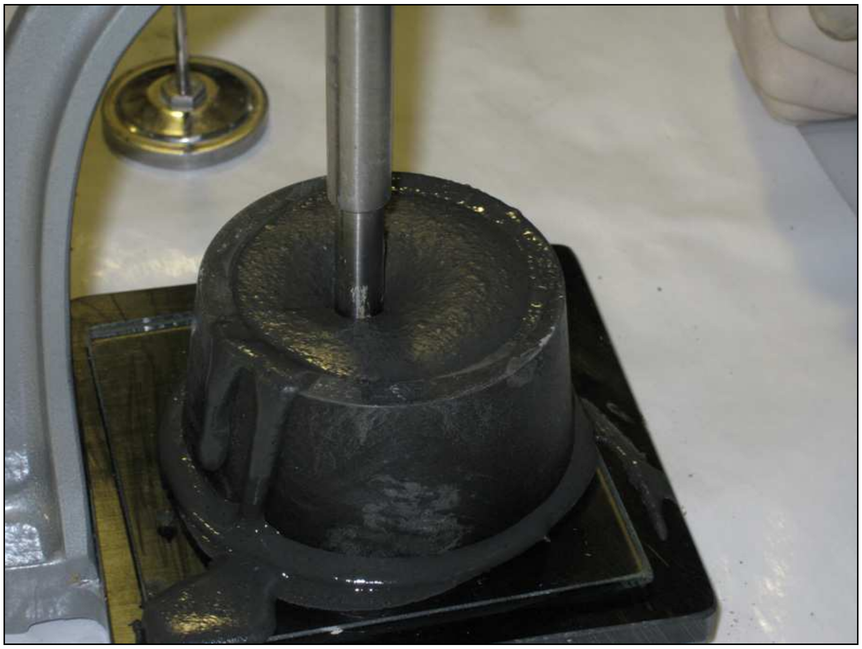


Figure 8-3. DuraLith Sample #10 Vicat sample.

Figure 8-4. DuraLith Sample #10 Slump sample.

The Vicat needle plunger was dropped at 9.35 min after mixing and had a penetration depth of 20 mm and again at 11.5 min for a penetration depth of 7.5 mm, after which the Vicat testing was stopped. The initial setting time was estimated to be less than 9 min since a Vicat needle drop penetration depth of more than 25 mm was not obtained. At approximately 19 min after mixing, the sample temperature was 23 °C. At times between 21 and 23 min after mixing was ceased, the temperature probe could only be inserted into the sample about 1 inch but recorded temperatures ranging from 23°C to 23.5°C.

After team discussions, the mixer operator explained that he could tell that the bottom sample section was hardening up faster than the top section during the 3.25 min mix. After continued team discussions, it was decided to generate the high liquids bench-scale sample next since the baseline sample set-up so quickly.

Sample #11 –DuraLith Modified Baseline Formulation with 20 wt % Water– Section 8-2.2
The binder materials were thoroughly mixed in the overpack drum and the activator solution was weighed out into the 6-gal bucket. The supplemental water for the sand moisture difference (164g) and the additional water necessary to adjust the baseline formulation to the high liquids formulation (1525 g) was added to the simulant and mixed. Then the binder materials were added and the sample was mixed for 3 min. Within 30 sec the Vicat sample was collected and within 90 sec two 50-Cent slump samples were collected.

The mold was removed from slump Sample #11a and 30 sec later the mold for slump Sample #11b was removed. For both the slump samples, the bottom of the sample stuck to the table surface and the top section of the sample remained in the sample mold with a string of sample attaching the top and bottom sections of the sample as shown in Figure 8-5. When the string of sample broke, significant sample remained in the mold and the material was very sticky. Therefore the sample slump was not measured as only part of the sample remained on the surface to measure.

Figure 8-5. DuraLith Sample #11 slump samples.

The Vicat cylinder was dropped on the Vicat sample 4.5 min after mixing and had a penetration depth of 29 mm. At 5.75 min after mixing a 2-inch diameter by 4-inch tall sample was collected. At 6.5 min after mixing, the Plexiglas divider could not be inserted into the 4.5-gal sample because the sample was already too hard. The Vicat cylinder was dropped one more time and had a penetration depth of 5mm ,7 min after mixing. The Vicat cylinder was replaced with the needle plunger and dropped on the sample again 10.5 min after mixing with a penetration depth of 30.5 mm. The needle was dropped again at 16 min after mixing with a penetration depth of 11 mm. The final needle drop occurred at 22.5 min after mixing with a penetration depth of 6.5 mm. The calculated initial setting time for Sample #11 was 12 min. A sample temperature was collected 12.3 min after mixing and measured 22 °C, however the temperature probe could only be inserted into the sample about 2 inches.

The rest of the afternoon was used to generate the second batch of activator solution and discuss the previous generation of Sample #10 and Sample #11. The DuraLith technology provider explained that Class F fly ash could be substituted for 70% of the BFS component in the binder materials to prolong the cure time. Therefore, arrangements were made to purchase a quantity of the Class F fly ash that afternoon.

He also explained that if fumed silica was added separately as the last dry component, it could help prolong the curing process and that the addition of boric acid would also prolong the curing process. The DuraLith technology provider spent the afternoon running the calculations for the new formulations. New soil moisture content calculations were also run for a new batch of fine sand as the new bag was very wet compared to the bag previously used.

The new 4.5-gal DuraLith modified formulations, the calculated component weights, and the actual component weights are presented in Table 8-4.

Table 8-4. DuraLith modified 4.5-gal formulations.

Component	Weight %	4.5 Gal Baseline Calculated Component Weight, Kg	Sample #12 Actual 4.5-Gal Baseline Component Weight, Kg	Sample #13 Actual 4.5-Gal Baseline Component Weight, Kg	Sample #15 Actual 3.5-Gal High Solids Component Weight, Kg
Activator Solution	37.72	13.31	13.31	13.31	10.24
Binder Materials					
Blast Furnace Slag	45.15	9.91	2.973	2.973	2.28
Class F Fly Ash			6.937	6.937	5.32
Copper Slag	3.19	0.70	0.70	0.70	0.54
Metakaolin Clay	18.22	4.00	4.00	4.00	3.07
Fine Sand	30.25	6.64	6.64	6.64	5.09
Ground Zeolite – 5A	1.59	0.35	0.35	0.35	0.27
Fumed Silica	1.59	0.35	0.35	0.35	0.27
Totals	**100.00**	**21.95**	**21.95**	**21.95**	**16.84**
Water –wt % (Quantity)			20 wt % (1338 g)	20 wt % (1338 g)	16.45 wt % (65.15g)
Boric Acid			--	114.8 g	--

Sample #12 –DuraLith Baseline Modified Formulation with 20 wt % Water– Section 8-2.3

The binder materials were thoroughly mixed in the overpack drum (except the fumed silica) and the activator solution was weighed out into the 6-gal bucket. The supplemental water for the soil moisture difference (-187 g) and the additional water necessary to adjust the baseline formulation to the modified baseline formulation of 20 wt % water (1525 g) was added to the simulant and mixed, then the binder materials were added and the sample was mixed for 1.5 min. The fumed silica was then added and the sample was mixed for an additional 1.5 min.

The 2-inch diameter by 4-inch tall sample was collected 24 sec after mixing, the Vicat sample was collected 33 sec after mixing, and the five 50-Cent slump samples were collected within 1 min and 55 sec after mixing. The temperature for Sample #12 was 19°C three min after mixing was completed and the Plexiglas divider was inserted into the sample 4 min after mixing was stopped. The Vicat sample was replaced 3.45 min after mixing due to seepage of the sample out the bottom of the Vicat sample mold.

The mold of slump Sample #12a was removed 4.8 min after mixing was stopped. The sample flowed into a shallow pool that poured off the table surface. The mold for slump Sample #12b was removed 17 min after mixing and the material slumped 78 mm; the mold for slump Sample #12c was removed 21.35 min after mixing and the material slumped 68 mm; and the mold for slump Sample #12d was removed 26.67 min after mixing and the material slumped 55 mm. The sample mold for slump Sample #12e was pulled 30 min after mixing but did not release from the sample mold as shown in Figure 8-6.

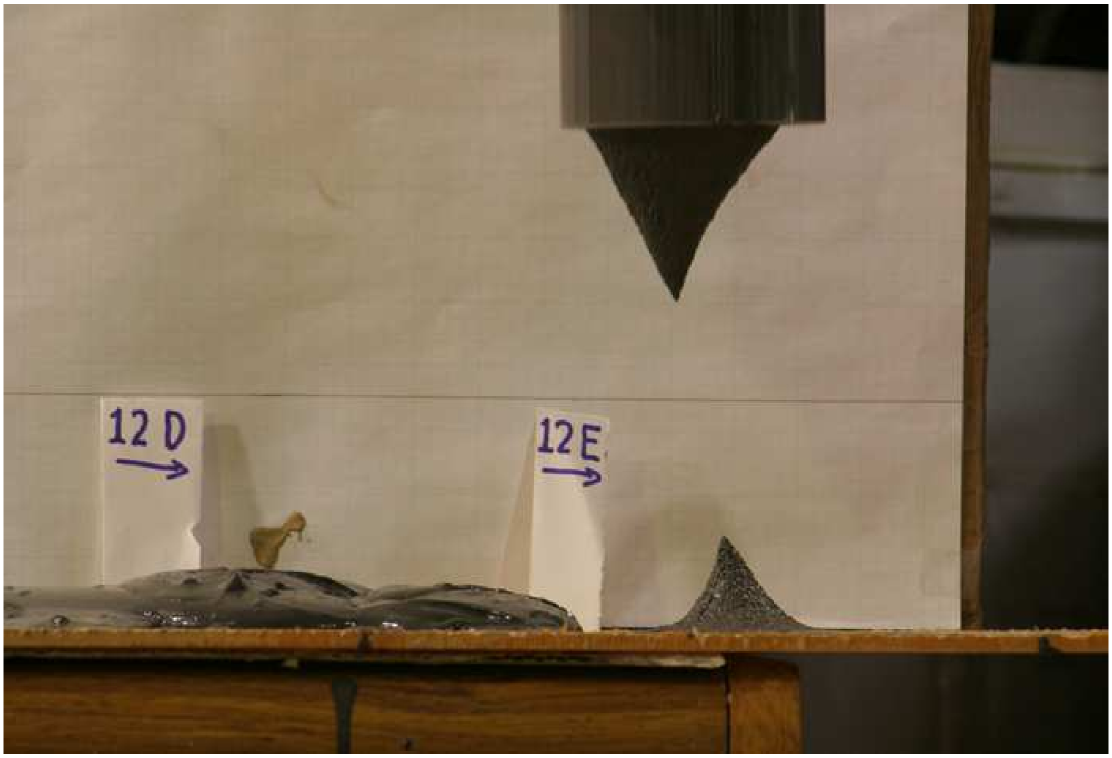


Figure 8-6. DuraLith Slump Sample #12d after the sample mold was pulled.

The Vicat cylinder was dropped into the sample 33 min after mixing and dropped to the bottom of the sample and the material stuck to the cylinder. The second cylinder drop occurred 40 min after mixing and had a penetration depth of 21.5 mm and the material was a little less sticky. The Vicat cylinder was dropped for the last time 46 min after mixing and had a penetration depth of 5 mm. Then the cylinder was replaced with the Vicat needle plunger and three measurements were made: 1 at 53 min, another at 68 min, and the last at 78 min after mixing with penetration depths of 40 mm, 28 mm and 13 mm, respectively. The initial setting time was calculated for Sample # 12 of 70 min. A summary of the bench-scale Vicat drop tests is presented in Table 8-6 at the end of this report section.

The sample reached a temperature of 21.5°C at 25.53 min after mixing. Small lumps of fumed silica were noticed in the slump and Vicat samples during testing after the 1.5 min silica mix time, so the mixing time for future samples was increased after the addition of the fumed silica. A picture of the dry fumed silica is shown in Figure 8-7.

Figure 8-7. Dry fumed silica in DuraLith Sample #12.

Sample #13 –DuraLith Baseline Modified Formulation with 20% Water plus 0.75 wt % Boric Acid– Section 8-2.4

Sample #13 was generated using the same formulation as Sample #12 except for the addition of boric acid at 0.75 wt % of the dry binder materials. The boric acid was added to the supplemental water and Sample #13 was mixed like the previous samples by adding the supplemental water to the activator solution and then adding the binder materials, except the fumed silica, and mixed for 1.5 min. The fumed silica was then added and the sample was mixed for 5 more min.

The molds were removed from slump Samples #13a, #13b, #13c, #13d, and #13e at 3.17 min, 18.83 min, 20.15 min, 24.67 min, 26.67 min, and 27.67 min after mixing, respectively, with slumps measuring approximately 70 mm, 58 mm, 56 mm, 43 mm, and 38 mm, respectively. It took approximately 20 sec for slump Sample #13e to drop from the sample mold. A picture of slump samples for Sample #13 is shown in Figure 8-9.

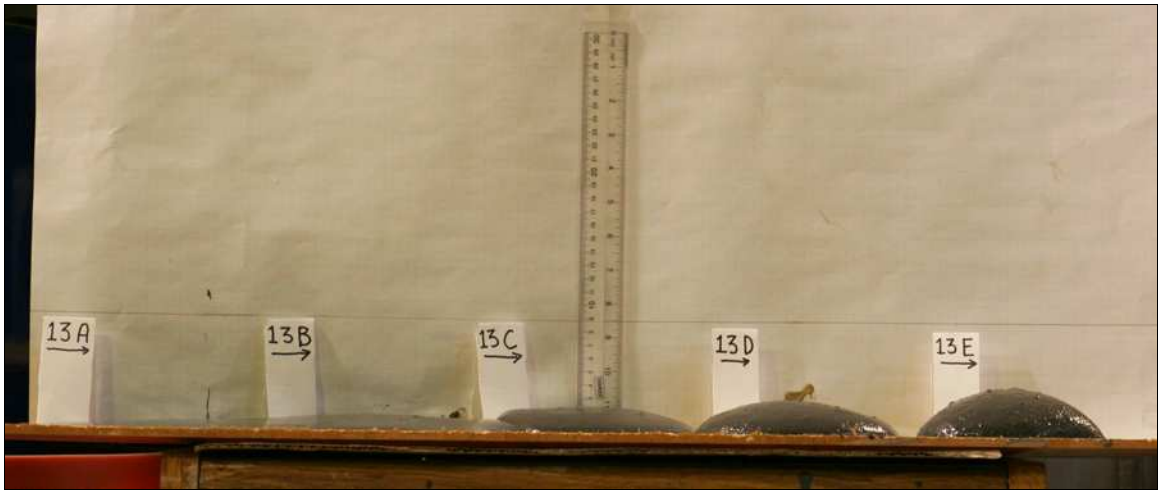


Figure 8-9. Slump sample for DuraLith Sample #13.

The Vicat cylinder was dropped on the sample 3 times at 29.6 min, 36.67 min, and 44.25 min after mixing. The first cylinder dropped to the bottom of the sample while the second and third drops had penetration depths of 28.5 mm and 5 mm, respectively. The Vicat cylinder was changed out to the needle plunger and testing continued. The needle was dropped onto the sample 5 times at 54.25 min, 64.25 min, 69.25 min, 74.25 min, and 79.25 min after mixing. The drops resulted in the needle penetrating to the bottom of the sample for the first drop, while the next four drops resulted in penetration depths of 31.5 mm, 19.5 mm, 19.5 mm, and 11.5 mm, respectively. The initial setting time calculated for Sample #13 was 44 min

The sample reached a temperature of 21.8°C at 21.5 min after mixing and an unmixed agglomeration of fumed silica particles approximately ¼-inch in size was observed in one of the slump samples.

Sample #15 –DuraLith High Solids Modified Formulation with 16.45 wt % Water – Section 8-2.5
Because there was not quite enough activator solution left from batch #2 to make a 4.5 gal sample, Sample #15 was generated using 3.5 gal and 16.45 wt % water instead of 20 wt % water like Samples #12 and #13. Consequently, this sample was considered the high solids formulation. All the binder materials, including the fumed silica, were blended thoroughly in the overpack drum; the activator solution was weighed into the 6-gal bucket and the supplemental water was added and mixed; and then the dry binder materials were added to the bucket and mixed for 4 min. The 2-inch diameter by 4-inch tall sample and the Vicat sample were collected within 30 sec after mixing and the 50-Cent slump samples were collected within 2 min after mixing. No lumps or dry material were observed in the collected samples or in the bucket and the sample consistency was workable.

The mold for slump Sample #15a was removed 14 min after mixing with a slump height of 83 mm; the mold for Sample #15b was removed 18 min after mixing with a slump height of 78 mm; the mold for Sample #15c was removed 1 min later and had a slump height of 76 mm; the mold for Sample #15d was removed 21.25 min after mixing with a slump height of 60 mm; and the mold for Sample #15e was removed 23.5 min after mixing with a slump height of 40 mm. A picture of all 5 slump tests is shown in Figure 8-10.

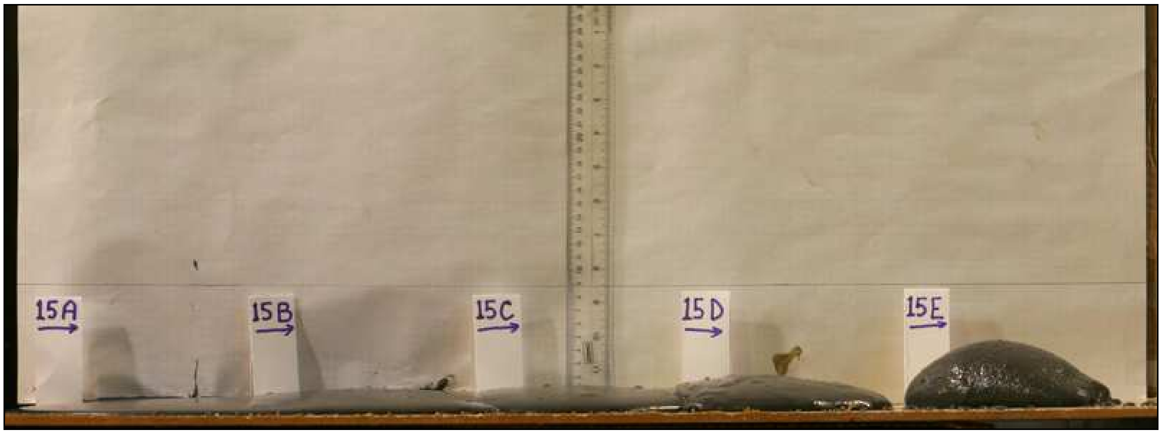


Figure 8-10. Slump sample for DuraLith Sample #15.

The Vicat cylinder was dropped twice at 33.6 min and 39.6 min after mixing with penetration depths of 15 mm and 3 mm, respectively. The Vicat cylinder was replaced with the Vicat needle which was dropped three times at 51.6 min, 64.6 min, and 74.6 min after mixing with penetration depths of 25 mm, 11.5 mm, and 7 mm, respectively. The initial setting time for Sample #15 was 51.6 min when the needle penetration depth was actually 25 mm.

Table 8-5 shows the DuraLith 50-Cent rheometer slump test data

Table 8-5 . DuraLith bench-scale 50-Cent rheometer slump test data.

Sample Number	50-Cent Slump Tests			Sample Molds Removed - Time after mixing, min
	Initial Slump Height, mm	Final Slump Height, mm	Slumping Height, mm	
10	88	--	--	--
11a	88	--	--	--
11b	88	--	--	--
12a	88	**	**	4.8
12b	88	10	78	17
12c	88	20	68	21.35
12d	88	33	55	26.67
12e	88	--	--	31.42
13a	88	18	70	18.83
13b	88	30	58	20.15
13c	88	32	56	24.67
13d	88	45	43	26.67
13e	88	50	38	27.67
15a	88	5	83	14
15b	88	10	78	18
15c	88	12	76	19
15d	88	22	66	21.25
15e	88	48	40	23.5

-- Sample did not come out of sample mold completely. ** Sample was too runny and was removed from table surface.

When comparing the 50-Cent slump data presented in Table 8-5, Samples #13 and #15 seem to provide the best DuraLith formulation slump results as related to the longest set-up times and all the samples actually came out of the sample molds. Samples #10 and #11 set-up so quickly that the samples would not come out of the sample molds, either partially or completely. Sample #12a was so thin that it ran off the edges of the test table and Sample #12d was so thick that it did not release from the sample mold.

Table 8-6. DuraLith bench-scale Vicat cylinder drop and needle drop test data.

Sample Number	Vicat Tests				
	Cylinder Drop		Needle Drop		Initial Setting Time
	Penetration Depth, mm	Time after mixing, min	Penetration Depth, mm	Time after mixing, min	Time, min
10	6	5.08	--	--	< 9
10	--	--	20	9.35	
10	--	--	7.5	11.5	
11	29	4.5	--	--	12
11	5	10.5	--	--	
11	--	--	30.5	10.5	
11	--	--	11	16	
11	--	--	6.5	25.5	
12	40	33	--	--	70
12	21.5	40	--	--	
12	5	46	--	--	
12	--	--	40	53	
12	--	--	28	68	
12	--	--	13	78	
13	40	29.6	--	--	67

13	28.5	36.67	--	--	
13	5	44.25	--	--	
13	--	--	40	54.25	
13	--	--	31.5	64.25	
13	--	--	19.5	69.25	
13	--	--	19.5	74.25	
13	--	--	11.5	79.25	
15	15	33.6	--	--	52
15	3	39.6	--	--	
15	--	--	25	51.6	
15	--	--	11.5	64.6	
15	--	--	7	74.6	
-- Vicat Test Apparatus used either cylinder or needle component for individual drop tests – not both.					

When comparing the Vicat cylinder drop test data, Samples #12, #13, and #15 had comparable penetration depths between 5 mm and 3 mm at times ranging from 46 min and 39.6 min and initial setting times ranging from 52 to 70 min. Samples #10 and #11 had set so quickly that the Vicat cylinder tests were completed approximately 5 and 10 min after mixing and had initial setting times of 12 min and less. These sample formulations did not provide enough time between mixing and set-up to be functional for scale-up testing.

DuraLith Drum-Scale Solidification Testing - Section 8.3

As stated previously, the drum-scale testing was performed to validate bench-scale DuraLith formulations and to provide a curing temperature profile for a large cylindrical waste form. Power requirements were also monitored for the ribbon mixer during mixing. After Sample #14 was generated, the team decided that the ribbon mixer should not be used to generate the engineering-scale demonstration samples because Sample #14 was poorly mixed using the ribbon mixer. The decision was made to generate 2 additional 51-gal drum samples in 80-gal containers using the MSE 20 Hp hydraulically driven drum mixer in an attempt to get adequate sample mixing for the DuraLith waste forms.

The modified drum-scale DuraLith formulations are presented in Table 8-7. None of the formulations included boric acid but the water content for Samples #14 and #16 was increased to 21 weight percent, and this was considered the new modified baseline formulation. Sample #17 was generated using 16.45% water by weight and was considered the high solids DuraLith formulation.

Table 8-7. DuraLith drum-scale formulations.

Component	Weight %	Calculated Component Weight, Kg	Sample #14 Actual 51-Gal Baseline Component Weight, Kg	Sample #16 Actual 51-Gal Baseline Component Weight, Kg	Sample #17 Actual 51-Gal High Solids Component Weight, Kg
Activator Solution	37.2	151.11	151.11	151.11	151.11
Binder Materials					
Blast Furnace Slag	8.43	33.66	33.66	33.66	33.66
Class F Fly Ash	19.67	78.76	78.76	78.76	78.76
Copper Slag	2.00	7.91	7.91	7.91	7.91
Metakaolin Clay	11.30	45.29	45.29	45.29	45.29
Fine Sand	18.80	75.17	75.17	75.17	75.17
Ground Zeolite – 5A	0.99	3.96	3.96	3.96	3.96
Fumed Silica	0.99	3.96	3.96	3.96	3.96
Totals	**100.00**	**399.82**	**399.82**	**399.82**	**399.82**
Water Weight Percent			21% (21.898 Kg)	21% (21.898 Kg)	16.45% (0 Kg)

Sample #14 - Drum-Scale DuraLith Sample Generation with 21 wt % Water – Section 8.3.1

The supplemental water was added to the ribbon mixer first and then the activator solution was added followed by the dry binder materials. The materials were fed to the ribbon mixer using the overhead crane and the conveyor belt, as was performed with the previous large-scale samples. Sample #14 was mixed for 12 min. Appendix B contains the outside temperature probe data and mixer power data.

The mixer was stopped once during the mixing process to clear lumps of dry material from the sides of the mixer and the mixer shaft. A bucket of the waste form was collected for the nine 2-inch diameter by 4-inch tall samples, the 5 slump samples, and one for the Vicat sample. Many lumps were present in the bucket sample. The remaining DuraLith waste form was poured into the 55-gal drum and it appeared that here was a layer of lumps approximately 1-inch deep on the surface of the sample. The Plexiglas divider with the 7 attached thermocouples was inserted into the 55-gal drum after the sample was relocated approximately 5.5 min after mixing.

The nine 2-inch diameter by 4-inch tall samples were placed into the sample containers within 2 min after mixing was completed; the slump samples were collected within 3 min after mixing; and the Vicat sample was collected 3.38 min after mixing was stopped. The mold was pulled from slump Sample #14a 17 min after mixing and had a slump height of 72 mm; the mold was pulled from slump Sample #14b 21 min after mixing and had a slump height of 63 mm; the mold was pulled from slump Sample #14c 22 min after mixing and had a slump height of 52 mm; the mold was pulled from slump Sample #14d 22.5 min after mixing and had a slump height of 44 mm; and the mold was pulled from slump Sample #14e 23 min after mixing and had a slump height of 37 mm. It took approximately 17 sec for slump Sample 14e to release from the sample mold. A picture of the slump sample for Sample #14 is shown in Figure 8-11. A picture of the lumps in slump Sample #14b is shown in Figure 8-12 during slump testing.

Figure 8-11. Slumps sample for DuraLith Sample #14.

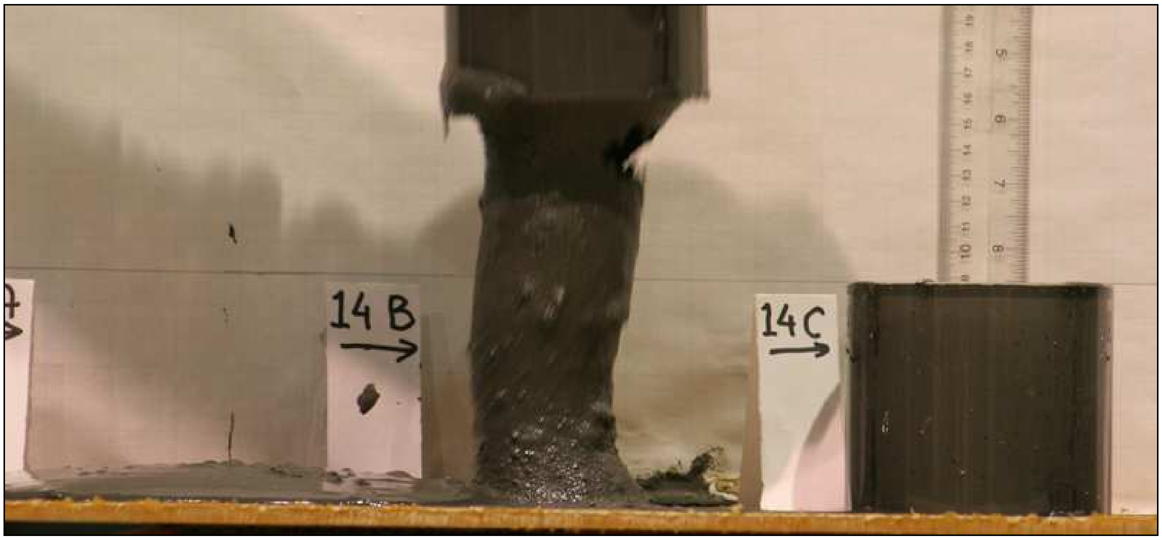


Figure 8-12. DuraLith Slump Sample #14b showing the many lumps in the sample.

The Vicat cylinder was dropped onto the Vicat sample 3.78 min after mixing with a penetration depth of 6 mm and then again at 3.83 min after mixing with a penetration depth of 7 mm. The Vicat cylinder plunger was changed to the Vicat needle plunger and testing resumed. The Vicat needle was dropped onto the Vicat sample 4.15 min after mixing and penetrated to the bottom of the sample; it was dropped again at 4.25 min after mixing with a penetration depth of 23mm; and once more 4.35 min after mixing with a penetration depth of 15mm; then Vicat testing was ceased. An initial setting was calculated for Sample #14 of 4 min. The sample was not as sticky as some of the previous samples generated and did not stick to the Vicat cylinder plunger.

At this point in time the 55-gal drum was checked for consistency and there were many lumps that appeared to be floating on the sample surface. Test personnel put on a pair of veterinarian gloves and reached an arm length into the drum to identify how far down in the drum sample that the lumps were present. The lumps were present as far down as could be reached and a picture of that investigation is shown in Figure 8-13. Figures 8-14 and 8-15 show the sample lumps before and after they were broken to determine if the lumps were dry or if they had been wetted during the mixing process. Notice the bubbles and lumps on the sample surface.

Figure 8-13. Investigation of lump depth in DuraLith Sample #14.

Figure 8-14. DuraLith Sample #14 lumps.

Figure 8-15. Broken lumps in DuraLith Sample #14.

A picture of Sample #14 was taken some time later and showed sample separation in the 55-gal drum and this is depicted in Figure 8-16.

Figure 8-16. DuraLith Sample #14 - separation of sample components.

After the generation of Sample #14, the team decided that the ribbon mixer did not mix the sample vigorously enough to incorporate the dry binder materials into the activator solution. At this point in time, a decision was made not to make the engineering-scale samples but to generate an additional 51-gal sample in an 80-gal drum using the MSE 20Hp hydraulically driven drum mixer because getting a larger scale sample with a good mix was more important than investigating the pourability and flowability of samples that were not adequately mixed.

Sample #16 - Drum-Scale DuraLith Sample Generation with 21 wt % Water – Section 8.3.2

The binder materials for the 51-gal sample were blended in the ribbon mixer and dropped into 55-gal storage drums. The blended dry materials were then put into twenty three 5-gal buckets and manually added to the activator solution and supplemental water while mixing for the generation of sample #16. Sample #16 was generated using a water weight percent of 21%. It took approximately 8 min to add the dry binder material to the activator solution and the waste form was mixed for 10.22 min at speeds ranging from 300 revolutions per minute (rpm) to 760 rpm. The mixing speed was measured using a photo tachometer. Four viscosity samples were collected during the mixing period: the first at 3 min 17 sec, the second at 5 min 17 sec, the third at 7 min and 17 sec, and the fourth at 9 min and 35 seconds into the mixing period. The resulting viscosity values were 2,950 cP; 2,450 cp; 2,450cP; and 2,500 cp, respectively.

A bucket of the DuraLith mixture was then collected for sampling and the sample was removed from the mixer. A picture of Sample #16 during the mixing process is shown in Figure 8-15. The slump samples were collected first, 11.28 min after mixing and the Vicat sample was collected next, 12.55 min after mixing was stopped and then nine 2-inch diameter by 4-inch tall samples were collected 13.09 min after mixing.

Figure 8-15. Generation of DuraLith Sample #16.

Sample #16a was so thin that it ran off the table surface after the sample mold was removed and had to be scrapped from the table surface; the same was true for slump samples #16b and #16c. The mold for slump sample #16d was pulled 50.72 min after mixing and had a slump height of 72 mm while the mold for slump sample #16e was pulled 60.72 min after mixing and had a slump height of 58 mm. Slump Samples #16d and #16e are shown in Figure 8-16. Notice how shiny the surface of the slump samples is more than 1 hour after mixing and even though no lumps are visible in the slump samples small lumps were present in the waste form. A summary of the slump test for the drum-scale samples is presented in Table 8-8 at the end of this section.

Figure 8-16. DuraLith Slump Samples 16d and 16e.

The Vicat cylinder was dropped onto the Vicat sample 3 times at 66 min, 81 min, and 86 min after mixing with penetration depths of 40 mm, 9.5 mm, and 4.5 mm, respectively. The Vicat cylinder was then changed and the Vicat needle drop tests began. The Vicat needle was dropped two times at 101 min and 111 min after mixing with the needle penetrating to the bottom of the sample. The Vicat needle was dropped an additional 8 times with penetration depths ranging from 32 mm to 0 mm and had an initial setting time of 132 min. A summary of the Vicat drop tests are included at the end of this report section in Table 8-9.

Sample #16 had the longest working time for any of the DuraLith waste forms generated during the test sequence so it was decided to make one more 51-gal drum sample at the initial baseline water weight percent of 16.45. That sample was generated the following week when PNNL, WRPS, and DuraLith personnel were no longer at the MSE test facility.

Sample #17 - Drum-Scale DuraLith Sample Generation with 16.45 wt % Water – Section 8.3.3

Sample #17 was generated in the same manner as Sample #16: the binder components were first blended in the ribbon mixer, dropped into 55-gal storage drums, and then placed into twenty 5-gal buckets. The activator solution was generated in Building 50 and brought to the RRF and mixing was initiated at a mixing speed of 290 rpm. No supplemental water was added to Sample #17 and it took approximately 9 min to add the buckets of dry binder materials to the activator solution. The mixing speed was increased to 600 rpm after the addition of the seventh bucket of binder materials and was increased to 800 rpm after bucket 14 and to 1300 rpm by the time all the buckets of binder material were added. Sample #17 was mixed for 10 min and three viscosity samples collected during the mixing period.

Viscosity samples were taken at 2 min and 35 sec into the mixing period, at 4 min and 38 sec, at 6 min and 26 sec, and again at 8 min and 37 sec, resulting in viscosity values of 15,000 cP; 23,000 cP; 15,560 cP; and 26,000cP, respectively. The viscometer spindle was changed between the second and third readings, which may be why the third viscosity value was lower than the second. Temperature readings were also collected periodically during and after the mixing period and the samples reached the highest temperature of 29 °C 28 min after mixing was stopped. This was the last temperature reading collected as it was hard to remove the temperature probe from the sample.

A bucket sample was collected within a min after mixing was stopped and the slump samples were collected from the bucket within 2 minutes after mixing. The Vicat and the nine 2-inch diameter by 4-inch tall were collected within 3 min after mixing. The Plexiglas divider was inserted into the sample 6.35 min after mixing.

The first slump mold was removed from Sample 17a 10 min after mixing. The mold was removed from Sample 17b 11.5 min after mixing, from Sample 17c 13.5 min after mixing, from Sample 17d 15.5 min after mixing, and from Sample 17e 18 min after mixing. Part of the slump Sample 17a dripped off the sample table so a slump height was not measured. All the slump samples melded together during the slump tests making it hard to get a true slump height so these slump heights were not reported. Figure 8-17 shows a picture of Sample 17 slump samples. All the slump samples had a skin on top and a dull finish for the sample section that was exposed when it was in the sample mold as shown in Figure 8-18. Also notice the lumps in the sample.

Figure 8-17. DuraLith Sample #17 slump samples.

Figure 8-18. DuraLith Sample 17 - slumps showing dull circular sample tops after mold removal.

The 2-inch diameter by 4-inch tall samples and the Vicat sample also had a dull finish on top of the sample surface. Figure 8-19 shows a picture of the 2-inch diameter by 4-inch tall samples, which was taken approximately 22 min after mixing.

Figure 8-19. Top surface of the 2-inch diameter by 4-inch tall DuraLith samples.

Figure 8-20. The first Vicat cylinder drop.

The first Vicat cylinder drop penetrated to the bottom of the sample. The sample appeared to be solid but the cylinder plunger dropped easily through the skin on the sample surface to the bottom of the sample mold and is shown in Figure 8-20. The material was also very sticky. The Vicat cylinder was dropped a total of 5 times with the second drop penetrating to the bottom of the sample but much slower. The third, fourth, and fifth drops had penetration depths of 33 mm, 14 mm, and 5 mm. The Vicat cylinder testing was completed and the Vicat needle drop testing was initiated with the needle dropping 34 mm into the sample. The second, third, and fourth drops penetrated the sample 15.5 mm, 7 mm, and 2.5 mm. The fifth needle drop resulted with a penetration depth of less than 0.25 mm, which barely marked the sample surface. The initial setting time for Sample #17 was 63 min.

Table 8-8 . DuraLith drum-scale 50-Cent rheometer slump test data.

Sample Number	50-Cent Slump Tests			Sample Molds Removed - Time after mixing, min
	Initial Slump Height, mm	Final Slump Height, mm	Slumping Height, mm	
14a	88	16	72	17
14b	88	25	63	21
14c	88	36	52	22
14d	88	44	44	22.5
14e	88	51	37	23
16a	88	--	--	26.72
16b	88	--	--	30.72
16c	88	--	--	34.73
16d	88	16	72	50.72
16e	88	30	58	60.72
17a	88	Not measured	Not measured	10
17b	88	Not measured	Not measured	11.5
17c	88	Not measured	Not measured	13.5
17d	88	Not measured	Not measured	15.5
17e	88	Not measured	Not measured	18

-- Sample did not come out of sample mold completely. ** Sample was too runny and was removed from table surface.

Although slump sample and a Vicat sample were collected for Sample #14, the data is probably suspect due to the poor mixing

Table 8-9. DuraLith drum-scale Vicat cylinder drop and needle drop test data.

Sample Number	Vicat Tests				
	Cylinder Drop		Needle Drop		Initial Setting Time
	Penetration Depth, mm	Time after mixing, min	Penetration Depth, mm	Time after mixing, min	Time, min
14	6	3.78	--	--	4
14	7	3.83	--	--	
14	--	--	40	4.15	
14	--	--	23	4.25	
14	--	--	15	4.35	
16	40	66	--	--	132
16	9.5	81	--	--	
16	4.5	86	--	--	
16	--	--	40	101	
16	--	--	40	111	
16	--	--	32	126	
16	--	--	20.5	136	
16			18	152	
16			12.5	162	
16			9	172	

Sample Number	Vicat Tests				
	Cylinder Drop		Needle Drop		Initial Setting Time
	Penetration Depth, mm	Time after mixing, min	Penetration Depth, mm	Time after mixing, min	Time, min
16			5	202	
16			2.5	232	
16	--	--	0	262	
17	40	23.25	--	--	63
17	40	28.25	--	--	
17	33	34.25	--	--	
17	14	38.25	--	--	
17	5	41.25	--	--	
17	--	--	34	58.25	
17	--	--	15.5	68.25	
17	--	--	7	83.25	
17	--	--	2.5	98.25	
17	--	--	< 0.25	117.25	

-- Vicat Test Apparatus used either cylinder or needle component for individual drop tests – not both.

Post Test Data - Section 9

Temperature curing profiles were obtained for the 55-gal drum samples after sample generation. The engineering-scale samples were also physically sectioned at the divider interface, inspected, and cored to obtain samples for leachability and compressive testing.

Curing Temperature Profiles – Section 9.1

Thermocouples were attached to the Plexiglas sheets that were inserted into the Ceramicrete and DuraLith 55-gal drum samples to collect a curing temperature profile for the cylindrical waste forms. Figure 9-1 shows the location of the thermocouples for Sample #5, the Ceramicrete sample, and Figure 9-2 shows the locations for Sample #13, the DuraLith sample. The thermocouple positions are the same for five of the seven thermocouples for both samples, however the thermocouple positions for Thermocouple #1 and Thermocouple #3 were switched for the DuraLith sample.

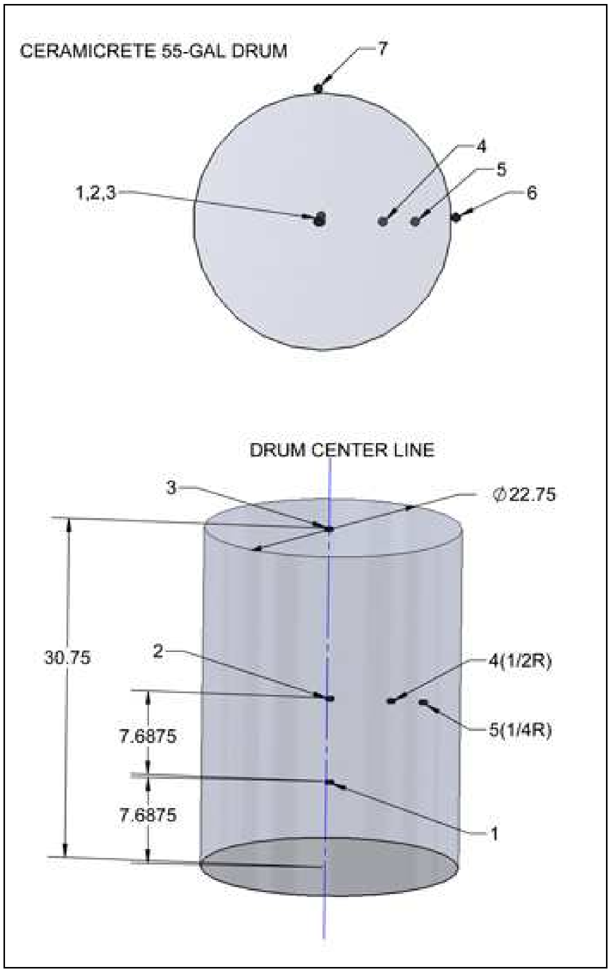


Figure 9-1. Ceramicrete thermocouple locations

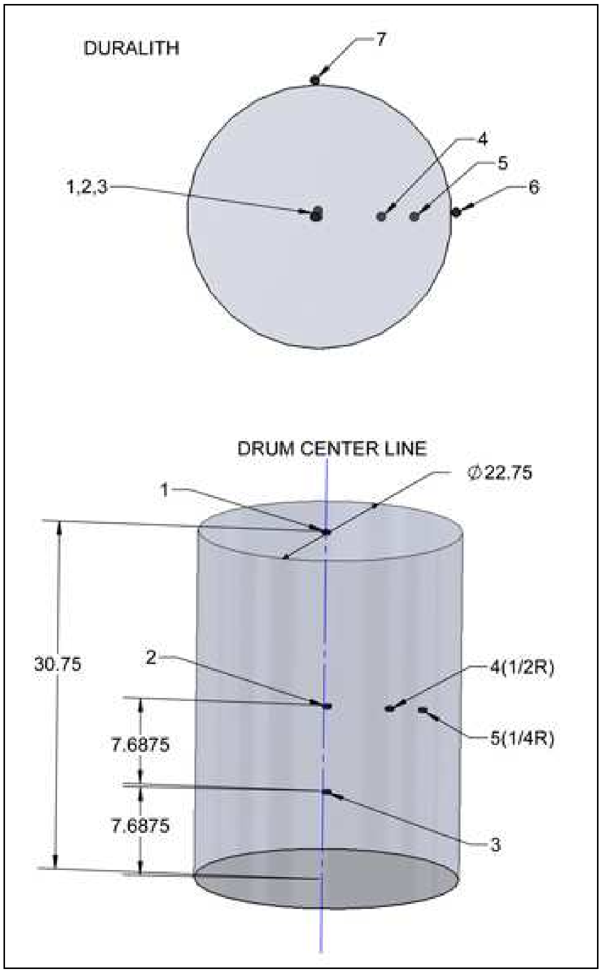


Figure 9-2. DuraLith thermocouple locations

Thermocouple positions 1, 2, and 3 lie along the centerline of the 55-gal drum samples while thermocouple positions 4 and 5 lie along the radius of the samples at approximately mid-height of the samples, and thermocouple positions 6 and 7 are located outside the drum at approximately mid height of the samples. After the temperature data was collected, it was graphed and it is presented in Figure 9-3 for the Ceramicrete Sample #5 and Figure 9-4 for DuraLith Sample #14.

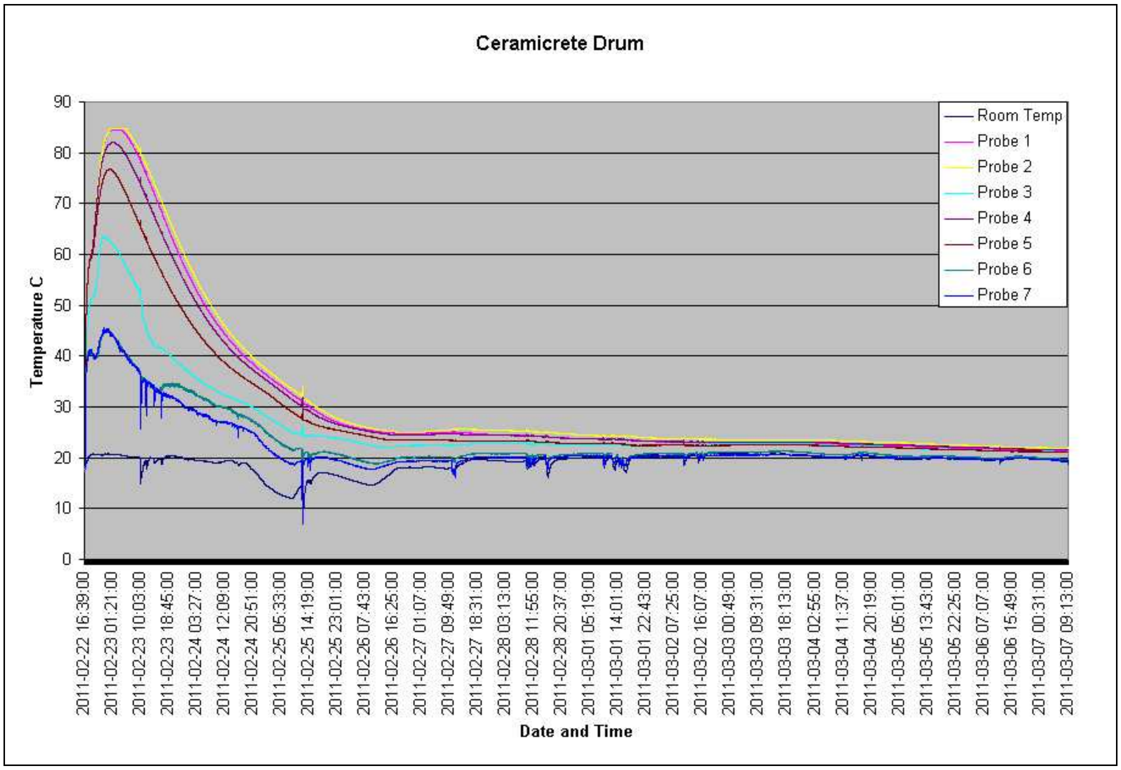


Figure 9-3. Ceramicrete Sample #5

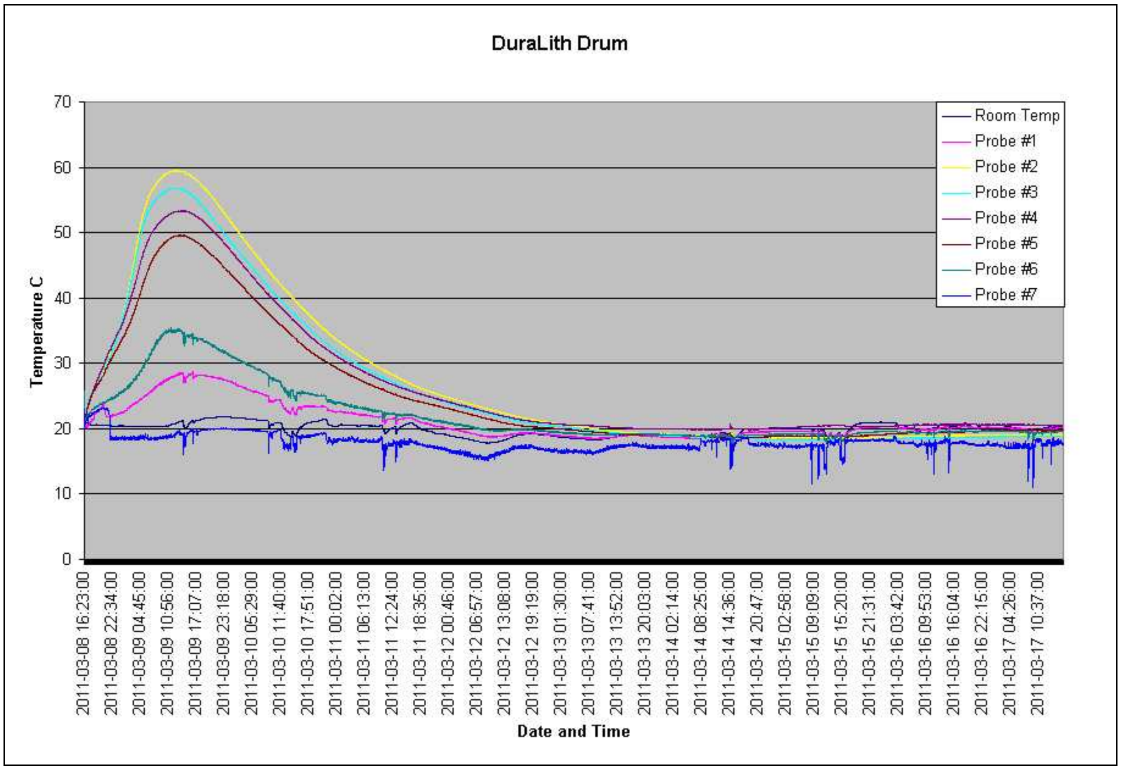


Figure 9-4. DuraLith Sample #14.

As expected the highest temperatures during the curing period were observed for thermocouple position 2, which was located along the center line of the sample at approximately mid height with the second highest temperatures recorded at the thermocouple position below thermocouple #2 along the centerline. Table 9-1 presents the earliest time that the maximum temperature was reached for each thermocouple during the curing period. The Plexiglas sheet with the attached thermocouple was inserted into the Ceramicrete 55-gal sample at 16:39 on February 22, 2011, and the Plexiglas sheet was inserted into the DuraLith 55-gal drum at 15:23 on March 8, 2011. The time stamp on the data logger was off by an hour for the DuraLith data because there was a change from Mountain Standard to Mountain Daylight time between temperature data collection for the drum samples. Thermocouple # 7 for the DuraLith sample was not functioning properly during the temperature data collection and should be treated as bad data. This is apparent when comparing the temperature for Thermocouple# 7 with the temperature for Thermocouple #6, which were both located on the outside of the drum. Also, all the temperature curing data for the DuraLith sample is suspect since the mixing for that sample was not adequate.

Table 9-1. Thermocouple maximum temperatures for the 55-gal drum samples.

Thermocouple Position	**Date and Time to reach Maximum Temperature Military Time, hour:min**		**Maximum Temperature, °C**	**Time After Thermocouple Insertion to Reach Maximum Temperature, hour:min**
Ceramicrete Sample #5				
Insertion date and time	2-22-11	16:39		
1	2-23-11	00:43	84.60	8:04
2	2-23-11	00:30	84.70	7:51
3	2-22-11	22:44	63.60	6:03
4	2-23-11	00:58	82.00	8:19
5	2-23-11	00:21	76.75	7:42
6	2-22-11	23:23	45.31	6:44
7	2-22-11	22:32	45.55	5:53
DuraLith Sample #14				
Insertion date and time	3-8-11	15:23		
1	3-9-11	16:12	28.73	23:49
2	3-9-11	12:15	59.48	19:52
3	3-9-11	12:17	56.82	19:54
4	3-9-11	14:12	53.41	21:49
5	3-9-11	14:10	49.63	21:47
6	3-9-11	11:26	35.38	19:03
7	3-8-11	20:31	23.23	4:08*
* Thermocouple malfunction.				

Ceramicrete Sample Inspection and Core Collection – Section 9.2

The Ceramicrete samples were allowed to cure for a period ranging from 53 days to 56 days and the DuraLith samples were slowed for a period ranging from 31 days to 42 days. The day before PNNL personnel arrived for the sample inspection and initial coring, the boxes were cut away from the engineering-scale test samples as shown in Figure 9-5. One core was collected from the top of Sample #6 and Sample #9 and two from the bottom of Sample #5 and sample dimensions were collected. Figure 9-6 shows Samples #6 and #9 while collecting the first core from Sample # 6. The tops of both Sample #6 and #9 were hard to the touch and showed a white salt precipitation on the surface. Sample #6 had more of the white precipitation on the surface than Sample #9.

Figure 9-5. Box being cut away from Ceramicrete Sample #8.

Figure 9-6. Coring of Ceramicrete Sample #6.

Figure 9-7 shows Sample #8. The top of Sample 8 was friable and easily flaked away if touched or disturbed. A close-up picture of the top of Sample # 8 is shown in Figure 9-8.

Figure 9-7. Ceramicrete Sample #8 after the box was removed.

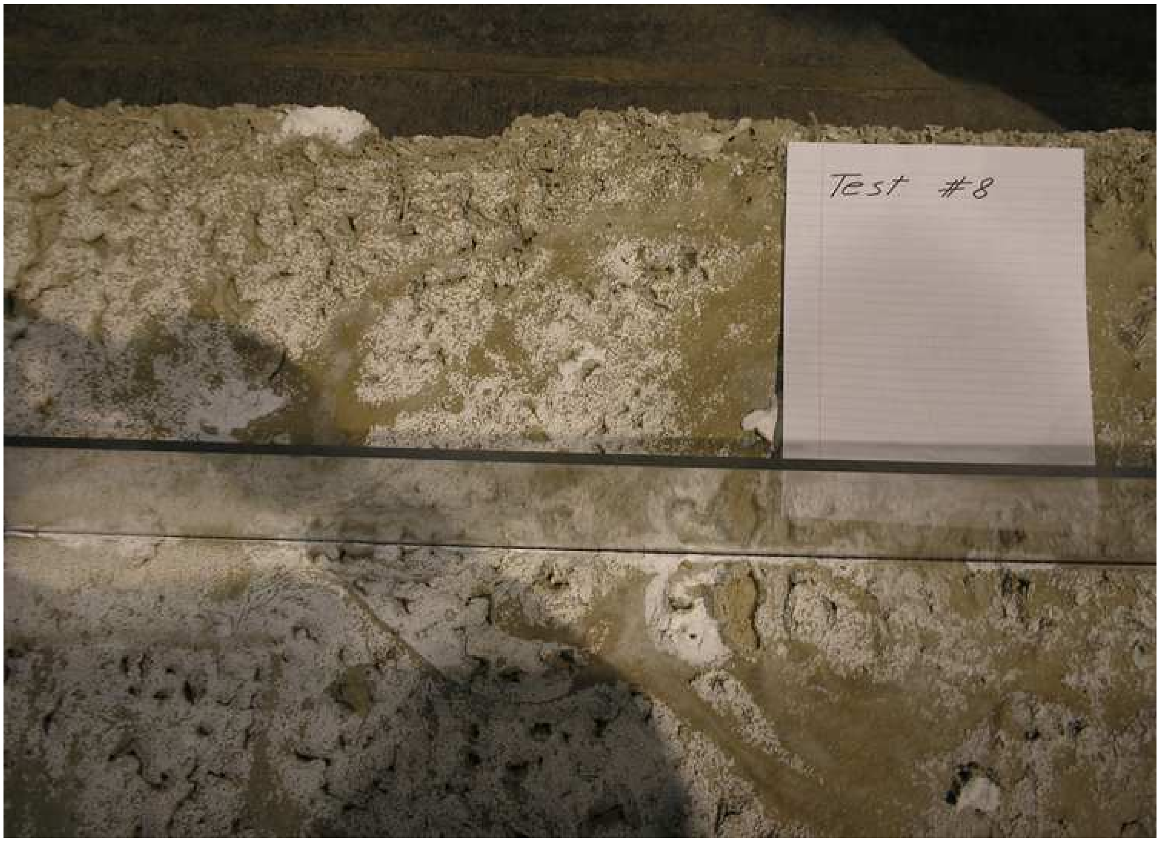


Figure 9-8. Top surface of Ceramicrete Sample #8.

The following day the team began with the physical inspection of the engineering-scale samples. Figure 9-9 shows the top sample section for Sample #8 and the top surface of the sample is pictured at the bottom of the photo. Notice the friable crust at the sample surface and the voids and the fracture in the top section of the sample.

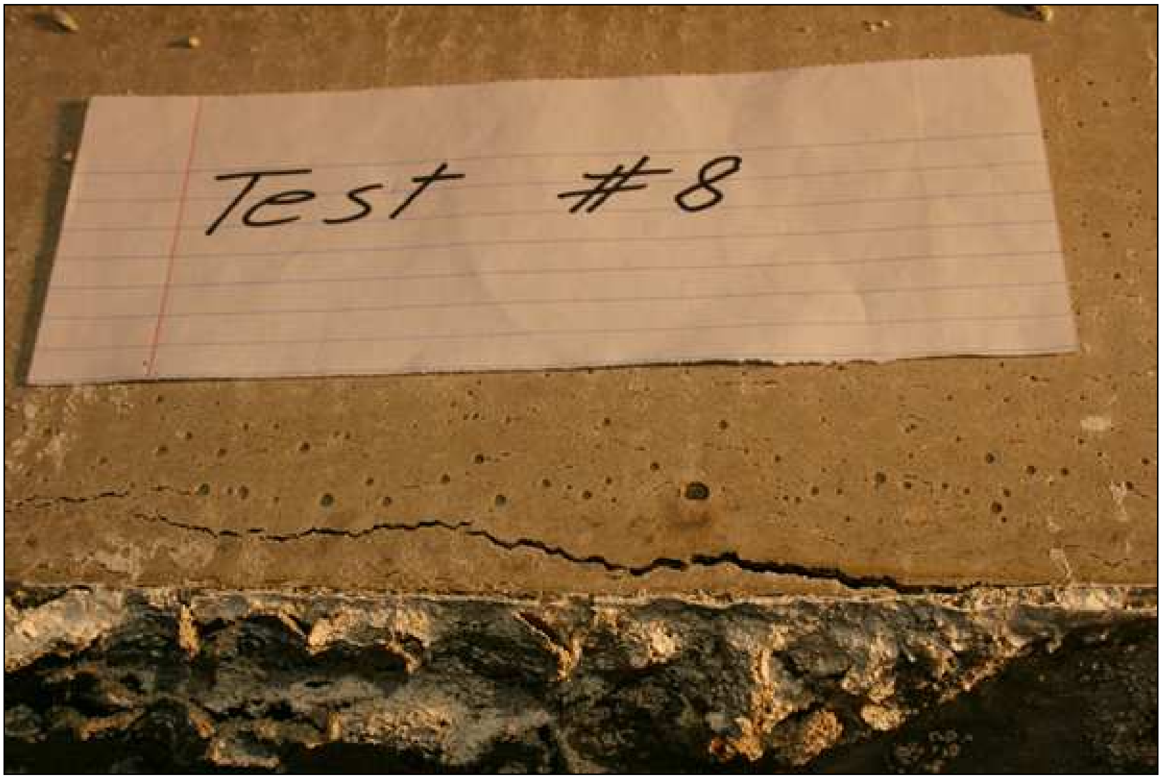


Figure 9-9. Close-up of the top section of Ceramicrete Sample #8.

Figure 9-10 shows the surface of Sample #9 and depicts the white precipitation and small fractures in the surface of the sample. Sample #9 had the hardest surface of the 3 Ceramicrete engineering-scale samples.

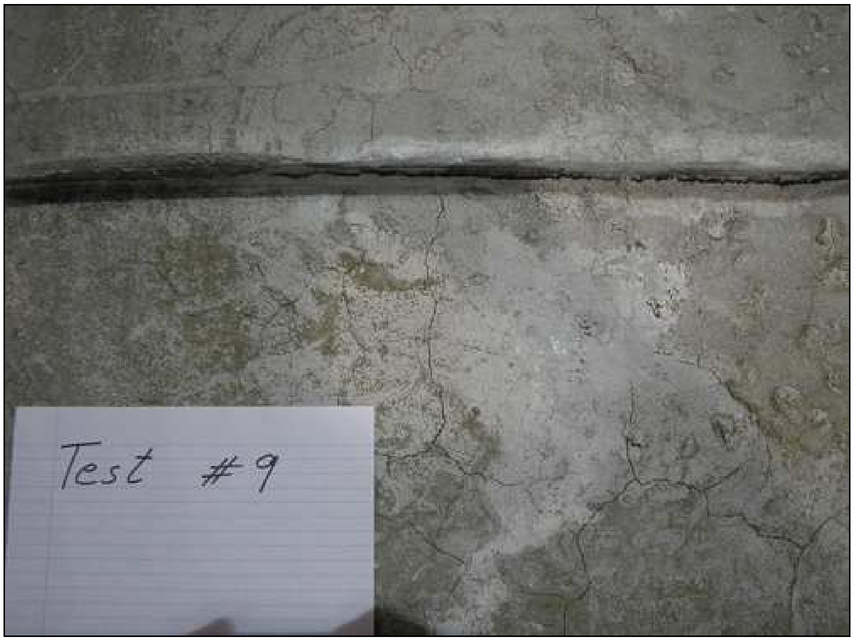


Figure 9-10. Surface of Ceramicrete Sample #9.

Figure 9-11 shows the top sample area of Sample # 9, with the voids and fractures present in the top section of the sample. Again, the top surface of the sample is shown by the arrow pointing to the hardened top surface.

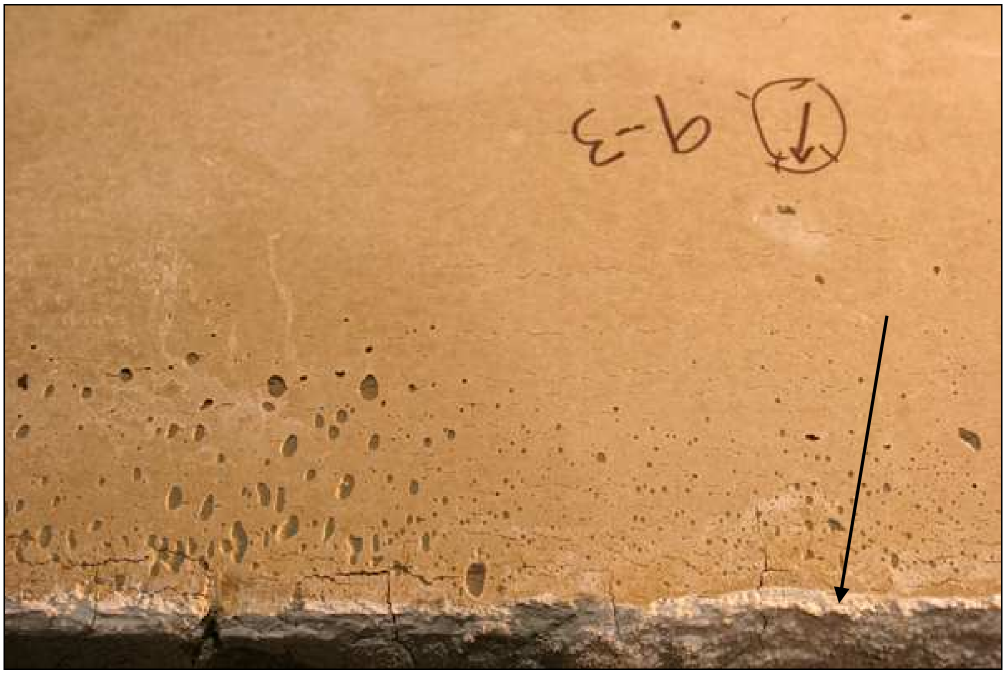


Figure 9-11. Close-up of the top section of Ceramicrete Sample #9.

The top surface of sample #6 is shown in Figure 9-12 and depicts the white precipitation and fracturing on the sample's surface. The surface of Sample # 6 was not quite as hard as the surface of Sample #9 but much harder than the surface of Sample #8. A picture of the top of Sample #6 is shown in Figure 9-13 and shows a fracture at the top core location.

Figure 9-12. Close-up of the top of Ceramicrete Sample #6.

Figure 9-13. Interior of the right hand side of Ceramicrete Sample #6 after coring.

A picture of the top surface of Sample #5, the Ceramicrete 55-gal drum sample, is shown in Figure 9-14. Notice the amount of white precipitation on the sample surface. Sample # 5 is also shown in Figure 9-15 when the sample was being divided for core collection.

Figure 9-14. Top of Ceramicrete Sample #5.

Figure 9-15. Ceramicrete Sample #5 being divided for core collection.

Figure 9-16 shows the interior of Sample #5 and Figure 9-17 shows a close-up of the same sample piece. Notice how uniform the sample's consistency is at the sample edges where the Plexiglas sheet did not divide the sample at the edges. The whiter, indented areas pictured in the top right hand side of the picture were the location of the thermocouples attached to the Plexiglas divider.

Figure 9-16. Ceramicrete Sample #5 interior view.

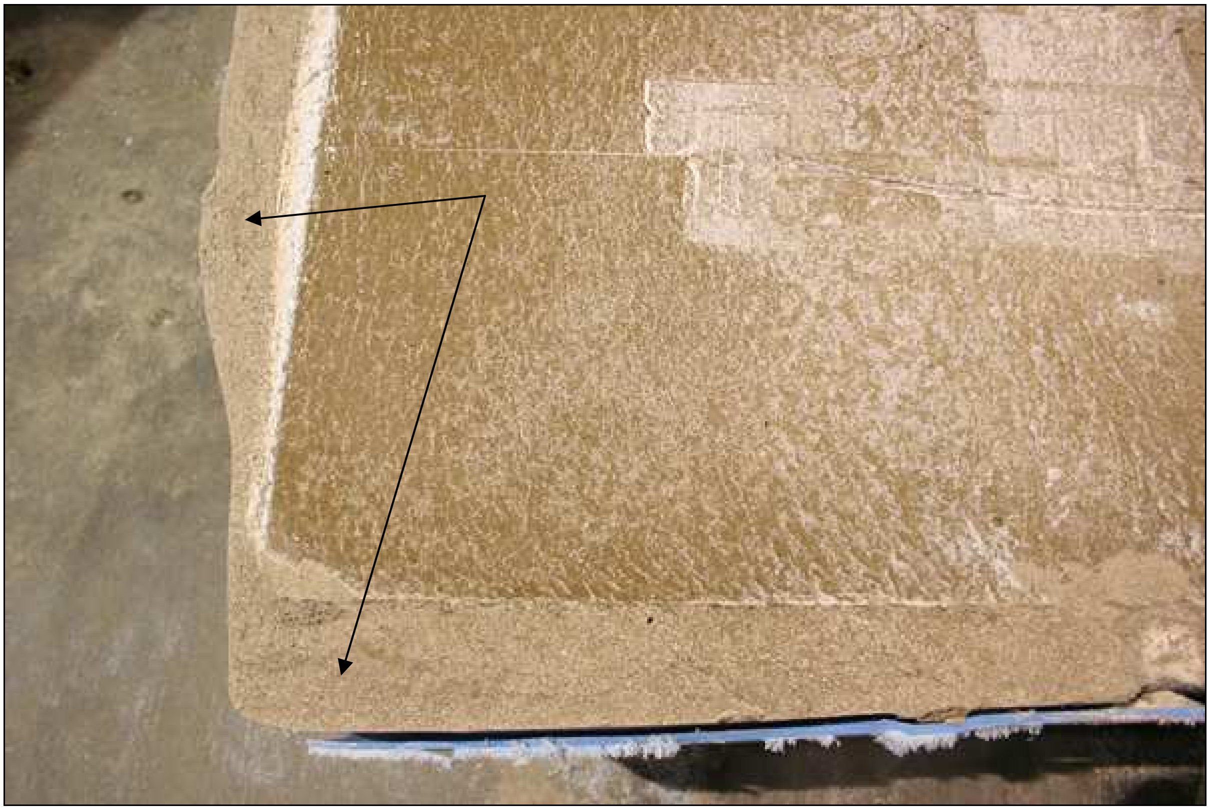


Figure 9-17. Close-up of Ceramicrete Sample # 5 showing the uniform mix at the sample edges.

Even though lumps were identified in the large-scale Ceramicrete waste forms during the mixing process, the waste forms appeared to be uniformly mixed and no lumps or unmixed areas were identified in the samples after the curing period.

DuraLith Sample Inspection and Core Collection – Section 9.3

The Plexiglas dividers and the drum containers were trimmed down in the drums so the samples could be turned over to collect the bottom core samples. The thermocouple wires were also cut from the Plexiglas divider for Sample #14. Pictures of the top of Samples #14, #16, and #17 are shown in Figures 9-18, 9-19, and 9-20, respectively, before coring was begun and Plexiglas and drums were cut flush with the samples.

Figure 9-18. The top of DuraLith Sample #14.

Figure 9-19. Top of DuraLith Sample 16.

Figure 9-20. Top of DuraLith Sample #17.

Notice how irregular the top surface of Sample #14 is compared to the top surfaces of Samples #16 and #17. Although all the top surfaces of the samples show white precipitation that was formed after the samples were generated.

Sample #14 was removed from the container first and broken up with a sledge hammer as no cores were collected from Sample #14 because of the poor mixing during the DuraLith test sequence. When the sample was inspected, the team was surprised at how well the sample cured; hardly any lumps were identified compared to those that were seen after the mixing process. A picture of the inside surface of Sample #14 is shown in Figure 9-21 and a close-up picture of the top sample section is shown in Figure 9-22. The top section has a larger amount of lumps that can be identified compared to the rest of the sample.

The sample also appeared to have areas that were damp and areas that were drier. A Sharpie was used to demark one of the areas between the damp and dry areas so it could be checked the following morning to determine if some of the sample areas were actually damp compared to the other areas that seemed drier as shown in Figure 9-23. The top of the sample, shown on the right hand side of the pictures, is a lighter gray and was drier than the darker gray section of the sample. Figure 9-24 show a picture of the same sample location the following morning after the sample was exposed to air and the sample had dried out proving that some of the sample areas were damp compared to the other areas. There were also areas in the sample with dark shiny specs. After investigation it was determined that the specs were actually small pockets of activator solution. A close-up picture of one of the large specs and several smaller specs of the activator solution pockets are shown in Figure 9-25 – the tan part of the picture is the finger tip of a leather glove.

Figure 9-21. Sample Section of DuraLith Sample #14.

Figure 9-22. Top section of DuraLith Sample #14.

Figure 9-23. DuraLith Sample #14 with a damp area demarked.

Figure 9-24. DuraLith Sample #14 the morning after the sample was removed from the container.

Figure 9-24. Activator solution pockets in DuraLith Sample #14.

Sample #16 also appeared to have areas of the sample that were damp and areas of the sample that were drier as shown in Figure 9-25. Arrows point to the difference in color: the blacker sections are damp and the brownish sections are drier. Notice the areas of unmixed material in the uneven edge pieces of the sample. The 20Hp drum mixer did a better job mixing the DuraLith samples but both Samples 16 and #17 were only mixed for 10 min. A longer mixing period was necessary to incorporate the dry binder materials into the activator solution. A close-up picture of Sample #16 with additional lighting is presented in Figure 9-26 that shows separation of the aggregate (fine sand) at the very bottom of the DuraLith sample generated using 21 wt % water. The area above shows a more uniform material.

Sample #17 was generated using 16.45 wt % water and Sample #17 did not show any aggregate settling at the bottom of the sample like Sample #16. A picture of Sample #17 while coring the outside radial sample is shown in Figure 7-27. Although Sample #17 seemed to have a better mix than Samples #14 and #16, there were still small pockets of the activator solution discovered in the sample. A picture of an activator pocket in one of the cores collected from Sample #17 is shown in Figure 7-28 and the interior of one half of Sample #17 is shown in figure 9-29. A picture of the sample was taken after the sample was cored and broken to examine the interior of Sample #17 to determine if the dry binder materials were incorporated and is shown in Figure 9-30. As can be seen from Figure 9-30, not all of the binder materials were incorporated into the sample matrix during the 10 min mixing period however a better mix was achieved for Sample #17 than for Samples #14 and #16.

Figure 9-25. DuraLith Sample #16 showing the damp and dry sample sections.

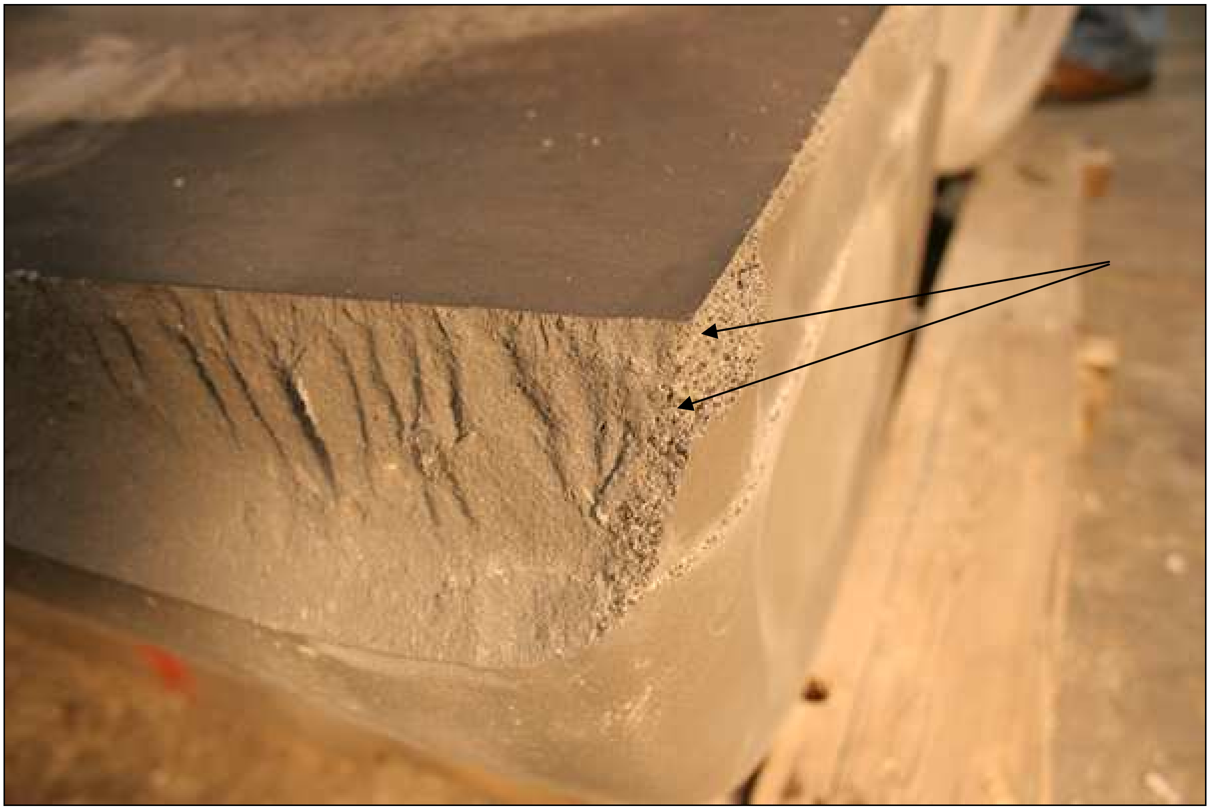


Figure 9-26. Bottom section of DuraLith Sample #16 showing aggregate settling.

Figure 9-27. Coring radial sample for DuraLith Sample #17.

Figure 9-28. DuraLith Sample #17 core with a pocket of activator solution.

Figure 9-29. Interior view of half of DuraLith Sample #17.

Figure 9-30. DuraLith Sample #17 interior view showing unmixed binder materials.

Core Locations for the Drum and Engineering Scale Samples – Section 9.4

During the physical inspection of the drum-scale and engineering-scale samples, measurements were taken of the samples. Measurements were also taken during the coring process to identify the cored locations in the samples. That information was used to develop the three-dimensional (3-D) drawings for the samples that show the sample dimensions and core locations. The 3-D drawing for the Ceramicrete 55-gal Sample #5 is presented in Figure 9-31. The 3-D drawings for the Ceramicrete 11 ft^3 Sample #6, the Ceramicrete 9 ft^3 Sample #7, the 55-gal DuraLith Sample #16, and the 55-gal DuraLith #17 are presented in Figures 9-32, 9-33, 9-34, and 9-35, respectively.

The cored samples were shipped to PNNL for compressive strength and leachability testing and those results will be incorporated into this test report.

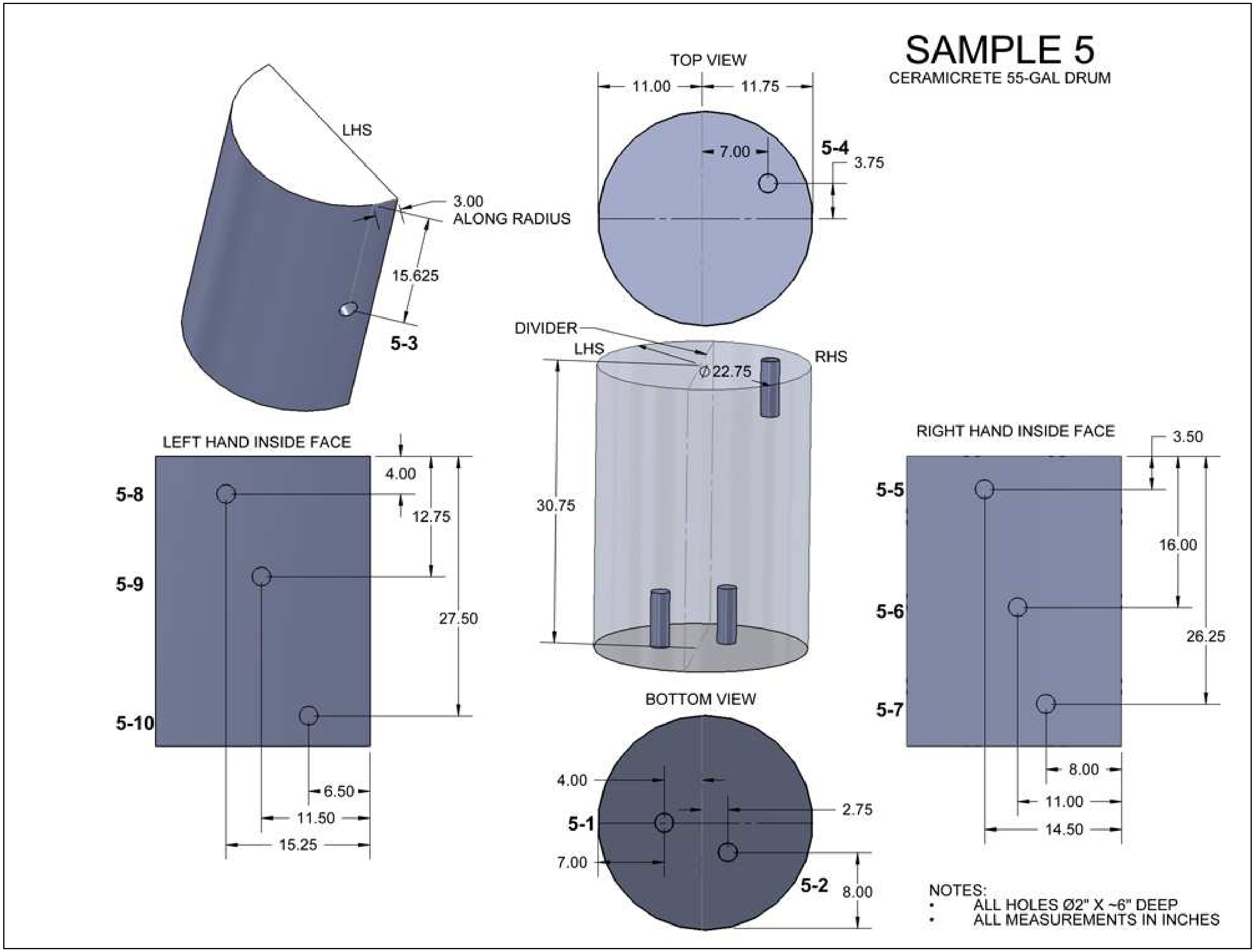


Figure 9-31. Core Sampling Locations for the Ceramicrete 55-gal drum Sample #5.

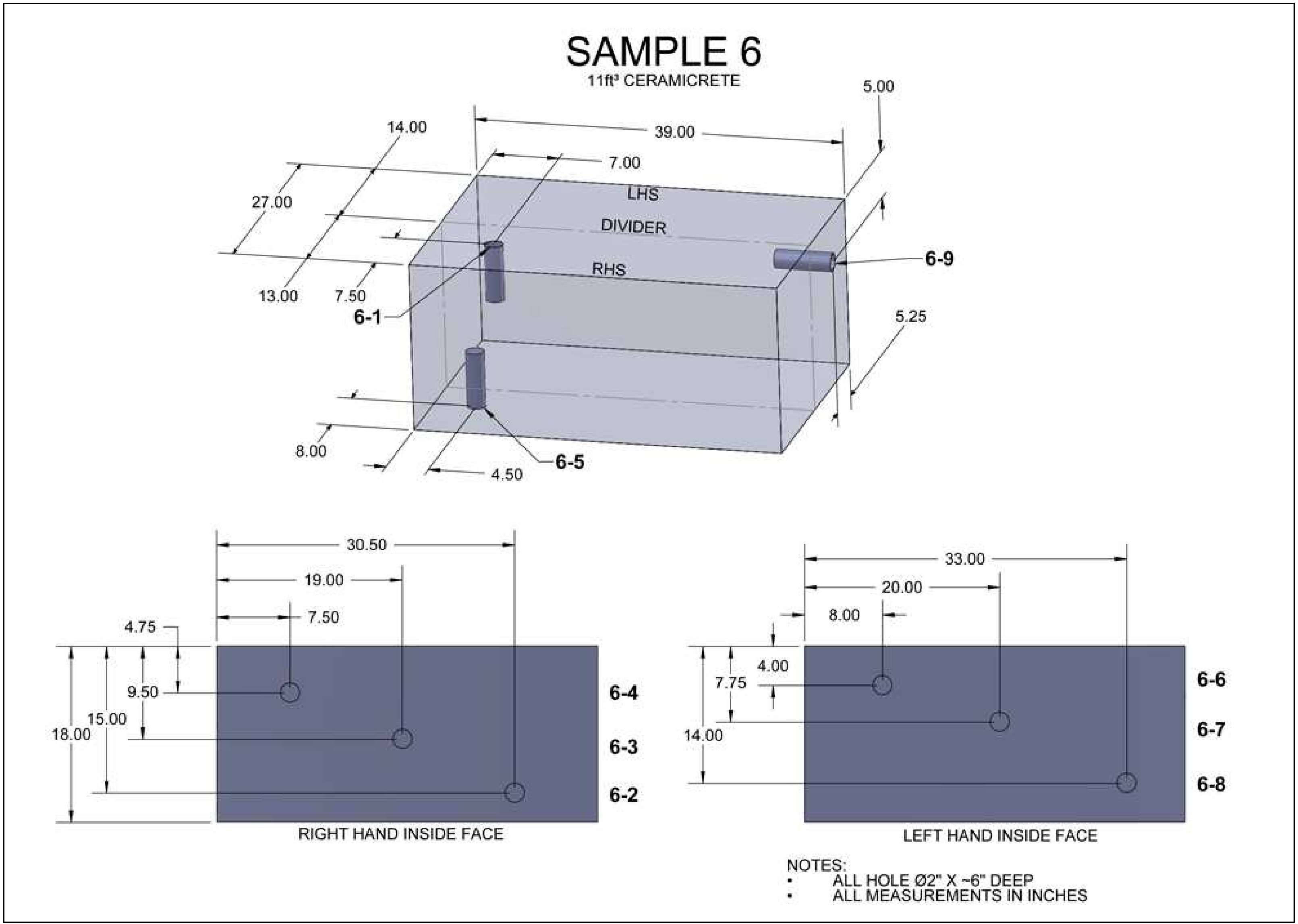


Figure 9-32. Core Sampling Locations for the Ceramicrete 11ft^3 Sample #6.

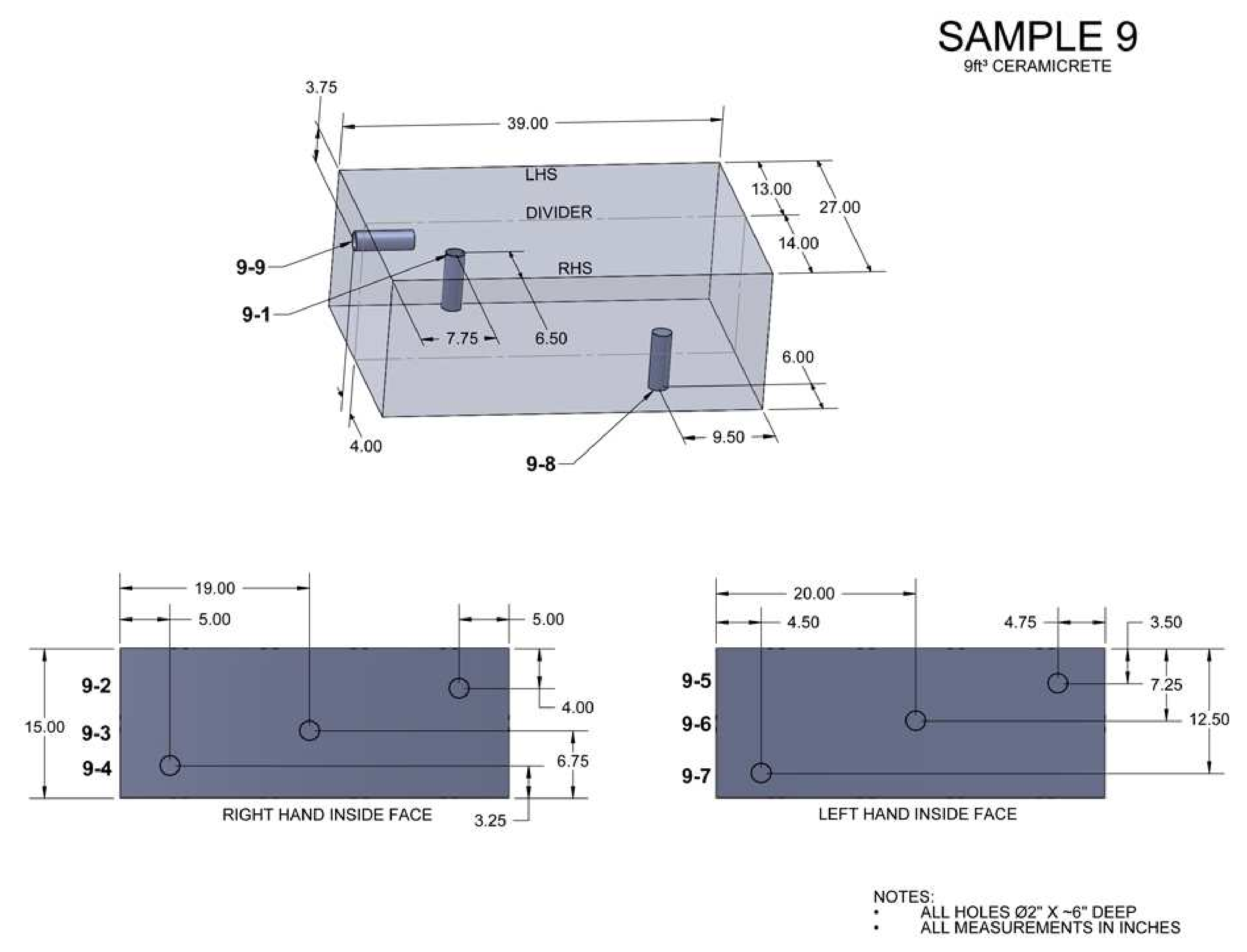


Figure 9-33. Core Sampling Locations for the Ceramicrete 9 ft³ Sample #9.

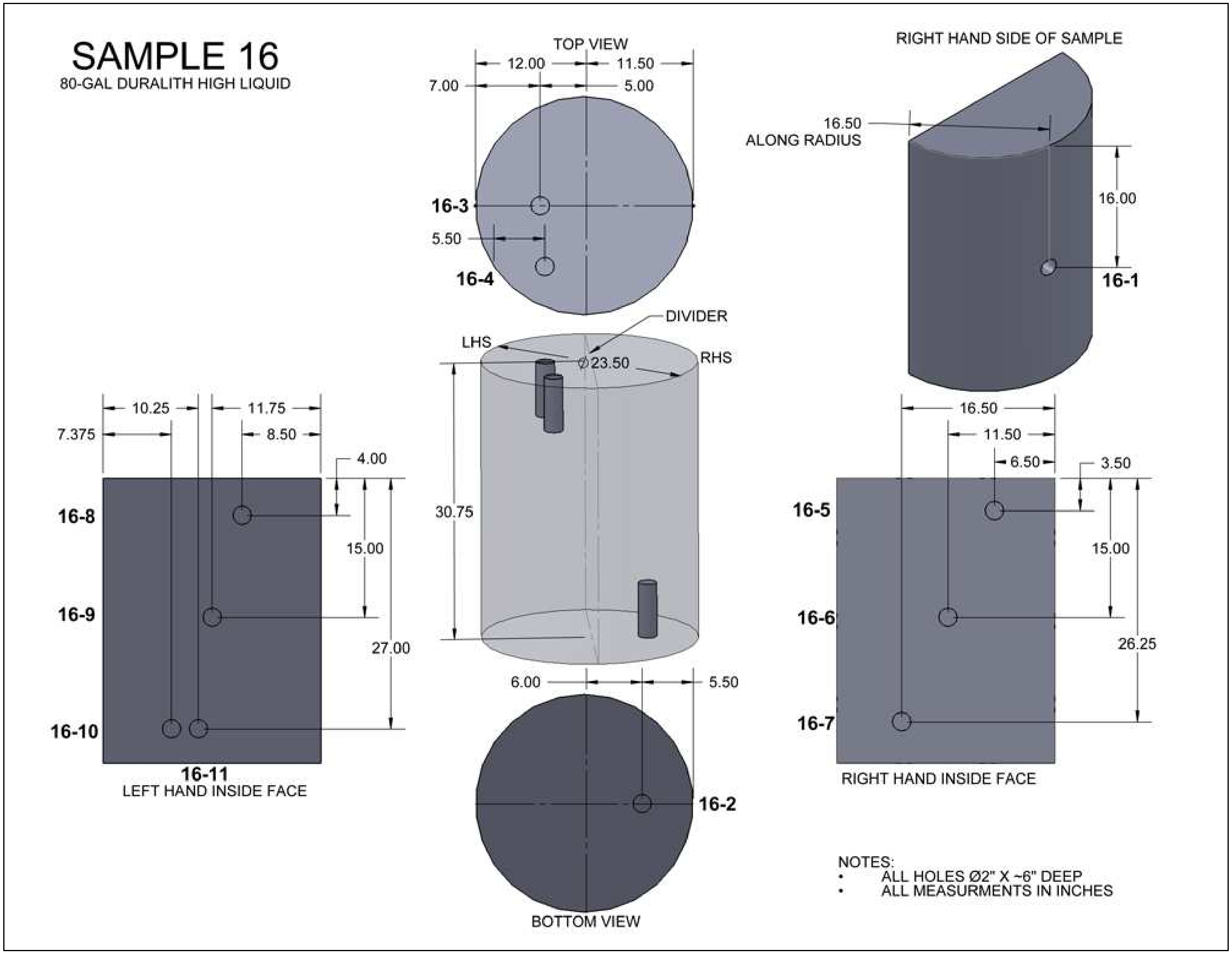


Figure 9-34. Core Sampling Locations for the DuraLith 55-gal drum Sample #16.

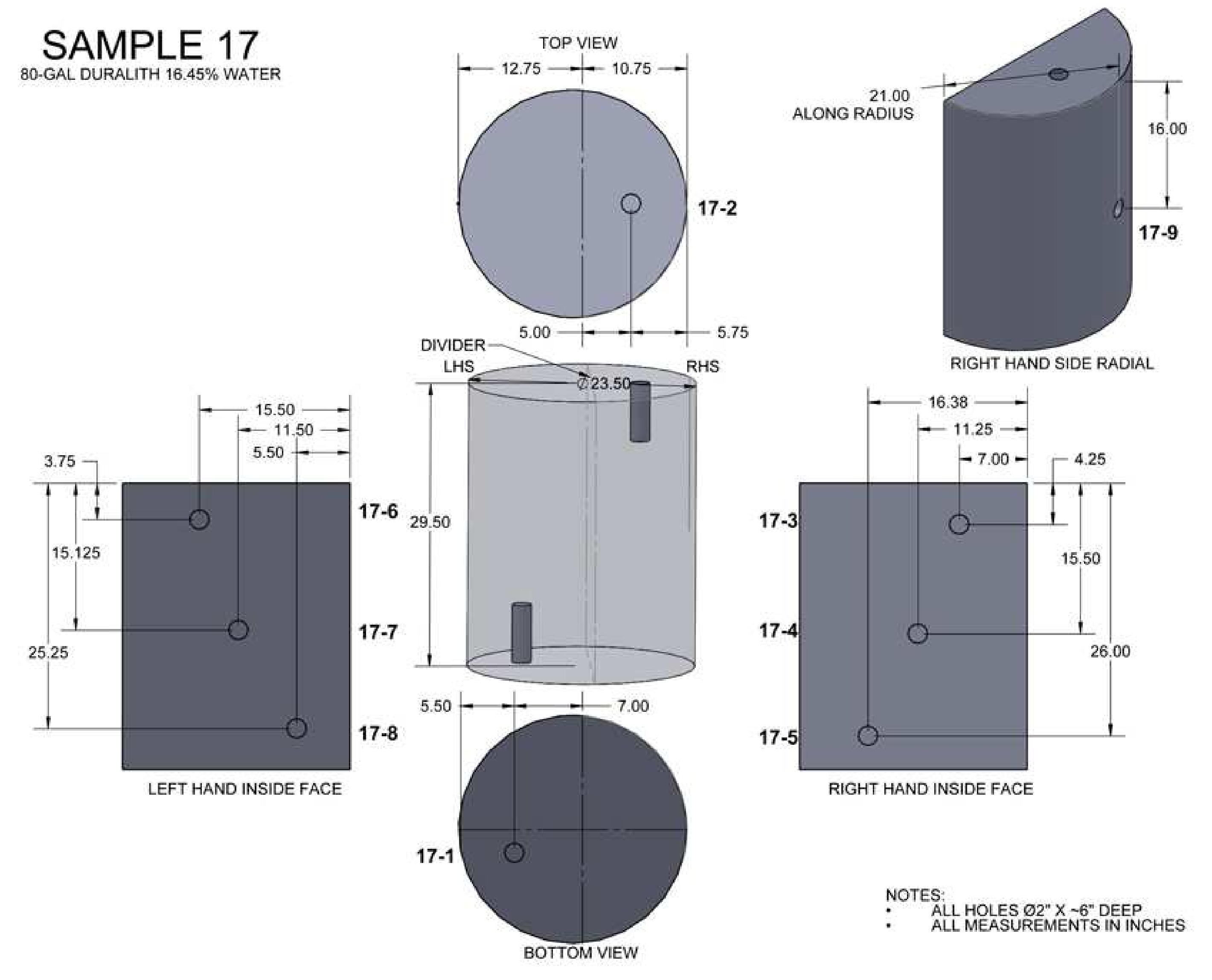


Figure 9-35. Core Sampling Locations for the DuraLith 55-gal drum Sample #17.

Conclusions – Section 10

During the test sequence to evaluate the Ceramicrete and DuraLith waste forms many parameters were discovered that relate to the process methodologies for each of the waste forms. The most important observation found during the Engineering-Scale demonstration was that the 10 ft^3 ribbon mixer did not provide enough energy to sufficiently mix the 55-gal drum samples or the engineering-scale box samples. All of the samples generated using the ribbon mixer had lumps of varying size and moisture content in the waste forms after the mixing process was completed and some damp materials built up around the mixing shaft for some of the samples.

The large-scale Ceramicrete samples had some lumps after mixing but the one DuraLith sample that was mixed using the ribbon mixer had many lumps throughout the entire 55-gal waste form. When the large-scale Ceramicrete samples were physically inspected after the curing period, no lumps or areas of unmixed material were identified in the solidified waste forms. The lumps seemed to incorporate into the waste form during the curing period. When the 55-gal DuraLith drum sample was physically examined after the curing period, several areas of unmixed dry material were discovered in the solidified waste form. The test team was actually surprised that there were not many more masses of unmixed dry material visible in the waste form. Many of the lumps seemed to incorporate into the waste form as the sample cured.

The two additional 55-gal drum DuraLith samples were mixed using the 20Hp hydraulically driven drum mixer for a 10 min mixing period and those samples also had some lumps in the waste form matrix. Additional mixing would be required to ensure a homogeneous mixture but due to concerns of the samples curing very quickly, the 55-gal drum samples were only mixed for 10 min. The mixer may have been able to completely incorporate the dry materials into the waste form matrix but since the samples were mixed for such a short period of time the time required for complete mixing was not identified during the test sequence.

Several additional mixers were used during the test sequence for the Ceramicrete and DuraLith solidification processes including the Collomix 5-gal bucket mixer. The Collomix mixer did effectively mix the Ceramicrete bucket samples. Some lumps were identified in the DuraLith 5-gal samples but those samples were only mixed for a period ranging from 3 to 6.5 min while the Ceramicrete samples were mixed for a period ranging from 14 to 20 min.

The ½ Hp tank mixers that were used to mix both of the simulant liquid waste streams and the activator solution for the DuraLith process had more than enough power to provide sufficient mixing for the liquid solutions. The $^1/_{15}$ Hp Lightnin mixers were also able to sufficiently maintain the consistency of the activator solution for the bucket-scale samples. The DuraLith activator solution requires constant mixing for a period of at least 24 hours and during the make-up of the first batch of activator solution the mixer failed with a possible maximum 12 hour period when the solution was not being mixed. However when mixing was reestablished, the solids in the bottom of the mixing tank and the crust on the sample's surface were easily incorporated into the solution.

Hydrogen generation was also identified as a potential problem during the production of the DuraLith activator solution and hydrogen concentration readings were collected three times when the activator solution for Sample # 17 was generated. Hydrogen concentration readings were collected immediately after the last batch of fumed silica was added to the activator solution, 8 minutes later and again 4.25 hours after the first reading with corresponding hydrogen concentration values of 0.15%, 0.05% and 0.00%, respectively. It appears that hydrogen is generated early during activator solution make-up and decreases over a short period of time. Gas bubbles were also observed coming to the surface of the activator solution early in the mixing process and were used as a visual confirmation of the hydrogen generation.

There was a big difference in the small 2-inch diameter by 4-inch tall samples collected from the Ceramicrete bench-scale bucket samples compared to those collected from the Ceramicrete 55-gal drum and engineering-scale box samples. The 2-inch diameter by 4-inch tall samples collected from the bucket samples had a salt solution that leaked out of the closed samples while the 2-inch diameter by 4-inch tall samples collected from the large-scale sample actually expanded out of the top of the sample containers. The test team initially surmised that sample disturbance after mixing caused the small samples for Sample # 6 to expand out of the containers after observing the 2-inch diameter by 4-inch tall samples the morning after mixing. However, all of the 2-inch diameter by 4-inch tall samples collected from the Ceramicrete large-scale samples expanded out of the containers. There may be several explanations for the sample expansion: mixing was not vigorous to completely mix the waste forms to allow the magnesium oxide to react; air was incorporated into the waste forms during the mixing process; the addition of boric acid to retard the set-up time did not allow the magnesium oxide to completely react in the waste form mixtures; or other unidentified parameters.

The sample surface for the 3 engineering-scale box Ceramicrete samples were very different for Sample #8 (the 2-ft by 2-ft by 6-ft box) when compared to Samples #6 and #9 (the 2-ft by 2-ft by 3-ft box). After the samples were mixed and moved to the curing area, the box lids were not placed on Samples #6 and #9 but the lid was placed on Sample #8. When the samples were checked the morning after they were mixed, #6 and #9 had white precipitation at the sample edges and at the divider and sample interface. They also had white precipitation growths on the top surface that resembled the solidified liquid that leaked out of the bench-scale 2-inch diameter by 4-inch tall samples. When the lid was removed from Sample #8, a large amount of liquid condensation (~ 1 gallon) was spilled on the floor and the sample had minimal white precipitation around the box edges and at the divider and sample interface. During the physical inspection of the samples, the top surface of Sample # 6 and Sample # 9 were relatively hard with varying amounts of the white precipitate but the surface of Sample # 8 was pitted and very friable for approximately the top inch of the sample.

The overhead crane and conveyor belt were used to deliver the dry materials to the ribbon mixer for blending and to deliver the blended dry materials to the liquid simulant waste in the ribbon mixer for mixing. During real applications a conveyor belt should not be used for delivery of dry materials and was only used during testing due to budget and schedule restraints. A spiral feeder or pneumatic system with load cells or could be used for a weight based computerized delivery system that would ensure exact component weight delivery.

Recommendations – Section 11

Additional mixing studies will be necessary to determine better mixing techniques using a more powerful mixer for the Ceramicrete and DuraLith wasteforms since the ribbon mixer did not adequately mix the large-scale samples. A pug mixer or paddle mixer which, have more than one mixing shaft or a high shear type of mixer may provide the mixing energy necessary to obtain uniform mixtures. The capacity of the mixer should be sized to mix 12 to 15 ft^3 so the 11 ft^3 engineering-scale samples could be easily accommodated. Also, additional formulation development may be necessary to obtain waste form mixtures that produce a longer working time to ensure a uniformly mixed waste form.

During previous Ceramicrete work, MSE monitored both temperature and pH during the mixing process to determine when the magnesium oxide and potassium phosphate fully reacted within the Ceramicrete mixtures. To ensure proper reaction times for the Ceramicrete mixtures, MSE recommends that both parameters, pH and temperature, be monitored during any follow on Ceramicrete formulation testing espically if boric acid is added to delay the set time of the mixtures. Follow on testing should also be undertaken to determine if covering the large-scale Ceramicrete samples after mixing and during the early curing process has a negative impact on sample curing.

References – Section 12

1. Gong, W., Lutze, W., and Pegg, I., 2010. *DuraLith Alkali-Aluminosilicate Geopolymer Waste Form Testing for Hanford Secondary Waste*, Report No. VSL-10R2140-1.

2. Maloney, D., Johnson, M., Dirkmaat, P., Wagh, A., and Natarajan, R., 2006. *Performance Demonstration of chemically Bonded Phosphate Ceramics: Hanford Secondary Waste and Idaho Sodium Bearing Waste.*

3. ASTM Designation C187 -10 – *Standard Test Method for Normal Consistency of Hydraulic Cement,* ASTM International, West Conshohocken, PA, DOI: 10.1520/C0187-10, www.astm.org.

4. ASTM Designation C191-08 - *Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle*, ASTM International, West Conshohocken, PA, DOI: 10.1520/C0191-08, www.astm.org.

5. Pashias, N. and Boger, D.V., and Summers, J. and Glenister, D.J., 1996. *A fifty cent rheometer for yield stress measurement*, The Society of Rheology, Inc.

6. ASTM C308-00 (reapproved 2005) - *Standard Test Method for Working, Initial Setting and Service Strength Times of Chemical Resistant Resin Mortars,* ASTM International, West Conshohocken, PA, DOI: 10.1520/C0308-00, www.astm.org.

Appendix A.
Equipment Information and Pictures

Tank Mixers used for simulant and activator solution

Leeson Electrical Corp. Grafton, WI, Model # - GC17FC3D

½ horse power (Hp) with an 8” propeller and 4 foot shaft

Dayton Electric Manufacturing Co – Chicago. IL

Model # 6K342H, ½ Hp, with an 8” propeller and 4 foot shaft

3 - Lightnin Mixers
SPX Process Equipment - Rochester NY for Leeson Electrical Corp - Grafton, WI

Model # G2U05R. 2300 rpm, $^{1}/_{15}$ Hp, 2 ft shaft with 3” propeller

Large Scale Mixers used for drum and box samples
10ft^3 Ribbon mixer, 5Hp
Euro Drive Inc.
Model # DFT100L4

Conveyor Belt
E-Z Lift Conveyors – Denver CO
Model # BB-050 – 12 ft belt bucket conveyor

20 Hp Hydraulically Driven Drum Mixer
Hepsco Hydraulic Engineered Products – Charlotte, NC
6000 psi working pressure
62.5” reinforced shaft, 15” propeller

Electric Fork Lift
Multiton MIC Corp. – Richmond, VA
Model SM-20, 2205 lb capacity with barrel holding assembly

Small Scale Mixer used for bench-scale samples
Collomix, Gmbh – Gaimersheim, Germany, Model # CX 22 Duo,
800 Watt, 0 – 520 rpm under load

Walk-in Laboratory Hood
10-ft high by 14-ft wide by 7-ft deep with 125-fpm of face velocity across the front opening of the hood providing 18 air exchanges in the hood per minute

Overhead Crane
Wright 10 ton overhead crane, Crane Hoist Engineering Corp – Crane, IN

Core Drill
Dymodrill Model # 4094
Milwaukee Electric Tool Corp
Brookfield, WI

Core Barrel
Dry Vacuum hole saw
Model # 2 ¼ DVH
Diamond Products.com

Scales

Drum Scale
Intercomp Corporation – Minneapolis, MN
Model # CW250,
Range 500Kg,
Accuracy 0.2 Kg

Mettler Instrument Corporation –
Highstown, NJ
Toledo Model #
SG32001
Range 0 - 32,100g,
Accuracy 0.1g

Mettler Instrument Corporation –
Hightstown, NJ
Model # PJ400
Range 0 - 400g,
Accuracy 0.01g

Dust Control Systems

Donaldson Company Inc. – Torit Division – Minneapolis, MN
Torit trunk line porta-trunk
300 cfm

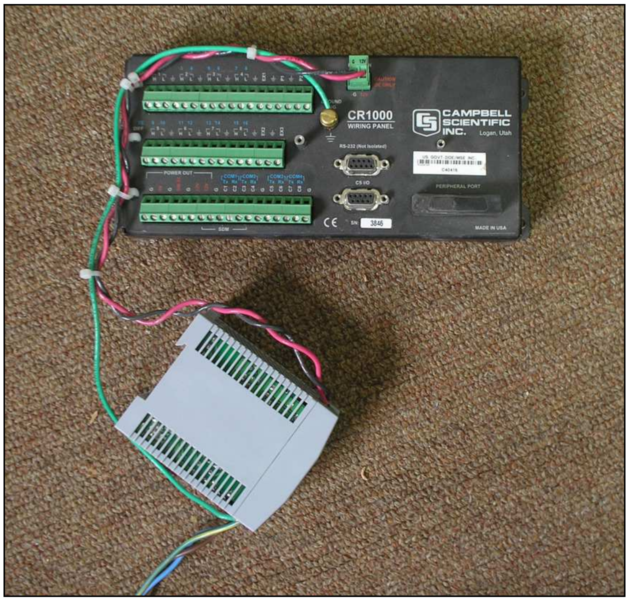
Nederman Portable Air Control System - Sweden
Model 641
300cfm

Miscellaneous Equipment

Brookfield Viscometer
Engineering Labs Inc – Middleton, MA,
Model DV-E

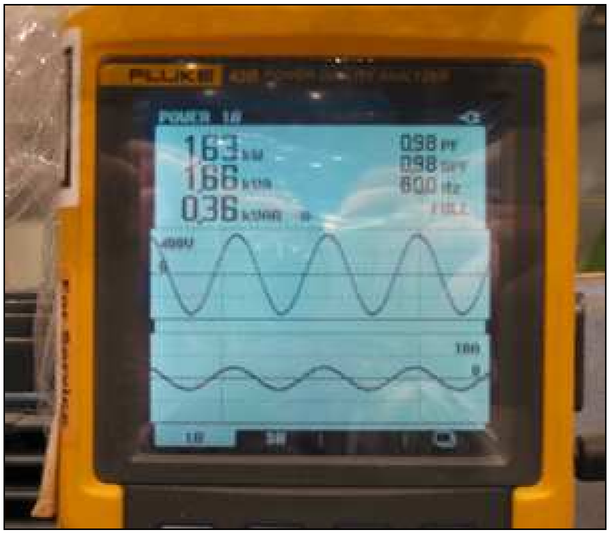
Vicat Test Apparatus
Humboldt Manufacturing Company – Norridge, IL
Model H-3050

Lab Timers
Cole Parmer – dual timer clock
CE Model 895



Data Logger
Campbell Scientific Incorporated – Logan UT
Model CR1000

Power Quality Analyzer
Fluke Corporation –
Everett, WA
Model 43B



Thermocouple Thermometer (outside of the ribbon mixer)
Cooper Instrument Corporation
Electro-Therm, Model # HT680A

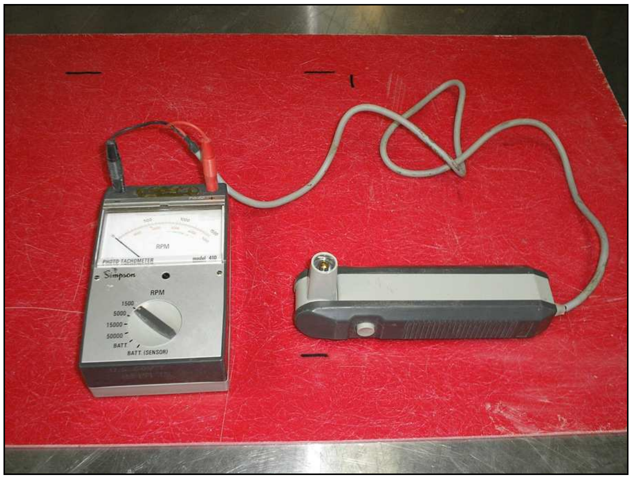
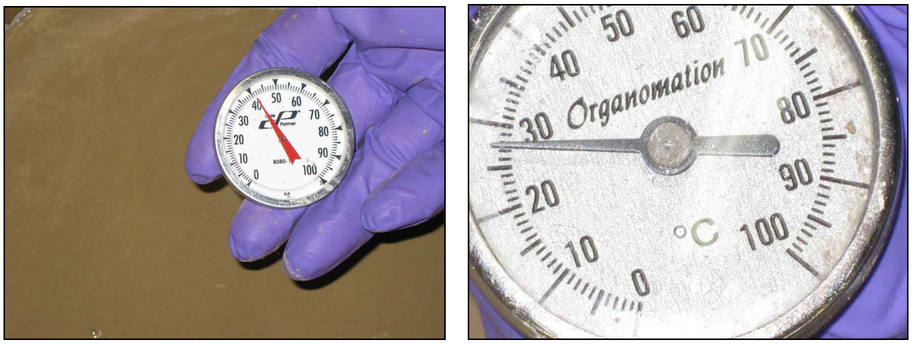


Photo Tachometer
(RPM Gauge for 20 Hp drum mixer)
Simpson Electric Company – Elgin, IL
Model # 410



Temperature Probes

Cole Parmer
Model #8080-12
(0-100 °C)

Organomation
(0 - 100°C)

Hydrogen Air Sampling Pump
Gastec, Inc (Sensidyne) – Clearwater, FL
Model 800
30 hydrogen tube with a Range 0.05 to 2%

Appendix B.
Outside Temperature Probe Data and Mixer Power Data

Table B-1. Sample #5 temperature probe and power data.

Mixing Time, min	Probe A, Degrees C	Probe B, Degrees C	Power, KW	PF
0	18.4	21.7	1.64	0.99
2:00	18.4	20.2	1.64	0.99
4:00	18.4	20.8	1.64	0.99
6:00	18.4	22.1	1.64	0.99
8:00	24.4	23.8	1.64	0.99
10:00	26.0	25.1	1.64	0.99
12:00	27.6	26.2	1.65	0.99
14:10	29.0	27.8	1.65	0.99
16:00	30.4	29.1	1.65	0.99
18:00	31.7	30.4	1.65	0.99
20:00	33.1	31.6	1.64	0.99
22:12	34.3	32.7	1.63	0.99
24:00	35.2	33.7	1.64	0.99

Table B-2. Sample #6 temperature probe and power data.

Mixing Time, min	Probe A, Degrees C	Probe B, Degrees C	Power, KW	PF
0	22.9	22.7	1.66	0.99
1:00	21.5	21.8	1.67	0.99
2:00	20.5	21.8	1.67	0.99
3:00	20.6	20.8	1.68	0.99
4:00	21.0	21.1	1.69	0.98
5:00	21.7	21.7	1.68	0.98
6:00	22.4	22.2	1.68	0.98
7:00	23.1	23.0	1.68	0.98
8:00	23.9	23.6	1.68	0.98
9:00	24.7	24.3	1.67	0.98
10:00	25.5	25.1	--	--
11:00	26.4	25.8	1,67	0.98
12:00	27.1	26.2	1.67	0.98
13:00	28.2	27.2	1.67	0.98
14:00	28.7	27.6	1.67	0.98
15:00	29.5	28.7	1,67	0.98
16:00	30.1	29.3	1.67	0.98
17:00	31.0	30.1	1.67	0.98
18:15	31.8	30.6	1.67	0.98
19:00	32.3	31.2	1,67	0.98
20:00	33.0	32.1	1.67	0.98
21:00	33.7	32.8	1.67	0.98
22:20	34.6	33.3	1.67	0.98

Table B-3. Sample #8 temperature probe and power data.

Mixing Time, min	Probe A, Degrees C	Probe B, Degrees C	Power, KW	PF
0	22.2	23.3	1.60	0.99
1:00	21.3	21.7	1.60	0.99
2:00	19.8	20.6	1.60	0.99
3:00	19.8	20.2	1.60	0.99
4:13	20.2	20.5	1.60	0.99
5:00	20.7	20.8	1.60	0.99
6:00	21.4	21.3	1.60	0.99
7:00	21.9	21.8	1.60	0.99
8:10	22.6	22.4	1.59	0.99
9:00	23.0	22.9	1.60	0.99
10:00	23.5	23.4	1.59	0.99
11:00	24.0	23.8	1.59	0.99
12:10	24.6	24.6	1.59	0.99
13:00	25.2	24.8	1.59	0.99
14:00	25.9	25.1	1.59	0.99
15:10	26.8	25.8	1.59	0.99
16:00	27.2	26.2	1.59	0.99
17:00	27.8	26.7	1.60	0.99
18:00	28.6	27.8	1.60	0.99
20:00	30.4	29.9	1.60	0.99
21:18	31.2	30.4	1.60	0.99
22:30	32.0	31.2	1.60	0.99
23:20	32.6	31.7	1.61	0.99
24:00	33.1	32.1	1.60	0.99
25:25	33.9	32.9	1.60	0.99
26.25	34.4	33.4	1.60	0.99
27:27	35.0	33.8	1.60	0.99

Table B-4. Sample #9 temperature probe and power data.

Mixing Time, min	Probe A, Degrees C	Probe B, Degrees C	Power, KW	PF
0	22.5	23.8	1.60	0.99
1:00	21.3	21.9	1.61	0.99
2:30	21.7	21.9	1.60	0.99
3:10	22.5	22.6	1.61	0.99
4:30	23.1	23.4	1.61	0.99
5:30	23.2	23.3	1.61	0.99
6:00	23.9	23.8	1.61	0.99
7:00	24.4	24.4	1.61	0.99
8:00	24.9	24.8	1.61	0.99
9:00	24.7	25.6	1.61	0.99
10:00	25.7	26.1	1.61	0.99
11:00	26.3	26.2	1,61	0.99
12:00	27.1	26.8	1.60	0.99
13:00	27.9	27.6	1.61	0.99
15:00	29.5	29.2	1.61	0.99
16:00	30.3	30.0	1.61	0.99
17:20	31.4	31.1	1.61	0.99
18:15	32.1	31.6	1.61	0.99
19:00	33.1	32.4	1.61	0.99
20:14	34.0	33.3	1.61	0.99
21:00	34.5	33.9	1.62	0.99
22:20	35.0	34.4	1.61	0.99
23:10	35.8	35.1	1.61	0.99
24:00	36.5	35.4	1.61	0.99

25:05	37.7	36.1	--	--

Table B-5. Sample #14 temperature probe and power data.

Mixing Time, min	Probe A, Degrees C	Probe B, Degrees C	Power, KW	PF
0	17.9	18.3	1.73	0.99
1:00	17.9	--	1.73	0.99
2:30	18.2	18.4	1.73	0.99
3:10	18.4	18.7	--	0.99
4:30	18.6	18.8	1.73	0.99
5:30	18.7	18.9	1.74	0.99
6:00	18.7	18.9	1.74	0.99
7:00	18.9	19.2	1.73	0.99
8:00	19.0	19.2	1.72	0.99
9:00	19.1	19.3	1.73	0.99
10:00	19.2	19.4	1.73	0.99
11:00	19.3	19.4	1.74	0.99
12:00	19.4	19.6	1.73	0.99

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