SRNL-STI-2010-00427 Revision 0

Key Words: Reactor Vessel Grout
Low-pH Grout
Flowable Fill

Retention: Permanent

BLENDED CALCIUM ALUMINATE- CALCIUM SULFATE CEMENT-BASED GROUT FOR P-REACTOR VESSEL IN-SITU DECOMMISSIONING (U)

David B. Stefanko and Christine A. Langton

Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
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March 10, 2011

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Prepared for the U.S. Department of Energy
Under Contract No. DE- AC09-08SR22470

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REVIEWS AND APPROVALS

Authors:

D. B. Stefanko, SRNL / E&CPT / Advanced Characterization and Process Date

C. A. Langton, SRNL / E&CPT / Engineering Process Development Date

Technical and SRNL Project Review:

M. G. Serrato, Technical Reviewer and Project Manager, SRNL /ES&BT Date

SRNL Management Approvals:

A. B. Barnes, Manager, SRNL / E&CPT Date

S. L. Marra, Manager, SRNL / E&CPT Date

Customer Approvals:

J. K. Blankenship, SRNS, Area Completion Engineering, SDD Eng. Date

J. C. Musall, SRNS, Area Completion Engineering, SDD Eng. Date

EXECUTIVE SUMMARY

This report documents laboratory and scale-up testing of blended calcium aluminate - calcium hemihydrate grouts for P-Reactor vessel in-situ decommissioning (ISD).[1] Blended calcium aluminate - calcium sulfate hemihydrate cement-based grout was identified as candidate material for filling (physically stabilizing) the 105-P Reactor vessel (RV) because it is less alkaline[2] than portland cement-based grout which has a pH greater than 12.4. In addition, blended calcium aluminate - calcium sulfate hemihydrate cement compositions can be formulated such that the primary cementitious phase is a stable crystalline material.[3] A less alkaline material (≤ 10.5) was desired to address a potential materials compatibility issue caused by corrosion of aluminum metal in highly alkaline environments such as that encountered in portland cement grouts [Wiersma, 2009b, Wiersma, 2010, and Serrato and Langton, 2010]. Information concerning access points into the P-Reactor vessel and amount of aluminum metal in the vessel is provided elsewhere [Griffin, 2010, Stefanko, 2009a and Wiersma, 2009, Wiersma, 2010, Bobbitt, 2010, respectively]. Radiolysis calculations are also provided in a separate document [Reyes-Jimenez, 2010].

This work supports scope identified and authorized in TAR-SDD-2008-00133 [Musall, 2009a], TAR-SDD-2009-00231 [Musall, 2009b], and TT/QAP, SRNL-RP-2009-01248 [Stefanko, 2009b]. This work supports the SRS Reactor In-Situ Decommission Project and was funded by the American Recovery and Reinvestment Act.

Based on laboratory testing, 2:1 mixtures (by weight) of Ciment Fondu® to Plaster of Paris plus water had a slurry pH of 9 to 10. Water in contact with cured specimens also had a pH of 9 to 10. The primary reaction product for this cement system is ettringite, which is a thermodynamically stable crystalline solid. Amorphous aluminum hydroxide, which is compatible with the reactor materials of construction, is also present in the 2:1 Ciment Fondu® to Plaster of Paris mixtures. (Ciment Fondu® and Plaster of Paris are commercially available components.)

Grouts typically require inert fillers in addition to a suitable cement binder. A bimodal particle size distribution was selected for testing in the blended calcium aluminate – calcium sulfate cement grout based on earlier work on magnesium potassium phosphate flowable fills [Stefanko, Langton and Singh, 2010]. A Class F fly ash to quartz sand (ASTM C-404 masonry sand or

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[1] SRNS/SDD-Engineering made the decision to fill the R-Reactor vessel with a portland cement based grout based on the amount of aluminum metal estimated to have been left in the vessel [Wiersma, 2009 a and b and Wiersma, 2010].

[2] Water in contact with calcium aluminate cement phases has a pH ranging from 10 to 11 depending on impurities. Water in contact with hydrated calcium sulfate compounds such as calcium sulfate hemihydrate has a pH between 5.5 to 8+, depending on impurities. Consequently mixtures of these ingredients which hydrate to form stable cementitious materials were investigated for the P-Reactor fill application.

[3] Thermodynamically stable cementitious reaction products are an important feature of a durable material. Unstable reaction products that are initially cementitious but undergo phase changes and associated volumetric changes over time (densification or expansion) do not produce durable materials.

ASTM C-637 Grade 2 sand) ratio of 1:3 (by weight) was selected because it is effective in reducing segregation and enhancing flow behavior.

The blended calcium aluminate – calcium sulfate cement grout required a set retarder as indicated by static working times of less than 15 minutes. Citric acid and boric acid were effective set retarders. A lower dose of citric acid was required compared to boric acid for the same set delay. Boric acid was selected for the scale-up testing and subsequently the final mix because it was available at Gibson's Pressure Grouting Services, Inc., during the scale-up testing.

Based on laboratory bench-scale and scale-up testing a calcium aluminate - calcium sulfate grout formulation was recommended for scale-up testing at Gibson's Pressure Grouting Services, Inc. This mix was one of two special formulations considered as candidates for the P-Reactor vessel ISD. The other mix was based on magnesium mono potassium phosphate cement and is described elsewhere [Stefanko, Langton and Singh, 2010].

The recommended mix design was confirmed in the full-scale mixing, pumping, and ¼ scale vessel filling test. Selected results are also included in this report. SRNL Mix T12-1 (Ciment Fondu®, 9.06 wt. %; Plaster of Paris, 4.53 wt. %; ASTM C-637 gradation 2 quartz sand, 51.56 wt. %; Class F fly ash, 15.32 wt.%; KIM® 301, 0.135 wt. %; SIKA ViscoCrete® 2100, 0.092 wt. %; boric acid, 0.10 wt. % (0.75 wt. % of the binder); diutan gum, 0.015 wt. %; and water 19.18 wt. % is recommended for filling the SRS P-Reactor vessel. Ingredients and proportions for the recommended mix are listed below. (A formulation with a lower water to cementitious binder ratio was also designed and tested. This mix has lower hydraulic conductivity and higher strength. However, it was not recommended for filling the P-Reactor vessel because it was developed after the full scale processing and vessel mock up testing.)

Blended Calcium Aluminate–Calcium Sulfate Grout Recommended for Filling the P-Reactor Vessel.

Ingredient	Water to binder weight 1.41	
	(Lbs/yd^3)	**(Kg/m^3)**
Ciment Fondu® (Kerneos Aluminate Technologies)	304.3	180.5
Plaster of Paris (US Gypsum Company)	152.2	90.3
Class F Fly Ash ASTM C-618 (SEFA, Inc.)	514.8	305.4
ASTM C-404 Masonry sand or ASTM C-637 Sand for grout for pre-placed aggregate	1732.0	1027.6
Water	644.3	382.2
KIM 301® (Integral Water Proofing Admixture) (Kryton, International Inc.)	4.5	2.7
SIKA ViscoCrete® 2100 (W.R. Grace, Inc.)	3.1	1.8
Diutan Gum (CP Kelco, Inc.)	0.5	0.3
Boric Acid (Technical grade)	3.4	2.0
Total	3359	1993

* Proportions per unit volume were confirmed on large size batches.

Pre-blending of all of the solid ingredients is recommended. Pre-blending provides quality control under "factory" conditions and disperses the solid ingredients in each other. Overall this shortens the grout mixing time in the field and simplifies full-scale production of this special material. Pre-measuring the SIKA ViscoCrete® 2100 high range water reducer (HRWR) for each batch is also suggested. Chilled water is not necessary for the recommended mix for ambient and material temperatures up to 32°C provided that the grout is continually agitated and placed within an hour after solids addition. A minimum of 8 minutes of mixing (measured from the time all of the solids are added to the water) is required to achieve uniform properties at the full-scale mixing.

The mixing and pumping equipment used in the full-scale mixing and pumping tests are suitable for full-scale production, i.e., double tub 25 cubic foot paddle mixer with a 25 cubic foot agitated hold tank, PUMPAC hydraulically driven ball and seat pump with a two stage piston, and two inch flexible grout hose up to 400 ft in length. Based on the scale-up test results, the grout can be dropped at least 20 feet without segregating. Consequently a tremie is not necessary for filling the reactor vessel. In addition, the blended calcium aluminate – calcium sulfate cement grout formulation has a dynamic working time of more than one hour. Consequently, in an upset condition, grout in the mixer and hose can be re-circulated for up to one hour without adversely affecting fresh and cured properties while the process is brought back on line.

Post Script

On November 18 and 22, 2010, SRNS in conjunction with Baker Concrete Construction and Gibson's Pressure Grouting Services, Inc., successfully completed filling the 105-P Reactor vessel with the blended calcium aluminate - calcium sulfate grout recommended by SRNL in accordance with the SRS Reactor Facility In-Situ Decommissioning requirements and SDD-2010-00200, Revision 1, Grout Placement Strategy for 105-P Reactor Vessel [Griffin, 2010a]. A total of 118 cubic yards of material was placed in the vessel during the two days of fill operations (49 cubic yards on November 18 and 69 cubic yards on November 22). A photo of vessel filled to within 16 inches of the top is provided below (looking into an open circumferential sleeve position).

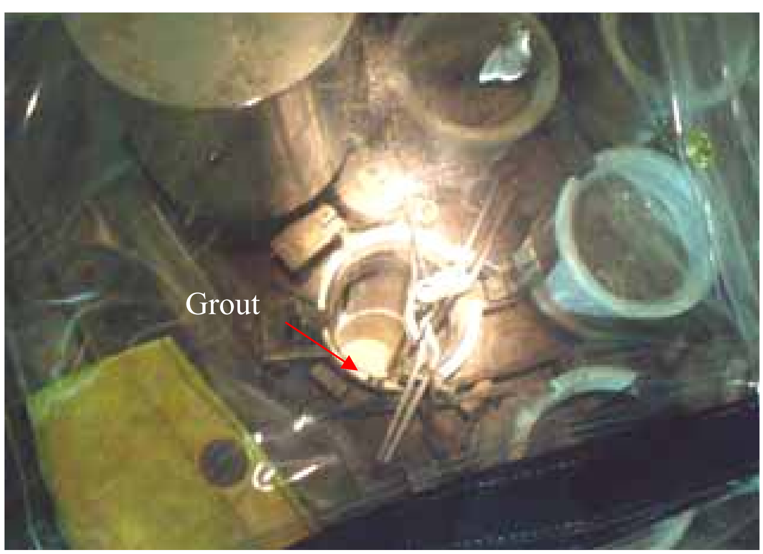

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS AND ABREVIATIONS

ALARA	As Low as Reasonably Achievable
ARRA	American Reinvestment and Recovery Act
ASTM	American Society for Testing & Materials
CAC	Calcium aluminate cement
CACS	Calcium aluminate – Calcium sulfate (hemihydrate)
DOE	Department of Energy
EARAIP	Early Action Remedial Action Implementation Plan
E&CPT	Environmental and Chemical Processing Technology
EDX	Energy Dispersive X-ray
EM	Environmental Management
ES&BT	Environmental Sciences and Bio Technology
HRWR	High Range Water Reducer
ISD	In-Situ Decommissioning
LLC	Limited Liability Corporation
PAOU	P-Area Operable Unit
PS&E	Process Science and Engineering
RH	Relative Humidity
RV	Reactor Vessel
SDD	Site Deactivation and Decommissioning
SEM	Scanning Electron Microscope
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
SRS	Savannah River Site
STI	Scientific Technical Information
STR	Subcontract Technical Representative
TAR	Technical Assistance Request
TT / QAP	Technical Task and Quality Assurance Plan
TTR	Technical Task Request
UPV	Ultrasonic Pulse Velocity
VMA	Viscosity Modifying Admixture
WSRC	Washington Savannah River Company
XRD	X-ray diffraction

Abbreviations

C	Celcius
cc	cubic centimeter
cu ft	cubic foot
cyd	cubic yard
ft	feet
g	gram
gal	gallon
gpm	gallon per minute
hr	hour
lbs	pounds
NM	not measured
min	minute
psi	pounds per square inch
s	seconds
wt	weight (wt.% = weight percent)

1.0 INTRODUCTION

1.1 Objective

The objective of this report is to document laboratory testing of blended calcium aluminate - calcium hemihydrate grouts for P-Reactor vessel in-situ decommissioning.[4] Blended calcium aluminate - calcium hemihydrate cement-based grout was identified as candidate material for filling (physically stabilizing) the 105-P Reactor vessel (RV) because it is less alkaline[5] than portland cement-based grout which has a pH greater than 12.4. In addition, blended calcium aluminate - calcium hemihydrate cement compositions can be formulated such that the primary cementitious phase is a stable crystalline material.[6] A less alkaline material (pH ≤ 10.5) was desired to address a potential materials compatibility issue caused by corrosion of aluminum metal in highly alkaline environments such as that encountered in portland cement grouts [Wiersma, 2009a and b, Wiersma, 2010, and Serrato and Langton, 2010]. Information concerning access points into the P-Reactor vessel and amount of aluminum metal in the vessel is provided elsewhere [Griffin, 2010, Stefanko, 2009 and Wiersma, 2009 and 2010, Bobbitt, 2010, respectively]. Radiolysis calculations are also provided in a separate document [Reyes-Jimenez, 2010].

This work supports scope identified and authorized in TAR-SDD-2008-00133 [Musall, 2009], TAR-SDD-2009-00231 [Musall, 2010], and TT/QAP, SRNL-RP-2009-01248 [Stefanko, 2009b]. This work supports the SRS Reactor Facilities In-Situ Decommissioning (ISD) Projects and was funded by the American Recovery and Reinvestment Act.

1.2 P-Reactor Vessel In-Situ Decommissioning

1.2.1 P-Area Reactor Vessel Description

SRNS committed to the Department of Energy to fill the reactor vessels in 105-P and 105-R with grout to the extent practicable as part of the SRS Reactor Facilities In-Situ Decommissioning Projects. The main tank (referred to as the reactor vessel) in each reactor was constructed of 304 stainless steel and is 16 feet in diameter and 16 feet in height. The tank is capped with Tube Sheets on the top and bottom which are approximately four and 3.5 feet in height, respectively. The top tube sheet is covered with a Plenum approximately 2 feet high. A steel shell around the reactor vessel forms a Thermal Shield around the tank with a Cooling Annulus of about 21 inches wide. The steel shell is surrounded by a five foot thick Biological Shield consisting of reinforced

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[4] SRNS/SDD-Engineering made the decision to fill the R-Reactor vessel with a portland cement based grout based on the amount of aluminum metal estimated to have been left in the vessel [Serrato, 2010 and Wiersma, 2010].

[5] Water in contact with calcium aluminate cement phases has a pH ranging from 10 to 11 depending on impurities. Water in contact with hydrated calcium sulfate compounds such as calcium sulfate hemihydrate has a pH between 5.5 to 8+ depending on impurities. Consequently mixtures of these ingredients which hydrate to form stable cementitious materials were investigated for the P-Reactor fill application.

[6] Thermodynamically stable cementitious reaction products are an important feature of a durable material. Unstable reaction products that are initially cementitious but undergo phase changes and associated volumetric changes over time (densification or expansion) do not produce durable materials.

concrete. These features, except for the biological shield, are illustrated for P-Reactor vessel in isometric view and cross-section in Figures 1-1 and 1-2, respectively [Vrettos, 2009]. A top view of the P-Reactor plenum is shown in Figure 1-3. The strategy for filling the P-Reactor vessel is to pull plugs in 3 to 8 permanent sleeves along the circumference of the vessel and to use these positions as grout entry and vent points in the vessel [Griffin, 2010a]. The details of the connection between the grout hose and reactor vessel were finalized after scale-up testing and final design of the grout placement [Griffin, 2010a].

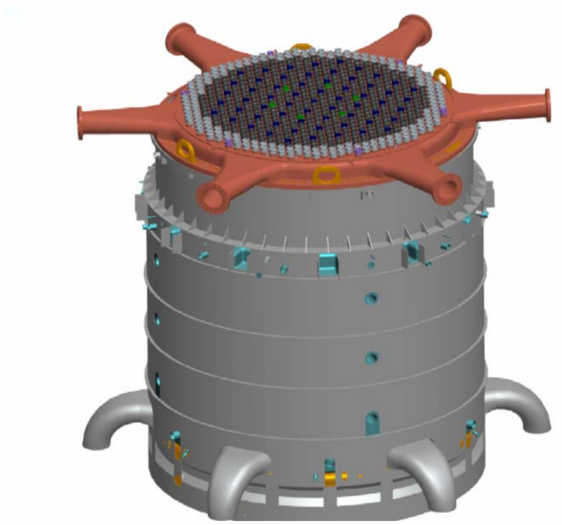

Figure 1-1. Isometric view of the SRS P-Reactor [Vrettos, 2009].

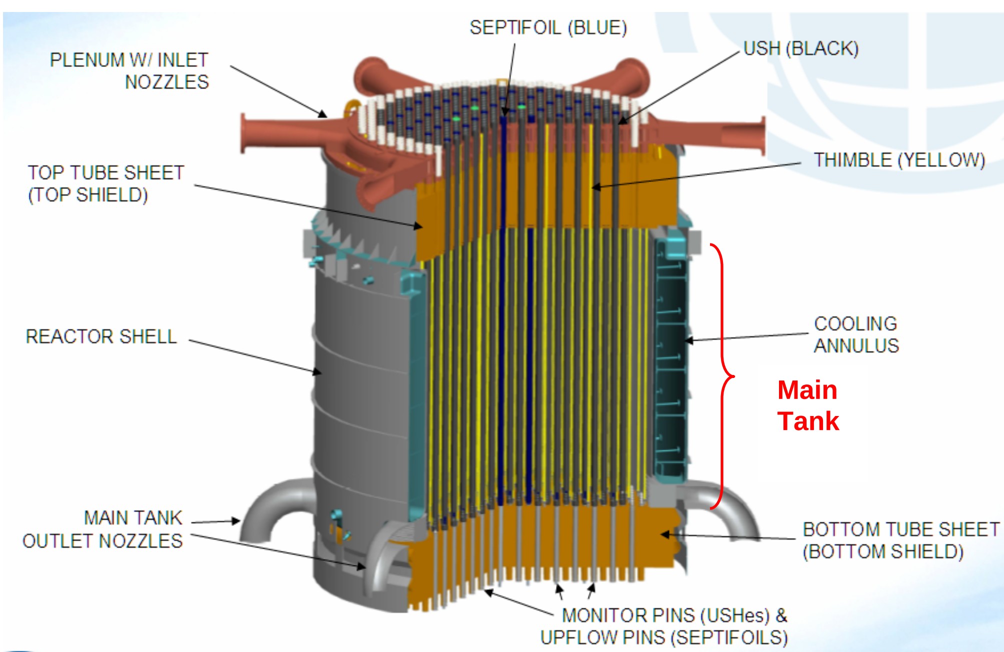

Figure 1-2. P-Reactor cross section [Vrettos, 2009].

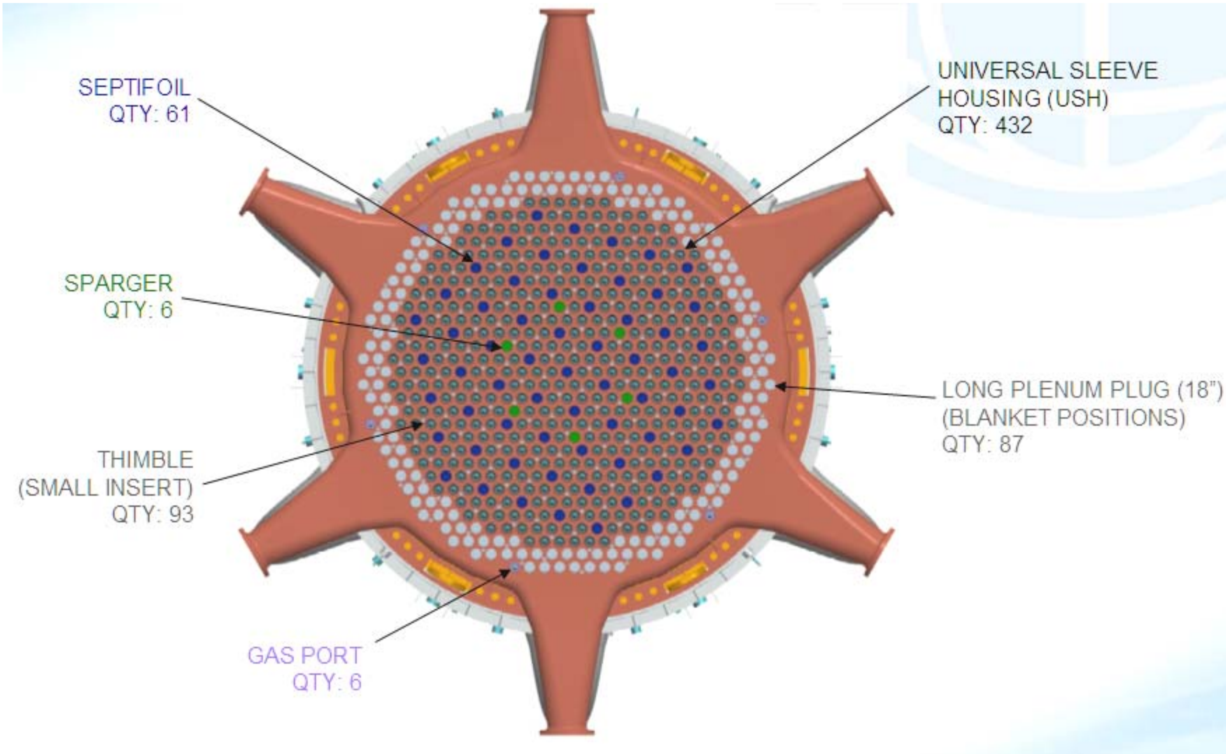

Figure 1-3. P-Reactor plan view [Vrettos, 2009].

1.2.2 In-Situ Decommissioning Fill Requirements

The in-situ decommissioning requirements for filling the RV are listed below [PAOU, 2008]:

- Fill the RV to the maximum extent practical with a stabilizing grout/fill material.
- Fill material shall have a minimum compressive strength of 50 psi and be non-corroding.

An additional minimum requirement is that the fill contain an integral water proofing agent [Blankenship, 2009].

Based on an initial understanding of the RV configuration and field conditions, the requirements were restated as engineering property attributes and criteria and are listed in Table 1-1.

Table 1-1. SRS ISD Reactor Vessel grout fill requirements.

Property	Requirement	Comments
Slurry Properties (Fresh Properties)		
pH	≤ 10.5	Aluminum corrosion rate [Weirsma, 2010]
Viscosity	< 350 cp (desirable)	Pumpable slurry (400 ft through 1 to 2 inch hose)
Yield Stress	pumpable	As low as possible without segregation
Self leveling	Yes	Reactor vessel entry points for vibrating the grout to achieve consolidation are limited
Flow Cone	< 50 s	Flowable, self leveling (desired)
Static Working Time	~30 minutes	Grout needs to remain fluid as the velocity decreases (to zero) as a function of distance from the discharge point in the reactor vessel
Dynamic Working Time	> 60 minutes	Longer is desired for recovery from upset conditions
Set Time	2 hr to 24 hr desired	Sufficient time to prevent settling
Density (wet unit weight)	80 to 140 lbs/cu ft	Pumpable through 1-2 inch ID hose Non cellular, "normal" weight material
Bleed water	None	Physically stable slurry is required
Segregation	None	Physically stable slurry is required
Maximum particle size	3 mm maximum	< 0.5 mm may be necessary pending further understanding of reactor vessel construction and test results
Cured Properties		
Compressive Strength		
3 days	200 psi minimum	50 psi required in regulatory documentation
28 days	200 psi minimum	
Adiabatic temperature rise	< 60°C	As low as possibly and still achieve compressive strength.
Maximum placement temperature	35°C	Suitable for mass pours

Pour schedules, lift heights, and total time to fill a reactor vessel were also important considerations in formulation development. Minimizing the number of lifts (start and stop cycles) and minimizing the total fill time impact the ISD project (ALARA, cost, schedule, waste generation).

2.0 CALCIUM ALUMINATE CEMENT SYSTEMS

2.1.1 Calcium Aluminate Cements

Commercially available calcium aluminate cements (CAC) were initially considered as the binder for a low pH reactor fill grout because they buffer the pH of water between 9 and 10 which was one of the requirements for P-Reactor Vessel grout [Weirsma, 2009a and b and Weirsma, 2010].[7] However, the hydrated calcium aluminate phases that initially form under ambient conditions when these cements come in contact with water, $CaO{\cdot}Al_2O_3{\cdot}10H_2O$ and $2CaO{\cdot}Al_2O_3{\cdot}8H_2O$, are thermodynamically unstable and convert over time to a non cementitious hydrogarnet, stratlingite ($3CaO{\cdot}Al_2O{\cdot}6H_2O$), which is the only stable hydrated phase in the system CaO-Al_2O_3-H_2O. This phase conversion is accompanied by the loss of strength and cementitious properties and is the reason calcium aluminate cements are not used as binders for ambient temperature applications.

2.1.2 Calcium Sulfo-aluminate Cement

Commercially available calcium sulfo-aluminate cement (CSAC) was also considered as a potential binder for a low pH reactor fill grout. [8] This cementitious system was described in the early 1900's and developed into commercial products in China in the 1970's. The primary clinker compounds (produced in the cement kiln) are yeelimite ($Ca_4Al_6O_{12}(SO_4)$), belite (Ca_2SiO_4), and ferrite phase (C_4AF) (listed in decreasing abundance). These cements are typically inter ground with additional calcium sulfate compounds[9] to achieve the desired final reaction product which is ettringite plus alumina gel (non crystalline aluminum hydroxide). The majority of the CSAC is produced in China where it is used in various types of construction and for producing rapid setting cements. The principle matrix phase in hydrated CSAC is ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}{\bullet}26(H_2O)$[10]. Non crystalline calcium- silica hydrates (C-S-H) and calcium aluminum / iron monosulfate phases along with a significant amount of unreacted clinker are also reported in typical formulations [Glasser and Zhang, 2001]. The conversion reactions which occur in hydrated calcium aluminate cement do not occur in CSAC at ambient conditions.

Calcium sulfo-aluminate cements and blends of calcium sulfo-aluminate cement and gypsum have been evaluated for stabilization of heavy metals [Peysson, et al., 2005] with good retention demonstrated for multivalent metals. Calcium sulfo-aluminate cements have also been evaluated as candidates for waste encapsulation [Zhou, et. al., 2006]. Fluid grouts with pHs between 10.5

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[7] These types of cements are typically used in high-temperature applications as refractory cements. Blends of these cements with portland cement and gypsum are used for ambient temperature applications as leveling compounds. However commercial formulations are designed for dry indoor conditions.

[8] About 40 % less CO2 is generated by the production of CSACs compared to portland cement and it can be produced at temperatures 200 to 300C lower that portland cement.

[9] 16 to 25 weight percent $CaSO_4$ is typical. The amount depends on the intended end use. Expansive formulations are also produced by blending the cement with $Ca(OH)_2$ which results in an ettringite microstructure that causes expansion or shrinkage compensation depending on the amount.

[10] $C_3A{\bullet}3C\boldsymbol{S}{\bullet}32H$ is an alternative representation representing CaO as C, Al_2O_3 as A, SO_4 as ***S***, and H as H_2O.

and 11 have been prepared from blends of Rockfast® (LaFarge product) calcium sulfo-aluminate cement and gypsum and tested for encapsulation of reactive metals [Hays and Godfrey, 2007].

2.1.3 Blended Calcium Aluminate – Calcium Hemihydrate Cement

Blends of calcium aluminate cement and other cements such as, belite cement, gypsum, portland cement + gypsum, slag cement, slag cement + sodium carbonate, calcium carbonate, and other reactive ingredients such as micro-silica and sodium silicate have been tested for various applications and are summarized elsewhere [Odler, 2000]. Given the acceptable pHs of calcium aluminate cements in contact with water (9 to 10) and gypsum cements in equilibrium with water (~6), blends of calcium aluminate cement and calcium hemihydrate ($CaSO_4 \bullet \frac{1}{2}H_2O$) were identified as potential candidates for the P-Reactor vessel grout.

Commercially available products that are blends of calcium aluminate cement and other materials were reviewed for suitability as reactor vessel fill materials. Pumpable, flowable, self-leveling, gypsum-based slurries are used as interior floor leveling materials, but all of the materials researched contained some portland cement which results in pHs of ~12.4.

The approach was to identify and test blends of commercially available calcium aluminate cements and calcium sulfate hemihydrate (Plaster of Paris) with the objective of forming ettringite as the primary cementitious phase. These ingredients were proportioned to provide enough calcium sulfate to form ettringite as the primary cementitious phase as the result of reaction with the calcium aluminate phases in the CAC. Excess aluminum forms alumina gel.
See Equation 1.

Equation 1. $$3CaAlO_4 + 3CaSO_4 \cdot \frac{1}{2}H_2O + XH_2O \longrightarrow Ca_6Al_2(SO_4)_3(OH)_{12} \bullet 26(H_2O) + Al(OH)_3$$

The Plaster of Paris used in this testing was obtained from US Gypsum Company, Chicago, IL. Two calcium aluminate cements were initially tested, Ciment Fondu® and Secar® 41. Both products are manufactured by Kerneos Aluminate Technologies, Chesapeake, VA. The primary calcium aluminate phase in both cements is $CaAlO_4$.[11] Ciment Fondu® was selected for the blends because it contains a small amount of dicalcium silicate which contributes to the microstructure and strength of the cured material. It was also less expensive than Secar® 41 which does not contain dicalcium silicate. In addition, inclusion of KIM® 301, an integral waterproofing reagent marketed by Kryton International Inc, was specified by SDD / SRNS [Blankenship, 2009] as an ingredient in the reactor fill grout.

2.2 Blended Calcium Aluminate – Calcium Sulfate Hemihydrate Cement Grouts

In order to reduce the heat generated from chemical reactions between the blended cement and water, chemically inert fillers were added to produce P-Reactor vessel fill grouts. Class F fly ash and quartz sand were selected as inert filler based on testing to develop a magnesium phosphate

[11] Ciment Fondu® also contains $12CaO \bullet 7Al_2O_3$, $2CaO \bullet SiO_2$ and $4CaO \bullet Al_2O_3 \bullet Fe_2O_3$. Secar® 41 also contains $2CaO \bullet Al_2O_3 \bullet SiO_2$.

cement grout for filling the SRS reactor vessels[12] [Stefanko, Langton, and Singh, 2011]. Two size fractions of quartz sand, ASTM C-404 masonry sand and ASTM C-637 Grading 2 sand, were tested. Because the P-Reactor vessel contains a dense array of flow obstructions (universal sleeve housings, thimbles, septifoils, spargers) coarse aggregate (3/8 inch granite gravel) was not included in the grout mix design.

Details of the proposed scale-up testing activities are provided elsewhere, G-SOW-G-00121 [Griffin, Langton and Stefanko, 2010].

[12] This combination of inert fillers provides a bimodal particle size distribution that contributes to achieving the desired flow properties, i.e., reducing bleed while producing highly flowable material.

3.0 EXPERIMENTAL METHOD

3.1 Test Methods

Material properties and test methods for evaluating these properties are listed in Table 3-1. Examples of flowable fill mixing and testing are provided in Figures 3-1 to 3-8.

Table 3-1. Properties and test methods for P-Reactor vessel fill grout.

Properties	Test Method
Spread / Flow	Modified ASTM D-6103 (Used 2 x 4 inch cylinder rather than 3 x 6 inch cylinder)
Static Working Time Static Gel Time (Screening)	Modified ASTM D-6103 Multiple 2 x 4 inch cylinders filled to 3 inch height at time zero. Spread measured selected time intervals Spread diameter reported
Dynamic Working Time (Screening)	Initial measurement same as Modified ASTM D-6103 Repeat Modified ASTM D-6103 using material recovered from test and returned to mixer for specified times
Flow	ASTM C-939 (flow cone)
Dynamic Working Time Using Flow Cone	Initial measurement same as Modified ASTM C-939. Repeat Modified ASTM C-939 using material recovered from test and returned to mixer for specified times. Repeat Modified ASTM
Set Time from Calorimeter	Determined from calorimeter data (acceleration in reaction rate) SRNL test method
Set Time (Screening)	Appearance of a rigid solid SRNL Ultrasonic Pulse Velocity (UPV) test method
Exothermic Reaction (adiabatic conditions)	SRNL adiabatic calorimeter method SRNL test method
Specific Heat	Energy balance method
Thermal Conductivity	Transient conduction calculation method
Bleed (Segregation)	Modified ASTM C-232 Estimate amount of liquid segregation after one hour
Compressive Strength	ASTM C-39 (2 x 4 inch cylinders) ASTM C-942 (2 inch cubes) ASTM C-39 (compression test cylinders) ASTM C-109 (compression test cubes)
Expansion (Screening)	Visual Examination of set material.
Chemical Compatibility	Slurry pH: pH paper Cured material in contact with water: SRNL pH Test Method

Figure 3-1. Hobart planetary mixer used for preparing samples.

Figure 3-2. Visual observation of liquid phase segregation.

Figure 3-3. ASTM D-6103 Flow Test and example of self-leveling grout. Modified test used smaller (2 x 4 inch) cylinders.

Figure 3-4. Static working time test samples. Modified after ASTM D-6103 by performing at selected time intervals.

Figure 3-5. Compressive strength cubes prepared per ASTM C-942 prior to stripping molds.

Figure 3-6. ASTM C-39 Compression Test Apparatus.

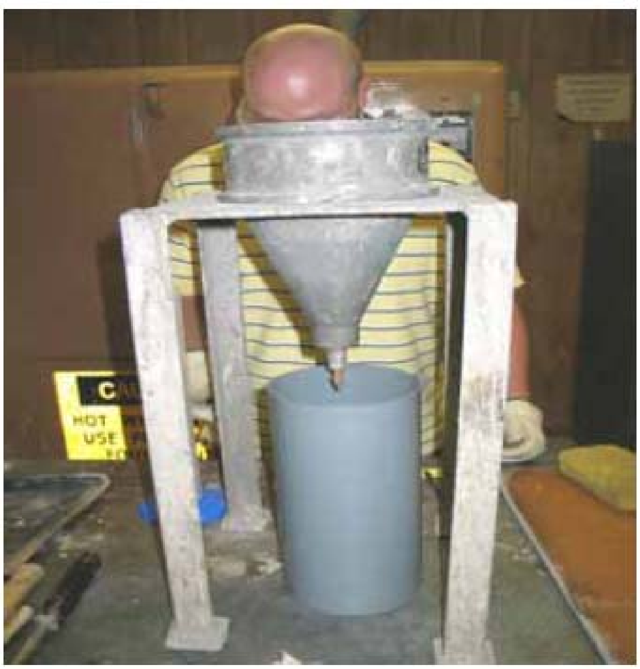


Figure 3-7. ASTM C-939 flow cone test.

Figure 3-8. SRNL adiabatic calorimeter.

3.2 Materials and Reagents

Materials used to formulate reactor vessel grouts and material suppliers are provided in Table 3-2.

Table 3-2. Materials used in laboratory and scale-up testing.*

Material	Supplier
Secar® 41	Kerneos Aluminate Technologies, Chesapeake, VA www.kerneosinc.com
Ciment Fondu®	Kerneos Aluminate Technologies, Chesapeake, VA www.kerneosinc.com
Plaster of Paris (calcium sulfate hemihydrate)	US Gypsum Company, Chicago, IL
Powder Filler	
Class F Fly Ash (< 3 wt. % carbon) Wateree Plant, SC and *Scherer Plant, GA*	SEFA Group, Lexington, SC 29073, 888.339.SEFA and *Boral Materials Technologies, Atlanta GA*
Sand Fillers	
Masonry Sand ASTM C-404	SCMI (South Carolina Mineral Industry) South Carolina Highway 125 Quarry
Quartz Sand ASTM C-637 Grading #2	*Standard Sand & Silica Co., Davenport, FL*
Additives	
Integral Water Proofing Reagent	
KIM® 301	Kryton International Inc., www.kryton.com
Set Retarders	
Boric Acid Technical grade, H_3BO_3	Reagents Inc. Charlotte, NC , 704-554-7474 *Alfa Aesar® www.alfa.com*
Citric Acid Monohydrate	Fisher Scientific, Fair Lawn, NJ, www.fishersci.com
Recover	W. R. Grace and Co., Cambridge, MA www.na.graceconstruction.com
Daratard 17	
Borax (sodium tetraborate)	Wal-Mart, www.20muleteamlaundry.com
Viscosity Modifiers	
Diutan Gum, KELCO-CRETE® DG	CP Kelco/ Huber Co., www.cpkelco.com
Cembinder® 8	EKA Chemicals, Inc., GreenBay, WI www.colloidalsilica.com
Cembinder® 50	
Bentonite (Prime-A-PAC)	Enviro Systems, Inc., Smyrna, GA, www.envirosys.us 770-333-0206
High Range Water Reducers	
SIKA ViscoCrete® 2100	SIKA Corporation, Lyndhurst, NJ, usa.sika.com
ADVA 408	W. R. Grace and Co., Cambridge, MA www.na.graceconstruction.com
Mid Range Water Reducers	
Superplast 1000	ICI, Miami FL (no longer in business)
WRDA 35	W. R. Grace and Co., Cambridge, MA www.na.graceconstruction.com
Water	SRS process water, SRS chilled process water (< 10°C) Smyrna, GA domestic water

*Materials in italics were procured by Gibson's Pressure Grouting Services Inc. and used in the scale-up and vessel fill mock up testing. These materials were also used for the full-scale production of the grouts used for filling the P-Reactor Vessel.

4.0 RESULTS: BLENDED CALCIUM ALUMINATE – CALCIUM SULFATE CEMENT GROUT

4.1 Screening Mixes

Initial screening of calcium aluminate and blended calcium aluminate - Plaster of Paris mixes was based on the pH of water in contact with the hydrated cements and the stability of hydrated phase assemblages. A pH of 9 to 10 was measured for water in contact with hydrated Secar® 41. A pH of 11 was measured for water in contact with hydrated Ciment Fondu®. However, Secar® 41 and Ciment Fondu®, calcium aluminate cements, both have initial hydrated phase assemblages that are known to undergo a conversion with time and temperature [Older, 2000] and [Taylor, 1997]. Consequently neither of these materials met the material stability requirement in Table 1-1.

Blends of calcium aluminate cements and Plaster of Paris were prepared and evaluated by the same criteria. The blends were proportioned to result in ettringite as the stable hydration product. The pHs of water in contact with the hydrated blended formulations were 9 to 10. The Ciment Fondu® – Plaster of Paris blend was selected for further development based on the lower cost of the Ciment Fondu®.

The second tier screening was performed to identify water to cement ratios and additives for obtaining flowable grouts to meet the P-Reactor production and placement requirements. The water to Ciment Fondu® plus Plaster of Paris ratio did not effect the set time but mixes with a higher water to cement ratio were initially more fluid. Selected results are listed in Table 4-1 and indicate that the reactor vessel grouting application requires a set retarder to achieve the required working time. Several set retarders were evaluated. Selected results are presented in Table 4-2.

Table 4-1. Summary of first and second tier screening for blended Ciment Fondu® – Plaster of Paris mixes.

Mix No.	Proportions (wt. %)	Water: Fondu+ Plaster of Paris	Fresh Properties	Set time	Compressive Strength (psi)	Unit Weight	pH
FG-2	Ciment Fondu® 9.29 Plaster of Paris 4.65 Class F-Fly Ash 30.15 Masonry Sand 30.02 Water 25.89	1.86	Very fluid but not pourable after 5 minutes static condition	< 60 min.	NM	NM	9-10
FG-3	Ciment Fondu® 9.24 Plaster of Paris 4.61 Class F-Fly Ash 30.05 Masonry Sand 30.13 Water 25.97	1.87	Not pourable after 5 minutes static condition	< 60 min.	NM	1.87 g/cc 115.6 lbs/cu ft	9-10
FG-9 FG-9-1	Ciment Fondu® 8.47 Plaster of Paris 4.25 Class F-Fly Ash 14.15 Masonry Sand 56.46 Water 16.67	1.31	Initial flow 6.25 inches Not pourable after 5 minutes	< 60 min.	1790 @ 4 days	NM	NM

NM = Not Measured.

Table 4-2. Summary of set retarder screening for blended Ciment Fondu® – Plaster of Paris mixes.

Mix No.	Proportions (wt. %)	Water: Fondu+ Plaster of Paris	Fresh Properties	Set time	Compressive Strength (psi)	Unit Weight	pH
FG-9-2	Ciment Fondu® 8.46 Plaster of Paris 4.24 Class F-Fly Ash 14.13 Masonry Sand 56.38 Water 16.64 **Boric Acid** 0.15	1.31	Fluid but not pourable after 5 minutes static condition Segregation / Bleed	NM	NM	NM	NM
FG-9-4	Ciment Fondu® 8.47 Plaster of Paris 4.25 Class F-Fly Ash 14.14 Masonry Sand 56.43 Water 16.66 **Recover®** 0.05	1.31	Initially fluid Not pourable after 5 minutes static condition Segregation	NM	NM	NM	NM
FG-9-7	Ciment Fondu® 8.47 Plaster of Paris 4.25 Class F-Fly Ash 14.13 Masonry Sand 56.38 Water 16.64 **Borax** 0.15	1.31	Fluid and pourable after 5 minutes but not after 10 minutes static condition Segregation / High Bleed	NM	NM	NM	NM
FG-9-26d	Ciment Fondu® 8.75 Plaster of Paris 4.36 Class F-Fly Ash 14.81 Masonry Sand 49.81 Water 21.84 SIKA VC® 2100 0.18 KIM 301 0.13 **Daratard® 17** 0.13	1.67	Initial flow = 8 inches No flow @ 15 minutes Segregation	NM	NM	NM	9.0 after mixing for 30 minutes
FG-9-26e FG-9-26e-1	Ciment Fondu® 9.04 Plaster of Paris 4.52 Class F-Fly Ash 15.33 Masonry Sand 51.59 Water 19.19 KIM® 301 0.14 SIKA VC® 2100 0.08 **Citric Acid** 0.11	1.42	Initial flow = 9 inches 8.63 inches at 15 min 7.63 @ 30 min 8.5 @ 45 min Segregation / Bleed	>15 to <24 hr	314 @ 1 day	124.6 lbs/cu ft	NM

NM = Not Measured.

Boric acid, borax, and citric acid were the most effective set retarders. Boric acid and citric acid were used in subsequent testing. Next, high range water reducers and mid range water reducers were also tested in an attempt to reduce the water to cement ratio to control segregation and bleed and also to achieve higher strengths and faster strength gain. Selected results are presented in Table 4-3. The polycarboxylate-type high range water reducers, SIKA ViscoCrete® 2100 and ADVA® 408 performed the best. However bleed and segregation were still observed. Therefore, viscosity modifying admixtures (VMA) were evaluated. SIKA ViscoCrete® 2100 was selected for further testing with VMAs.

Table 4-3. Summary of water reducing and high range water reducing admixture screening for blended Ciment Fondu® – Plaster of Paris mixes.

Mix No.	Proportions (wt. %)	Water: Fondu® + Plaster of Paris	Fresh Properties	Set time	Compressive Strength (psi)	Unit Weight	pH
FG-9-5	Ciment Fondu® 8.47 Plaster of Paris 4.25 Class F-Fly Ash 14.15 Masonry Sand 56.46 Water 16.67 **Superplast® 1000** 0.004	1.31	Fluid but not pourable after 5 minutes static condition. Much Segregation / Bleed	NM	NM	NM	NM
FG-9-6	Ciment Fondu® 7.54 Plaster of Paris 3.78 Class F-Fly Ash 12.58 Masonry Sand 50.21 Water 25.88 **WRDA® 35** 0.01	2.29	Initially fluid but not pourable after 5 minutes static condition Segregation / Bleed	NM	NM	NM	NM
FG-9-10	Ciment Fondu® 8.47 Plaster of Paris 4.25 Class F-Fly Ash 14.14 Masonry Sand 56.45 Water 16.66 **ADVA® 408** 0.03	1.31	Initially fluid not pourable after 5 minutes static condition	NM	NM	NM	NM
FG-9-8 FG-9-14	Ciment Fondu® 8.47 Plaster of Paris 4.25 Class F-Fly Ash 14.15 Masonry Sand 56.44 Water 16.67 **SIKA VC® 2100** 0.02	1.31	Fluid and pourable after 5 minutes Segregation / No Bleed No flow at 15 minutes	NM	NM	NM	NM
FG-9-16	Ciment Fondu® 8.47 Plaster of Paris 4.25 Class F-Fly Ash 14.14 Masonry Sand 56.43 Water 16.66 **SIKA VC® 2100** 0.05 (3x more SIKA VC® 2100 than Mix 9-8)	1.31	Fluid and pourable after 5 minutes No flow at 15 minutes Segregation Some bleed	NM	NM	NM	NM
FG-9-13	Ciment Fondu® 8.47 Plaster of Paris 4.26 Class F-Fly Ash 14.16 Masonry Sand 56.44 Water 16.65 **SIKA VC® 2100** 0.08 (4x more SIKA VC® 2100 than Mix 9-8)	1.31	Initial Flow = 9.0 inches @ 15 min. Static flow = 3.5 inches @ 15 min. No flow @ 30 min. High Bleed	< 1 hr	1230 psi @ 1 day	NM	NM

NM = Not Measured.

The combination of SIKA ViscoCrete® 2100 and Diutan gum was evaluated next because zero bleed mixes with acceptable rheology (initial flows) were obtained with these materials in the flowable structural fills used for the majority of the below grade reactor facility ISD. Selected results are presented in Table 4-4. Zero bleed blended calcium aluminate – calcium sulfate grouts with high initial flows could be produced with a combination of SIKA ViscoCrete® 2100 and Diutan gum. However, the short set times of < 1 hour indicate that additional set retardation is required to achieve the dynamic and static working times required for reactor vessel filling. Consequently, three types of admixtures, a set retarder (boric acid or citric acid), VMA, and HRWR are needed to meet the requirements for reactor vessel grout.

Table 4-4. Summary of high range water reducing and viscosity modifying admixtures for blended Ciment Fondu® – Plaster of Paris mixes.

Mix No.	Proportions (wt. %)	Water: Fondu+ Plaster of Paris	Fresh Properties	Set time	Compressive Strength (psi)	Unit Weight	pH
FG-9-22	Ciment Fondu® 8.47 Plaster of Paris 4.24 Class F-Fly Ash 14.14 Masonry Sand 56.42 Water 16.65 **SIKA VC® 2100 0.06** **Diutan Gum 0.02**	1.31	Static flow = 6 in. @15 min. No flow @ 30 min. No bleed No settlement	~1hr	NM	NM	NM
FG-9-23	Ciment Fondu® 8.32 Plaster of Paris 4.17 Class F-Fly Ash 13.90 Masonry Sand 55.47 Water 18.06 **SIKA VC® 2100 0.06** **Diutan Gum 0.02**	1.44	Static flow = 6.25 in. @ 15 min. No bleed No settlement	~1 hr	NM	NM	NM
FG-9-24	Ciment Fondu® 8.47 Plaster of Paris 4.24 Class F-Fly Ash 14.13 Masonry Sand 56.41 Water 16.65 **SIKA VC® 2100 0.08** **Diutan Gum 0.02**	1.31	Static flow = 6.63 in. @ 15 min. No bleed No settlement	~1 hr	NM	NM	NM
FG-9-25	Ciment Fondu® 8.32 Plaster of Paris 4.17 Class F-Fly Ash 13.90 Masonry Sand 55.46 Water 18.05 **SIKA VC® 2100 0.08** **Diutan Gum 0.02**	1.44	Static flow = 6.75 in. @ 15 min. Pourable @ 30 min. Not pourable @ 40 min. No bleed No settlement	~1 hr	NM	NM	NM

NM = Not Measured.

Alternative VMAs were also tested because of the unique cement-based system and unique application. Selected results are presented in Table 4-5. Cembinder® 50, a colloidal silica, and bentonite clay were not as effective as the Diutan Gum.

Table 4-5. Summary of alternative viscosity modifying admixtures for blended Ciment Fondu® – Plaster of Paris mixes.

Mix No.	Proportions (wt. %)		Water: Fondu + Plaster of Paris	Fresh Properties	Set time	Compressive Strength (psi)	Unit Weight	pH
FG-9-30	Ciment Fondu ® Plaster of Paris Class F-Fly Ash Masonry Sand Water **SIKA VC® 2100** **Cembinder® 50**	8.30 4.16 13.86 55.32 18.01 **0.08** **0.27**	1.44	Static flow @ 15 min. 5.63 in No flow @ 30 min. High Bleed and High Settlement	NM	NM	NM	NM
FG-9-42	Ciment Fondu® Plaster of Paris Class F-Fly Ash Masonry Sand Water **SIKA VC® 2100** **Bentonite**	8.30 4.16 13.86 55.32 18.00 **0.08** **0.28**	1.44	Static flow @ 15 min. 0 in No bleed No settlement	NM	NM	NM	NM

NM = Not Measured.

4.2 Laboratory Bench Scale-up and Test Results

Bench-scale up testing at SRS was performed to identify a grout mix design for full scale-up testing at Gibson's Pressure Grouting Services Inc., Smyrna, GA. Based on the results of the screening mixes, processing admixtures and the proportion of binder to inert fly ash and sand were selected for scale-up to a batch size of 0.5 cubic foot.

4.2.1 Citric Acid

Citric acid was used in the first set of bench scale-up tests because for an equivalent amount it provided longer set retardation compared to boric acid. KIM® 301 was also added to all of the mixes in bench scale-up tests.[13] Results are listed in Table 4-6. The amount of citric acid in Mix FG9-26E was twice the amount in FG9-26G. Both mixes met the requirements for reactor fill grout. Mix FG9-26G was selected for the bench scale-up testing.

The bench scale-up test consisted of making a 0.5 cubic foot batch and pouring the resulting grout into a pan that contained physical obstructions to impede flow. See Figure 4-1. The grout mixing procedure was as follows:

- Pre-blend the solid cementitious reagents including the KIM® 301
- Add solid boric acid set retarder to the mixing water in a one cubic foot Hobart mixer.
- Add the sand and then the fly ash
- Add the pre blended cementitious ingredients
- Add the liquid HRWR to the slurry during the first minute of mixing
- Mix for 10 minutes
- Pour the resulting grout into the test pan through a ASTM C-939 flow cone (1/2 inch funnel opening) and measure the time for the flow cone to empty. (The ASTM C-939

[13] KIM® 301 was included in the reactor fill grout mix at the request of SRNS SDD Engineering.

procedure requires that the flow cone be cleaned between measurements. However, this was not done so the increased times are probably less than measured.)

- Continue filling pan using flow cone and measure the time to empty for each addition. Record time of each placement. (The flow cone was not rinsed between placements.)

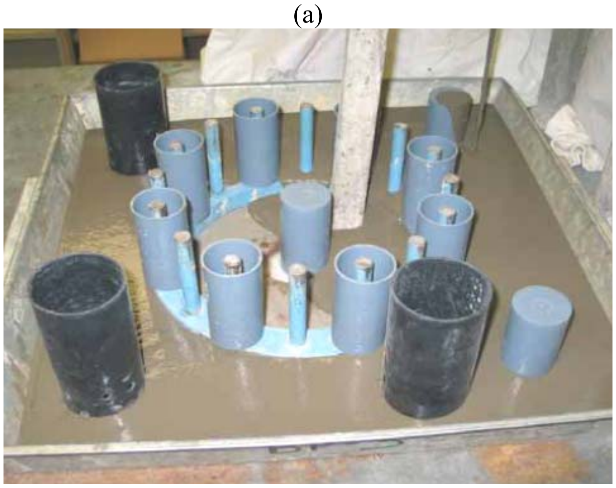
Table 4-6. Summary of bench scale-up testing with citric acid.

Mix No.	Proportions (wt. %)		Water: Fondu + Plaster of Paris	Fresh Properties	Set time	Compressive Strength (psi)	Unit Weight	pH
FG-9-26E	Ciment Fondu® Plaster of Paris Class F-Fly Ash Masonry Sand Water KIM® 301 Diutan Gum SIKA VC® 2100 Citric Acid	9.03 4.52 15.33 51.59 19.19 0.14 0.01 0.08 0.11	1.42	Static flow 9.0 in @ initial 8.13 @15 min 7.63 @ 30 min 8.5 @ 45 min No bleed No settlement	NM	NM	NM	9-10
FG9-26E1	Ciment Fondu® Plaster of Paris Class F-Fly Ash Masonry Sand Water KIM® 301 Diutan Gum SIKA VC® 2100 Citric Acid	9.05 4.52 15.32 51.58 19.19 0.13 0.01 0.08 0.11	1.42	Static flow 9.0 in @ initial 8.63 @15 min 7.63 @ 30 min 8.5 @ 45 min No bleed No settlement	~20 hr	314 @ 24 hr 753 @ 202 days	124.6 lb /cu ft	NM
FG9-26G	Ciment Fondu® Plaster of Paris Class F-Fly Ash Masonry Sand Water KIM® 301 Diutan Gum SIKA VC® 2100 Citric Acid	9.06 4.54 15.32 51.60 19.19 0.14 0.02 0.10 0.05	1.41	Initial flow = 8.5 inch 6.75 inches @ 30 min.	< 22 hr	726 @ 36 hr 1040 @ 202 days	NM	NM
FG9-26G2	Ciment Fondu® Plaster of Paris Class F-Fly Ash Masonry Sand Water KIM® 301 Diutan Gum SIKA VC® 2100 Citric Acid	9.05 4.53 15.32 51.60 19.20 0.14 0.02 0.09 0.06	1.41	Dynamic Flow Cone (after minutes of mixing) 29 s after 10 min. 30 s after 10 min. 29 s after 16 min. 31 s after 18 min. 32 s after 20 min. 32 s after 22 min. 35 s after 24 min. No bleed	< 22 hr	763 @ 5 days 1079 @ 201 days	NM	NM

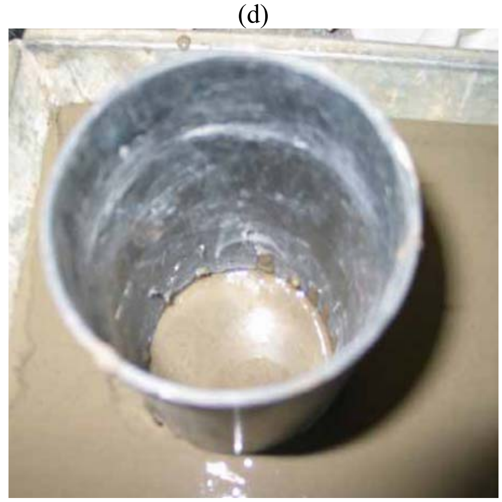
NM = Not measured

(a)

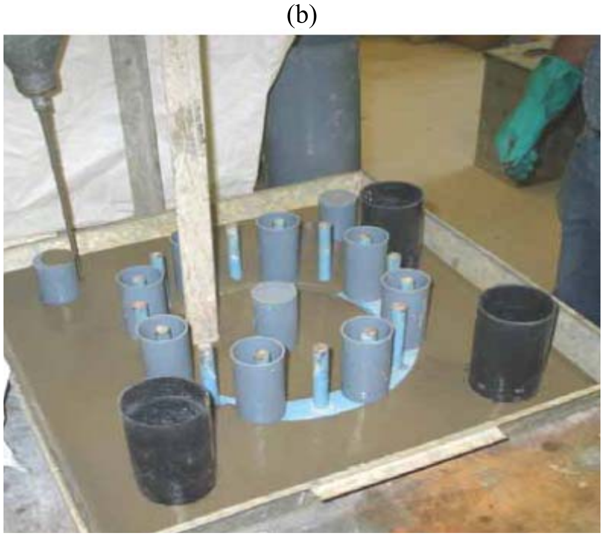
(d)



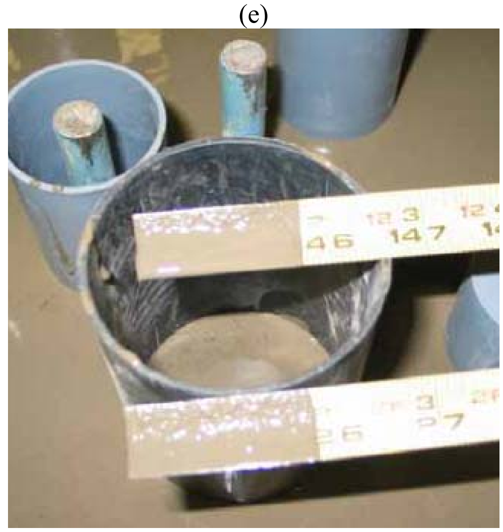
(b)



(e)



(c)



(f)

Figure 4-1. Bench scale-up flow test for citric acid formulation. Progressive filling of container with obstructions (a to c). Progressive filling of obstructions with 3/16 inch diameter holes (d to e) and 3/8 inch wide slit (f).

4.2.2 Boric Acid

The bench scale-up testing was repeated as described in Section 4.2.1 with boric acid as the set retarder.[14] Fresh and cured property results indicated that boric acid also resulted in mixes that met the requirements for P-Reactor vessel grout fill. The flow cone was filled eight times over a twelve minute period. Flows were measured for each batch. The time to empty the cone increased for each successive batch. (The ASTM C-939 procedure requires that the flow cone be cleaned between measurements. However, this was not done so the increased times are probably less than measured.) Results are presented in Table 4-7 and Figures 4-2 and 4-3.

Table 4-7. Summary of bench scale-up testing with boric acid.

Mix No.	Proportions (wt. %)	Water: Fondu + Plaster of Paris	Fresh Properties	Set time	Compressive Strength (psi)	Unit Weight	pH
FG-9-26F	Ciment Fondu® 9.03 Plaster of Paris 4.53 Class F-Fly Ash 15.27 Masonry Sand 51.41 Water 19.12 KIM® 301 0.14 Diutan Gum 0.02 SIKA VC® 2100 0.09 Boric Acid 0.39	1.41	Static flow 9.25 inch @ initial 8.5 @15 min 7.25 @ 30 min 8.0 @ 45 min Bleed after 24 hr	> 6 days	NM	124.5	NM
FG-9-26I	Ciment Fondu® 9.06 Plaster of Paris 4.52 Class F-Fly Ash 15.30 Masonry Sand 51.53 Water 19.16 KIM® 301 0.14 Diutan Gum 0.02 SIKA VC® 2100 0.09 Boric Acid 0.19	1.41	Static flow 8.5 in. @ initial 7.25 @ 30 min 6.5 @ 45 min No bleed No settlement	< 24 hr	564 @ 36 hr 600 @ 5 days 970 @ 202 days	124.5	NM
FG-9-26I2	Ciment Fondu® 9.04 Plaster of Paris 4.53 Class F-Fly Ash 15.30 Masonry Sand 51.53 Water 19.17 KIM® 301 0.14 Diutan Gum 0.02 SIKA VC® 2100 0.09 Boric Acid 0.19	1.41	Static flow 7.38 in. @ initial 6.25 in @ 15 5.75 @ 30 min 4.5 @ 45 min No bleed Dynamic/ Flow Cone (after minutes of mixing) 32 after 8 min. 33 s after 10 32 s after 11 33 s after 12 34 s after 14 35 s after 16 38 s after 17 39 s after 20	< 24 hr	598 @ 5 days 1200 @ 201 days	124.9	NM

[14] Two candidate mixes were identified for full scale-up testing. Another reason for testing boric acid is that it was the set retarder recommended for the other grout, a magnesium phosphate-based material recommended for the full scale-up evaluation. Two mixes were considered because this was the first flowable fill application of these uniquely modified materials.

(a) (b)

Figure 4-2. Bench scale-up flow test for boric acid formulation. Flowable grout placed in a container with obstructions (a). Grout flowing into obstructions via 3/16 inch diameter holes (b).

Figure 4-3. Static flow test results for Mix FG-26I (boric acid mix) per modified ASTM D-6103. Initial spread and spread after increasing times under static conditions.

4.3 Summary of Bench-Scale Testing

Both citric acid and boric acid were effective set retarders in laboratory bench scale-up testing of the calcium aluminate – calcium sulfate cement grouts. For an equivalent dose by weight, citric acid was more effective than the boric acid. However, boric acid was selected for the scale-up pumping and mock up vessel testing because it was inorganic. Also boric acid was found to be the most effective set retarder for the magnesium potassium phosphate grout and a supply for mock up testing had already been purchased.

The mixes retarded with citric acid and boric acid flowed around the obstructions and through 1.0 inch gaps between obstructions. Both grouts also flowed into the obstructions through 3/16 inch holes and 3/8 inch wide slits. See Figures 4-1 and 4-2. The mixes were not quite self-leveling but a faster fill rate would have provided faster flow and better leveling. Two corners were ¼ of an inch lower than the corner where the material was discharged. The diagonal corner was only 1/8 inch lower than the discharge point. The level inside and outside the cylinders was approximately the same.

4.4 Boric Acid Addition Confirmation

Tests were performed to identify the dose of boric set retarder in the blended calcium aluminate – calcium sulfate cement grout mix. Results of selected tests are presented in Table 4.8 and were used to finalize the mix design used in the scale-up testing and vessel mock up fill tests at Gibson's Pressure Grouting Services, Inc. The set times of mixes containing boric acid doses of between 0.35 and 1.0 weight percent of the cementitious binder (Ciment Fondu® + Plaster of Paris) set within 24 hours which met the acceptance criteria for reactor vessel filling. However, the dynamic working times for the mixes with 0.35 and 0.5 wt % boric acid additions were less than one hour.

A boric acid dose of 1.4 weight percent of the cementitious binder did not set for several days. However this mix did set some time after 20 days and had a compressive strength of 980 psi after curing for 194 days at 100% relative humidity.

Since the static and dynamic working times for mixes containing 0.7 and 0.8 wt. % of the binder were acceptable, a dose of 0.75 wt.% of the binder was selected for the pumping and vessel fill mock-up tests. At this dose, static and dynamic working time requirements were met without the use of chilled water.

Table 4-8. Summary of boric acid dose results.

Mix No.	Proportions (wt. %)	Boric Acid Wt % of total binder	Fresh Properties	Set time	Compressive Strength (psi)
T4-5	Ciment Fondu® 9.03 Plaster of Paris 4.53 Class F-Fly Ash 15.27 Masonry Sand 51.41 Water 19.12 KIM® 301 0.14 Diutan Gum 0.02 SIKA VC® 2100 0.09 Boric Acid as indicated Water : (Fondu + Plaster of Paris) = 1.41 Water: SIKA ViscoCrete® = ~ 208	0.35 Chilled water	Static flow 8.1 in. @ initial 7.6 @ 15 min 6.9 @ 30 min 4 @ 45 min No bleed/settlement Consistency of mortar after 1 hr of mixing	< 24 hr	824 @ 24 hr
T4-10		0.5 Ambient temperature water	Static flow 8.1 in. @ initial 7.5 @ 15 min 4.0 @ 30 min 0 @ 45 min No bleed/settlement Consistency of mortar after 1 hr of mixing Initial flow cone 30 s	< 24 hr	1030 psi @ 8 days 1533 psi @ 182 days
T4-6		0.53	Static flow 8.1 in. @ initial 7.0 @ 15 min 6.8 @ 30 min 5.9 @ 45 min No bleed/settlement Consistency of mortar after 1 hr of mixing	< 24 hr	908 psi @ 1 day
T6-2		0.7	Static flow 8.3 in. @ initial 7.4 @ 15 min 5.8 @ 30 min 4.3 @ 45 min Dynamic flow Initial flow cone = 29 s No bleed/settlement	< 24 hr	1230 psi @ 4 days
T4-15		0.8	Static flow 7.9 in. @ initial 6.3 @ 15 min 5.5 @ 30 min 4.9 @ 45 min Dynamic flow Initial flow cone = 33 s No bleed/settlement	< 24 hr	940 psi @ 7 days

Table 4-8 (continued). Summary of boric acid dose results.

Mix No.	Proportions (wt. %)	Boric Acid Wt % of total binder	Fresh Properties	Set time	Compressive Strength (psi)
T6-6	Ciment Fondu® 9.03 Plaster of Paris 4.53 Class F-Fly Ash 15.27 Masonry Sand 51.41 Water 19.12 KIM® 301 0.14 Diutan Gum 0.02 SIKA VC® 2100 0.09 Boric Acid as indicated Water : (Fondu + Plaster of Paris) = 1.41 Water: SIKA ViscoCrete® = ~ 208	0.79	Static flow after 10 min mixing 8.3 in. @ initial 7.3 @ 15 min 6.4 @ 30 min 5.9 @ 45 min Dynamic flow Initial flow cone = 40 s after 5 min mixing 30 s after 10 min mixing No bleed/settlement	< 24 hr	NM
T4-16		1.0	Static flow 8.5 in. @ initial 7.3 @ 15 min 6.0 @ 30 min 5.3 @ 45 min Dynamic flow Initial flow cone = 31 s No bleed/settlement	< 24 hr	1682 psi @ 183 days
T6-1		1.4	Static flow 8.68 in. @ initial 6.5 @ 15 min 6.8 @ 30 min 6.0 @ 45 min Dynamic flow Initial flow cone = 27 s Bleed Gelled within 24 hr but did not set for several weeks	> 20 days	980 psi @ 194 days

NM = not measured.

4.5 SRNL Calorimeter Results

Adiabatic temperature rise was measured at SRNL in one of two adiabatic calorimeters. A list of mixes, results, and experimental approach are documented in a report [Steimke, 2010]. Three mixes tested are shown in Table 4-9. The temperature rises were added to the temperature of the starting material to obtain the maximum temperature resulting from the cementitious reactions. This method of estimating the adiabatic temperature rise for complete reaction was used for comparison of materials. Because the majority of the reactions in the calcium aluminate – calcium sulfate – water system appear to be complete in 3 to 5 days, the estimate of the total heat generated is reasonable.[15]

[15] Steimke, et al., 2011, applied a factor of 1.4 to 1.5 to the calcium aluminate - calcium sulfate adiabatic calorimeter results based on prior experience with portland cement-based systems. A detailed analysis of the blended calcium aluminate – calcium sulfate system was not performed and the factor of 1.4 to 1.5 is probably overly conservative.

Table 4-9. Calorimeter Mixes with Boric Acid

Mix No.	Proportions (wt. %)	Water: Fondu+ Plaster of Paris	Set Time (hours)	Compressive Strength (psi)	Maximum Temp. rise in calorimeter (ºC)	Adiabatic Temperature Rise (ºC)
101H ½ the target amount of binder 0.75 wt. % boric acid based on binder Same mix as T4-18	Ciment Fondu® 4.61 Plaster of Paris 2.30 Class F-Fly Ash 17.98 Masonry Sand 55.30 Water 19.51 KIM® 301 0.14 Boric Acid 0.05 Diutan Gum 0.02 SIKA VC® 2100 0.09	2.83	2.5	190 @ 1 day 240 @ 6 days (T4-18)	17.3 (initial temp. = 23.4 ºC)	26 (69 J/mL) [Steimke, 2011]
102H Target amount of binder 0.75 wt. % boric acid based on binder Same mix as T12-1 & T10-1	Ciment Fondu® 9.06 Plaster of Paris 4.53 Class F-Fly Ash 15.32 Masonry Sand 51.56 Water 19.18 KIM® 301 0.14 Boric Acid 0.10 Diutan Gum 0.02 SIKA VC® 2100 0.09	1.41	12	760 @ 5 days (T12-1) 760 @ 5 days (T10-1)	35.5 (initial temp. = 23.5 ºC)	54 (130 J/mL) [Steimke, 2011]
103H ½ target amount of binder 83% more boric acid than 101H	Ciment Fondu® .61 Plaster of Paris 2.30 Class F-Fly Ash 17.97 Masonry Sand 55.28 Water 19.51 KIM® 301 0.14 Boric Acid 0.09 Diutan Gum 0.02 SIKA VC® 2100 0.09	2.83	26	Not set at 24 hr.	17.1 (initial temp. = 25.5 ºC)	24 (54 J/mL) [Steimke, 2011]

NM = not measured.

Figure 4-4 shows the temperature rise inside the calorimeter for the three mixes in Table 4-9. Mix 102H had two times more binder (Ciment Fondu® + Plaster of Paris) than mixes 101H and 103H. Consequently the adiabatic temperature rise was about twice of those mixes. The boric acid dose in Mix 103H was about 83 % greater than the dose in Mix 101H. Both mixes had equal proportions of binder. The set time for Mix 103H was about 10 times longer than that for mix 101H. The temperature rises for both mixes were about the same which was expected since they had identical proportions (except for the boric acid). Mixing times were also the same and performed in a Hobart planetary mixer at the same mixing speed setting.

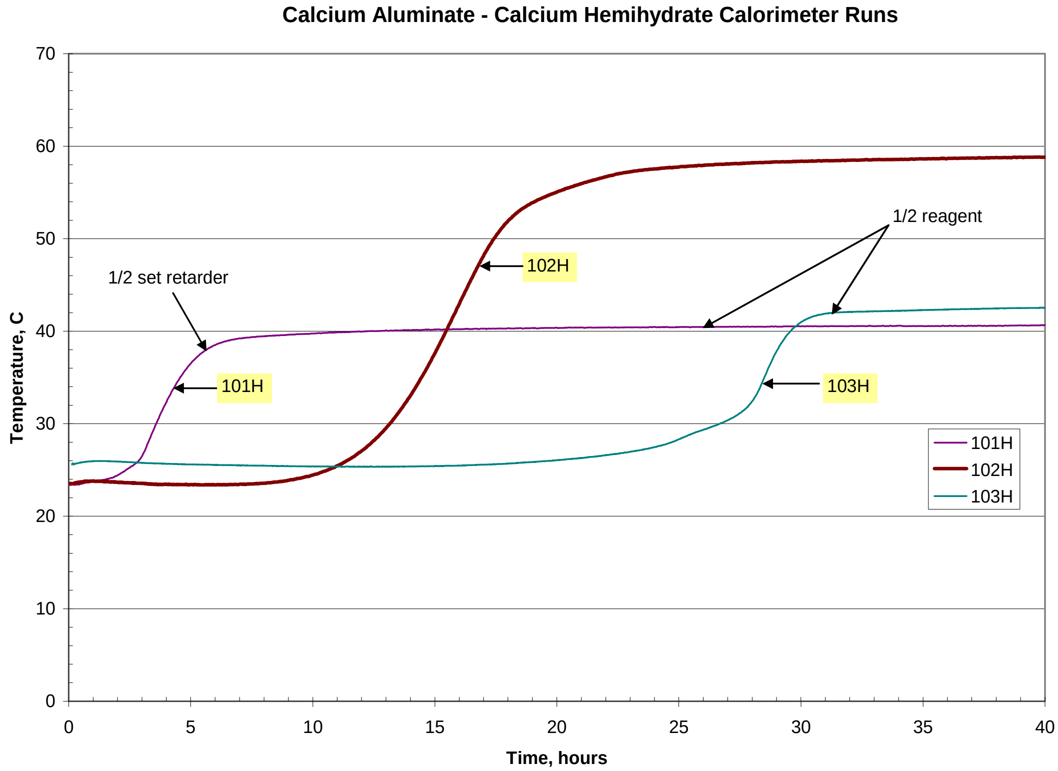


Figure 4-4. Adiabatic calorimeter result for selected mixes with different binder amounts and boric acid set retarder concentrations.

4.6 Scale-up Testing at Gibson Pressure Grouting Service, Inc.

The blended calcium aluminate – sulfate cement grout with boric acid set retarder was recommended for production scale-up and mock-up testing. The test objectives are described elsewhere [Stefanko, 2010] and include to:

- Confirm processability of the recommended blended calcium aluminate – sulfate cement grout including the boric acid dose
- Confirm the quality of grout produced with full-scale production equipment and methods.
- Prepare for full-scale P-Reactor vessel filling and included demonstration of blending and packaging of reagents, inert fillers, and processing admixture
- Identify a mixer (drum, paddle, colloidal or other) for the calcium aluminate – sulfate cement grout and prepare mixing specifications
- Identify a grout pump, demonstrate pumping at 3 flow rates through a 400 ft recirculation loop, and determine the effect of mixing and recirculation (up to 1 hr) on material properties
- Identify hose sizing requirements required for grout placement into SRS reactor
- Identify suitable equipment for adding / metering liquid admixtures to the mixer
- Identify process instrumentation and monitoring requirements for full-scale production
- Identify QA tests and sampling frequency for full-scale production

- Measure semi-adiabatic temperature rise for a one cubic yard monolith instrumented with thermocouples
- Demonstrate a dynamic working time and material properties for mixing up to 1 hour and evaluate contingencies for upset conditions
- Demonstrate grout flow and self-leveling in a ¼ scale vessel mock-up with representative flow obstructions
- Demonstrate a method for adding and metering water to mixer
- Demonstrate a method for adding dry solids to mixer
- Perform grout drop height test to identify any adverse effects on grout flow behavior and separation/segregation due to freefall
- Determine chilled water requirements

The testing was performed at Gibson's Pressure Grouting Services, Inc., Smyrna, GA during August and September, 2010. Details of the testing are provided in the Statement of Work, G-SOW-G-00121 [Griffin, Langton, and Stefanko, 2010]. The mix recommended for the scale-up and vessel fill mock-up testing is provided in Table 4-10. More details of the scale-up and vessel fill mock-up testing are provided elsewhere [Serrato and Langton, 2010 and Blankenship, 2010].

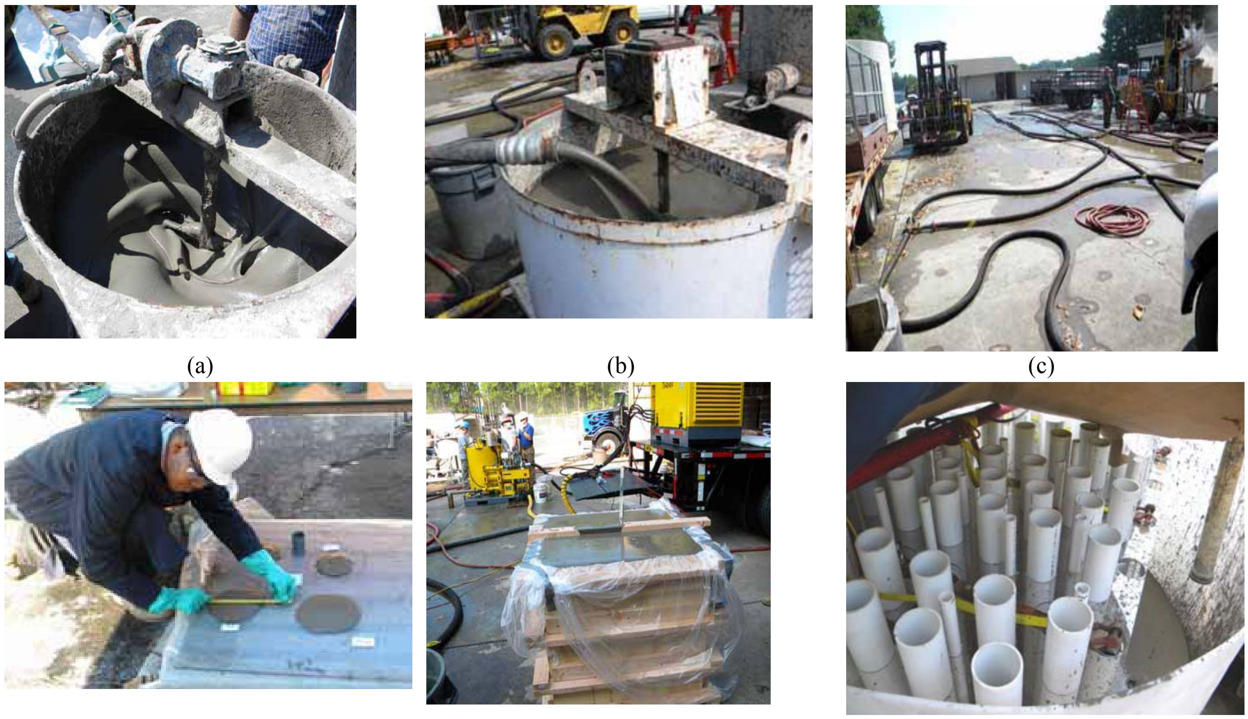
Table 4-10. Blended calcium aluminate – calcium sulfate cement grout recommended for scale-up and mock-up testing.

	Proportions			
Ingredient	Wt. %	(0.25 cu ft)	(1.0 cu ft)	(1.0 cyd)
Ciment Fondu®	9.09	2.82 lbs	11.3 lbs	304.6 lbs
Plaster of Paris	4.55	1.41 lbs	5.6 lbs	152.3 lbs
Class F Fly Ash	15.38	4.77 lbs	19.1 lbs	515.2 lbs
Sand	51.74	16.05 lbs	64.2 lbs	1733.4 lbs
Water	19.25	5.97 lbs 0.72 gal	23.9 lbs 2.87 gal	644.8 lbs 77.4 gal
KIM® 301	--	19.09 g	76.4 g	2061.7 g
Diutan Gum	--	2.16 g	8.6 g	233.3 g
SIKA ViscoCrete® 2100	--	12.95 g	51.8 g	1398.6 g
Boric Acid*	--	5.97 g	40.2 g	1085.4 g

*Boric can be adjusted between 0.5 and 1.25 wt. % of the binder depending on ambient temperature, reagent temperatures, and reactivity of the reagent batch.

4.6.1 Scale-up Test Results

The dry reagents for the mixing and pumping test were pre-blended and packaged in supersacks at Gibson's Pressure Grouting Services, Inc. Each sack contained 500 pounds of solid. The first mixer tested was a colloidal type. This mixer was too slow to incorporate the dry solids which were discharged from supersacks suspended above the mixing tank. Therefore a 25 cubic foot double tub paddle mixer was tested. The paddle blades were better at drawing the solids into the liquid which gave faster solids addition rate and shorter batch time. Photos of the mixing, pumping, static working time testing, and monolith and vessel filling are shown in Figure 4-5.



(a) (b) (c)

(d) (e) (f)

Figure 4-5. Scale-up Test. (a) Mixing Evaluation, (b and c) Re-circulating loop and Pump test, (d) Field static gel time test, (e) Semi-adiabatic temperature rise monolith, and (f) Mock-up vessel flow evaluation.

Once the mixer was selected, twenty five cubic feet (5 batches of dry reagents plus water) of grout were prepared for the pumping / recirculation loop test. A PUMPAC pumping system with a hydraulically driven ball and seat pump with a two stage piston was used. Grout was successfully pumped through 400 ft of 2 inch flexible hose which recirculated back to the agitator hold tank. Pump rates were 10, 20, 30 and about 53 gpm. The slowest pump rate was tested first then the rate was increased sequentially. The ambient temperature during the pumping test was 92.8°F. The grout temperature during mixing rose from 87.5°F to 96.5°F over a 68 minute period.

A 50 psi pressure loss was measured over 100 feet of 2 inch hose at the maximum flow rate. Pressure at the output of the pump was about 150 psi. Cold water was used to cool the mixer and hold tank prior to starting the test. Increasing recirculation time increased the fluidity of the mix as indicated by shorter flow cone measurements. The ASTM flow cone measurements were 24 seconds (30 minute) and 18.5 seconds (60 minute). Initial flows/spreads were 8.75 inch (30 minute) and 8.0 inch (60 minute).

After demonstration of pumping, dry reagents were blended to produce 6 cubic yards of grout for the ¼ scale vessel mock up demonstration and for filling a one cubic yard form for semi-adiabatic temperature measurements. Thermocouples were installed along a vertical support in the center of the plywood form. The thermocouples were spaced 8, 18, 24, and 30 inches from the bottom of the box. Temperature measurements were collected using a calibrated data logger over a period of 10 days. Results for the first 4 days are show in Figure 4-6. The temperature rise measured on the one cubic yard monolith was 53°C. This compares very well with the 54°C adiabatic temperature rise calculated for Mix 102H (Table 4-9) which has the same proportions as the monolith. The peak temperature occurs in about 10 hours which is consistent with results from laboratory samples.

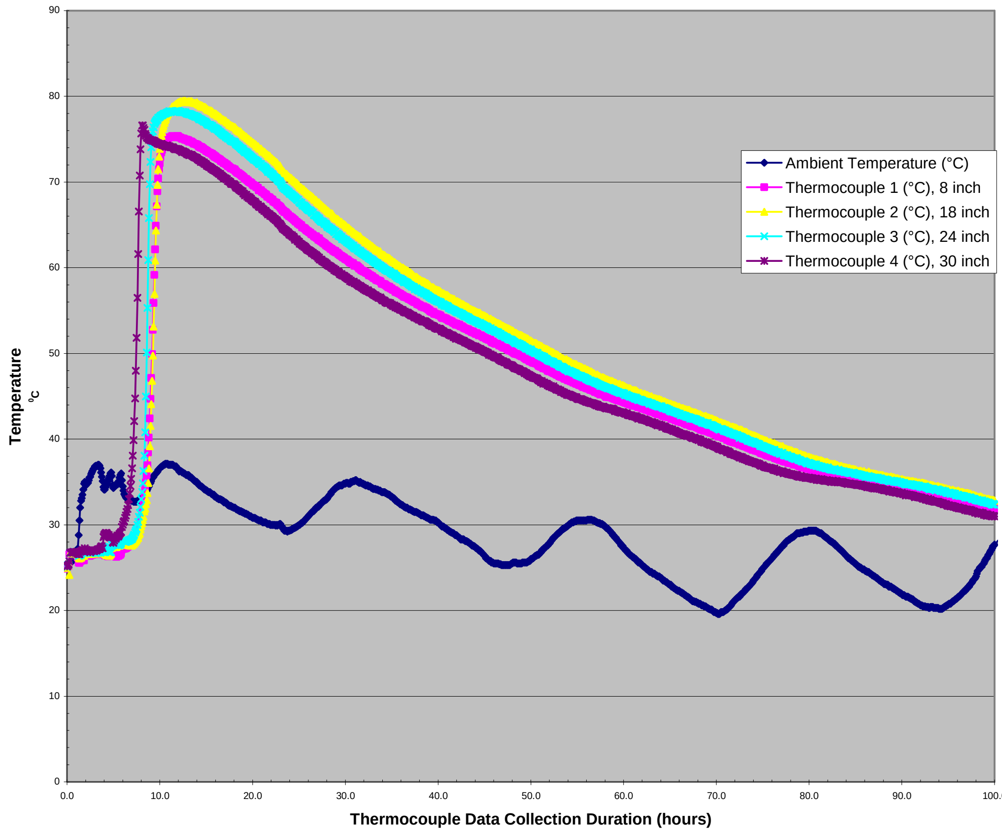


Figure 4-6. Blended calcium aluminate – calcium sulfate cement grout semi-adiabatic temperature results for one cubic yard monolith prepared on 9-2-2010.

Five cubic yards of the blended calcium aluminate - calcium sulfate cement grout were placed during the vessel fill mock up test, September 2, 2010. The grout was dropped about 20 ft (free fall) into the vessel. No segregation was observed and splatter was controlled by the SONO tube used as a guide for the grout stream. The flow rate was progressively increased from 20 gpm (run for 6 minutes) to 30 gpm (run for 4 minutes) to the maximum pump rate of about 50 gpm. The total height of the grout in the tank was about 24 inches. The grout flowed around simulated obstructions, i.e., 4 inch and 1.5 inch PVC pipes representing Universal Sleeve Housings and thimbles, respectively. The difference between level of the grout at the placement point to the opposite side of the tank was less than 1 inch. The number and positions of these obstructions represented the actual conditions in the P-Reactor vessel and were specified by SDD Engineering [Griffin, 2010]. Based on these results and information from samples collected from scale-up tests, the blended calcium aluminate – calcium sulfate grout was selected for the filling P-Reactor Vessel.

4.7 Blended Calcium Aluminate – Calcium Sulfate Grout Mineralogy and Microstructure

Mineralogy and microstructure characterization was performed on a sample taken from the one cubic yard block cast for temperature measurements as part of the mock-up test. See Figure 4- 7. The sample was prepared for powder pattern X-ray diffraction analysis by crushing cured grout to -100 mesh. Ettringite was identified as the primary crystalline cementitious phase. The fine aggregate in the grout was quartz and this mineral was also observed in the XRD patterns. See Figure 4-8. Trace amounts of mullite, $Al_6Si_2O_{13}$, from the fly ash (glass spheres which often contain mullite and cristobalite as refractory phases formed during quenching) was detected in some of the samples analyzed. Amorphous aluminum hydroxide is also present but does not show up in an XRD pattern. Anhydrous calcium aluminate phases in the Ciment Fondu® were also detected in trace amounts. However, the identification of the anhydrous phases is questionable because of the small quantities. Calcium sulfate hemihydrate, and calcium sulfate dihydrate were not present in the hydrated material.


Figure 4-7. Core drilling of the monolith. Samples used for XRD, SEM and strength.

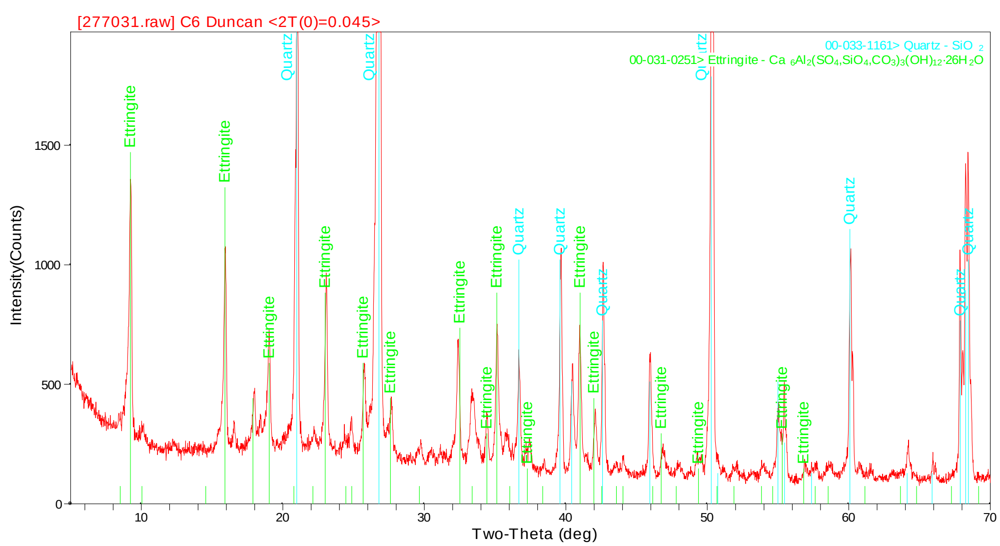
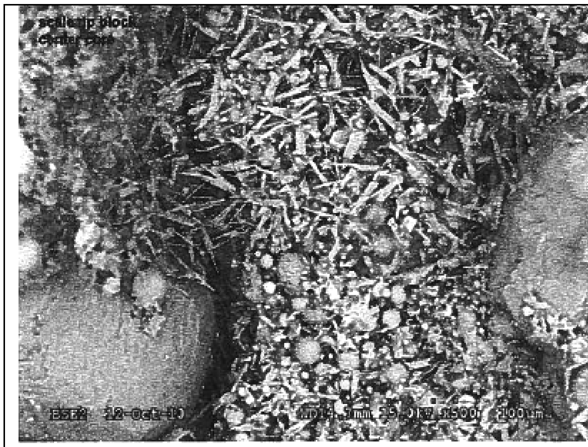


Figure 4-8. X-ray diffraction of hydrated blended calcium aluminate – calcium sulfate (2:1 by weight) cement grout. Ettringite is the only cementitious crystalline phase. Quartz sand, the fine aggregate in the grout is also present in the sample analyzed.

Scanning electron microscopy was used to characterize the microstructure of the blended calcium aluminate – calcium sulfate-based grout. Back scattered electron images are shown in Figure 4-9. Needles of ettringite form an interlocking matrix around fly ash particles (spherical) and quartz sand grains (irregular to equant grains). Amorphous aluminum hydroxide is present as an interstitial phase between the ettringite crystals and other particles. (See Figure 4-9 5000X magnification). Several morphologies were observed for ettringite; long well defined interlocking needles are embedded in short stubby needles.



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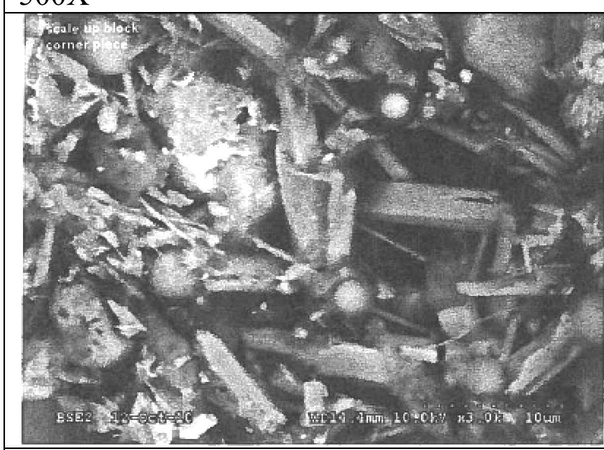

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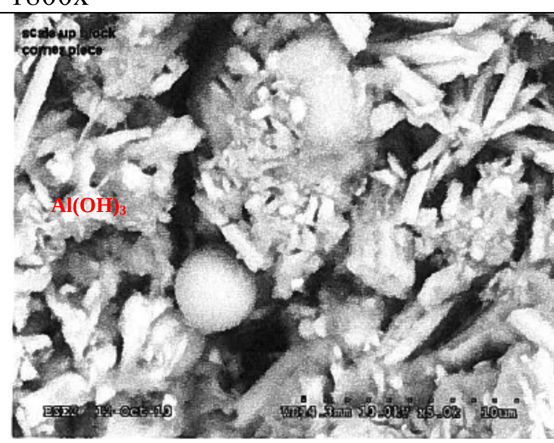

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Figure 4-9. Microstructure of the hydrated blended calcium aluminate – calcium sulfate cement-based grout.

The average compressive strength measured from cores taken from the monolith was 950 psi and the average saturated hydraulic conductivity was 3E-06 cm/s (measured by ASTM D-5084).

5.0 DISCUSSION AND CONCLUSIONS

Blended calcium aluminate – calcium sulfate cement met the chemical and mineralogical requirements for a reactor fill grout. The pH of water in contact with fresh and cured cement was 9 to 10 which met the requirement of < 10.5, and the primary cementitious phase was ettringite which is stable in this system. Aluminum hydroxide was also formed in the matrix and is compatible with the materials of construction for the reactor vessel and internal components. Ciment Fondu® and Plaster of Paris were identified as commercially available components which could be blended in a ratio of 2 to 1 by weight to produce a hydrated matrix consisting of ettringite and amorphous aluminum hydroxide. This blend of ingredients required a set retarder as indicated by static working times of less than 15 minutes. Citric acid and boric acid were effective set retarders. A lower dose of citric acid was required compared to boric acid for the same set delay. Boric acid was selected for the scale-up testing and subsequently the final mix because it was available at Gibson's Pressure Grouting Services, Inc. during the scale-up testing.

A grout fill requires inert fillers in addition to a suitable cement binder. The inert fillers used in the blended calcium aluminate – calcium sulfate cement grout were the same as those specified for the magnesium potassium phosphate flowable fill developed in an earlier study [Stefanko, 2010]. A bimodal particle size distribution was found to be effective in reducing segregation and enhancing flow behavior. Consequently, a mixture of Class F fly ash and quartz sand (ASTM C-404 masonry sand or ASTM C-637 Grade 2 sand) in a ratio of about 1:3 was selected for the blended calcium aluminate – calcium sulfate cement grout.

Based on laboratory bench-scale and bench scale-up testing and the mixing, pumping and ¼ scale mock up testing at Gibson's Pressure Grouting Services, Inc., a blended calcium aluminate – calcium sulfate cement grout with a water to binder ratio of 1.41 was selected as the reactor fill production grout. Proportions and fresh and cured properties are provided in Tables 5-1 and 5-2, respectively.

After the grout mock up testing, formulation adjustments to lower the water to binder ratio were tested. This work was performed because full-scale mixing (better agitation) resulted in more fluid grouts than what had been achieved during bench-scale mixing. These adjustments consisted of replacing water with ASTM C 637 gradation 2 sand, reducing the amount of diutan gum, and adding a small amount of additional HRWR (SIKA ViscoCrete 2100). This effort resulted in development of a second blended calcium aluminate – calcium sulfate cement grout with 12 wt.% less water. The proportions and properties are listed in Tables 5-1 and 5-2, respectively. Since full-scale testing was not performed on this formulation, it was not recommended as the production fill material. However, the reduction in water to binder resulted in higher compressive strengths and is expected to result in lower porosity and permeability. (This mix is very sensitive to the amount of SIKA ViscoCrete 2100. A small amount of additional SIKA ViscoCrete 2100 resulted in delaying set and lower early strengths.)

Table 5-1. Blended calcium aluminate – calcium sulfate grouts developed for P-Reactor vessel ISD.

Ingredient	Water to binder weight 1.41		Water to binder weight 1.24	
	(Lbs/yd^3)	(Kg/yd^3)	(Lbs/yd^3)	(Kg/yd^3)
Ciment Fondu® (Kerneos Aluminate Technologies)	304.3	180.5	304.3	180.5
Plaster of Paris (US Gypsum Company)	152.2	90.3	152.2	90.3
Class F Fly Ash ASTM C-616 (SEFA, Inc.)	514.8	305.4	514.8	305.4
ASTM C-404 Masonry sand or ASTM C-637 Sand for grout for pre-placed aggregate	1732.0	1027.6	1937	1150
Water	644.3	382.2	566.9	366.4
KIM® 301 (Integral Water Proofing Admixture) (Kryton, International Inc.)	4.5	2.7	4.5	2.7
SIKA ViscoCrete® 2100 (W.R. Grace, Inc.)	3.1	1.8	3.4	2.0
Diutan Gum (CP Kelco, Inc.)	0.5	0.3	0.17	0.1
Boric Acid (if needed) (Alfa Aesar)	3.4	2.0	3.4	2.0
Total	3359	1993	3487	2069

Table 5-2. Properties of P-Reactor vessel blended calcium aluminate –calcium sulfate cement grouts

Property	Water to binder weight 1.41	Water to binder weight 1.24
Slurry Properties (Fresh Properties)		
pH P-Reactor Vessel	9 to 10 fresh slurry and water in contact with cured sample	9 to 10 fresh slurry and water in contact with cured sample
Flow Cone	40 s (average)	41 s
Static Working Time	45 min.	45 minutes
Dynamic Working Time	2-4 hr	~ 4 hr
Set Time	~ 4 hr	~ 24 hr
Density (wet unit weight)	1986 kg/m^3 124 lbs/ft^3	2066 kg/m^3 129 lbs/ft^3
Bleed water	None	None
Segregation	None	None
Maximum particle size	1 mm maximum	1 mm maximum
Cured Properties Compressive Strength		
3 days	5.24 MPa 760 psi	4.55 MPa 660 psi
7 day	7.22 MPa 1047 psi	12.89 MPa 1870 psi
28 days	7.5 MPa 1084 psi	Not measured
Saturated Hydraulic Conductivity	3E-06 cm/s	4.1E-07 cm/s
Adiabatic temperature rise	54°C	~51°C estimate

6.0 RECOMMENDATIONS

SRNL Mix T12-1 (Ciment Fondu®, 9.06 wt. %; Plaster of Paris, 4.53 wt. %; ASTM C-637 gradation 2 quartz sand, 51.56 wt. %; Class F fly ash, 15.32 wt.%; KIM® 301, 0.135 wt. %; SIKA ViscoCrete® 2100, 0.092 wt. %; boric acid, 0.10 wt. % (0.75 wt. % of the binder); diutan gum, 0.015 wt. %; and water 19.18 wt. % is recommended for filling the SRS P-Reactor Vessel. A bimodal distribution of inert fillers (powder and sand) is recommended to achieve a low heat, stable slurry. The recommended mix is shown in Table 6-1.

Table 6-1. Recommended blended calcium aluminate – calcium sulfate cement grout for P-Reactor vessel ISD.

	Water to binder weight 1.41	
Ingredient	**(Lbs/yd^3)**	**(Kg/m^3)**
Ciment Fondu® (Kerneos Aluminate Technologies)	304.3	180.5
Plaster of Paris (US Gypsum Company)	152.2	90.3
Class F Fly Ash ASTM C-616 (SEFA, Inc.)	514.8	305.4
ASTM C-404 Masonry sand or ASTM C-637 Sand for grout for pre-placed aggregate	1732.0	1027.6
Water	644.3	382.2
KIM® 301 (Integral Water Proofing Admixture) (Kryton, International Inc.)	4.5	2.7
SIKA ViscoCrete® 2100 (W.R. Grace, Inc.)	3.1	1.8
Diutan Gum (CP Kelco, Inc.)	0.5	0.3
Boric Acid (Technical grade)	3.4	2.0
Total	3359	1993

* Proportions per unit volume were confirmed on large size batches.

Pre-blending of all of the solid ingredients is recommended for quality control and for simplifying full-scale production of this special material. Pre-measuring the SIKA ViscoCrete® 2100 HRWR for each batch is also suggested.

The recommended mix design does not required use of chilled water for ambient temperatures up to 32°C provided the grout is continually agitated and placed within an hour after solids addition.

The mixing and pumping equipment used in the full-scale mixing and pumping test are suitable for full-scale production, i.e., double tub 25 cubic foot paddle mixer and 25 cubic foot agitator tank, PUMPAC hydraulically driven ball and seat pump with a two stage piston, and two inch flexible grout hose.

A minimum of 8 minutes of mixing (measured from the time all of the solids are added to the water) is required to achieve uniform properties during full-scale mixing.

7.0 QUALITY ASSURANCE

Work was performed in accordance with TT/QAP SRNL-RP-2009-01248, Revision 0 using calibrated laboratory and test equipment. Results are recorded in Laboratory Notebooks SRNL-NB-2009-00166 (mix formulations), SRNL-NB-2010-00120 (scale up), WSRC-2004-NB-0064, and SRNL-NB-2009-00162 (calorimeter data).

8.0 ACKNOWLEDGEMENTS

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W. L. Mhyre, 717-5N
J. C. Musall, 707-25B
F. M. Pennebaker, 773-42A
W. Pope, Jr., 717-5N
M. G. Serrato, 773-42A
D. B. Stefanko, 773-43A
J. L. Steimke, 786-5A
J. T. Waymer, 717-5N
STI