SRNL-STI-2010-00333 Revision 0

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

Retention: Permanent

MAGNESIUM MONO POTASSIUM PHOSPHATE GROUT FOR P-REACTOR VESSEL IN-SITU DECOMMISSIONING

David B. Stefanko, Christine A. Langton

Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
Aiken, SC 29808

And

Dileep Singh

Argonne National Laboratory
Argonne, IL 60439

January 5, 2011

Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
Aiken, SC 29808
Prepared for the U.S. Department of Energy
Under Contract No. DE- AC09-08SR22470

SRNL
SAVANNAH RIVER NATIONAL LABORATORY
TM

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

SRNL-STI-2010-00333 Revision 0

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

Retention: Permanent

MAGNESIUM MONO POTASSIUM PHOSPHATE GROUT FOR P-REACTOR VESSEL IN-SITU DECOMMISSIONING (U)

David B. Stefanko, Christine A. Langton

Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
Aiken, SC 29808

And

Dileep Singh

Argonne National Laboratory
Argonne, IL 60439

January 5, 2010

Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
Aiken, SC 29808
Prepared for the U.S. Department of Energy
Under Contract No. DE- AC09-08SR22470

EXECUTIVE SUMMARY

Results of laboratory tests to evaluate magnesium mono potassium phosphate grout for P-reactor vessel in-situ decommissioning are provided in this report. Magnesium mono potassium phosphate cement-based grout was identified as candidate material for filling (physically stabilizing) the 105-P Reactor vessel (RV) because it is less alkaline than portland cement-based grout (pH of about 12.4) [Singh, 2009]. A less alkaline material ($\leq$ 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, 2009, Wiersma, 2010, Serrato, et al., 2010].

This work supports scope identified and authorized in TAR-SDD-2008-00133, TAR-SDD-2009-00231, and TT/QAP, SRNL-RP-2009-01248. This work supports the SRS Reactor In-Situ Decommissioning (ISD) Projects.

Argonne National Laboratory (ANL) researchers have considerable experience with magnesium mono potassium phosphate grouts. Consequently, D. Singh, ANL, was funded by EM 30/44 to provide consultation and to modify the Ceramicrete® magnesium mono potassium phosphate cementitious system for the SRS reactor vessel application. Results of the ANL and SRNL testing are presented in this report.

The formulations evaluated at ANL used Class C fly ash and general purpose quartz sand as fillers. Class C fly ash does react with water and possibly with phosphate so this material is not completely inert in the magnesium mono potassium phosphate system. However, it does provide certain benefits to the grout properties and enables the use of higher doses of boric acid set retarder which extends the working time of the resulting materials. The formulations developed by ANL had good placement properties and compressive strengths. However, the reaction rates for the cementitious components were slow and the temperature was still rising after two weeks at which time it was approaching the upper limit for reactor vessel ISD. In addition, although the slurries had pHs of 6 to 8, the pH of water in contact with samples of cured material taken from the adiabatic calorimeter were about 11.2 which is higher than the 10.5 limit recommended for filling the SRS P-Reactor vessel which contains aluminum metal components [Wiersma, 2009].

The testing performed at SRNL focused on evaluating commercially available magnesium mono potassium phosphate packaged products (Bindan Corporation Mono-Grout SR products), modifying these products (modified Mono-Grout SR mixes), and formulating magnesium mono potassium phosphate grouts from customized blends of reactive and inert materials. Modifications of the Mono-Grout SR products focused on mixtures of the Mono-Grout SR binder and inert fillers. Inert fillers were added to dilute the reactive reagents and thereby reduce the temperature rise resulting from exothermic reactions, to improve the flow and reduce segregation. Special graded quartz sands, glass beads, bauxite beads, and locally available masonry sand in addition to inert Class F fly ash were added to the modified SRNL mixes. In addition, an integral water proofing admixture and an inorganic set retarder were also included in the mixes.

Formulations that use inert fillers, i.e., Class F fly ash or silica flour and silica sand or other inert sand are preferred over formulation that include a low reactivity filler. Inert fillers are better suited to controlling the temperature of a mass pour, i.e., the total heat generated from the reactive components and the rate of heat generation. Consequently mixes containing Class F fly ash and silica sand are recommended over mixes containing Class C fly ash.

A mix containing 14 wt. % Bindan SR 3.10 binder, 12.2 wt. % water (boric acid is in the packaged product), 19.3 wt. % Class F fly ash and 54.3 wt. % inert sand-size aggregate) and 1.0 wt.% of the binder KIM integral water proofing reagent is recommended for scale-up testing. The mix design for a one cubic yard batch is provided below:

Ingredient	Lbs/cuft	Lbs/cuyd
Bindan SR3.10 Binder	18.9	510.2
Class F fly ash	26.0	701.0
KIM 301	0.19	5.1
ASTM C 33 masonry sand	73.2	1976.4
Chilled water (10°C)	16.5	446.2
Boric Acid (technical grade)	As needed	As needed
Set retarding admixture if required such as W. R. Grace Daratard 17	As needed	As needed
Total	134.8	3639.9

This mix contains a bimodal distribution of inert fillers (powder and sand) which was beneficial in obtaining both flowable stable slurries and high inert fill loadings. Laboratory bench-scale testing indicated that the water requirement is sensitive to the specific inert fillers used (particle size distribution, surface roughness, moisture content and surface saturated dryness, etc.) and to temperature. Consequently, chilled water (< 10°C, i.e. < 50°F) is required for scale-up testing and for full-scale production of magnesium mono potassium phosphate grout formulations. Up to 11 wt.% additional water (percent of the total amount of water) may be added to the base mix to achieve flow cone results of less than 40 seconds. Both of these modifications result in mixes that meet the fill requirements.

Commercially available binder blends (packaged binder products) are preferred because this allows commercial suppliers to apply their expertise and quality control to formulating these materials. The best results were obtained with Bindan Corporation SR 3.10 Binder. This binder is recommenced for scale-up testing.

Stable slurries (one that does not segregate) can also be achieved with the ANL mixes containing Class C fly ash, quartz sand, and magnesium mono potassium phosphate binder. However, the water demand will be higher and organic admixtures may be required.

The ability to make field adjustments in the amount of sand and fly ash is recommended so field conditions can be addressed and slight modifications to the mix can be made on site.

An alternative low pH grout system should be developed in case the scale-up testing of the magnesium mono potassium phosphate system is found to present problems that can not be

overcome in time to meet the project schedule. Calcium aluminate – gypsum based cement which hydrates to form ettringite as a primary phase is a potential candidate for meeting the reactor vessel fill requirements.

The laboratory testing described in this report is the first part of a phased program for evaluating magnesium mono potassium phosphate-based grouts for reactor vessel ISD. Because industry does not have experience with pumping magnesium mono potassium phosphate cementitious grouts or concretes or in mass pours, scale-up testing is required. Details of the scale-up testing are provided elsewhere, G-SOW-G-00121 [Griffin, 2010]

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS

ANL	Argonne National Laboratory
ASTM	American Society for Testing & Materials
cP	centipoise
DOE	Department of Energy
EARAIP	Early Action Remedial Action Implementation Plan
E&CPT	Engineering and Chemical Processing Technology
EDX	Energy Dispersive X-ray
EM	Environmental Management
ISD	In-Situ Decommissioning
LLC	Limited Liability Corporation
MKP	Mono Potassium Phosphate
MPO	Memorandum Purchase Order
PAOU	P-Area Operable Unit
PS&E	Process Science and Engineering
Psi	pounds per square inch
RH	Relative Humidity
RV	Reactor Vessel
S	seconds
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
WSRC	Washington Savannah River Company

1.0 INTRODUCTION

1.1 Objective

The objective of this report is to document laboratory testing of magnesium mono potassium phosphate grouts for P-Reactor vessel in-situ decommissioning.[1] Magnesium mono potassium phosphate cement-based grout was identified as candidate material for filling (physically stabilizing) the 105-P Reactor vessel (RV) because it is less alkaline than portland cement-based grout (pH of about 12.4) [Singh, 2009]. A less alkaline material ($\leq$ 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, 2009, Wiersma, 2010, and Serrato, et al., 2010]. Information concerning access points into the P-Reactor vessel and amount of aluminum metal in the vessel is provided elsewhere [Stefanko, 2009 and Wiersma, 2009 and Bobbitt, 2010, respectively].

Fresh and cured properties were measured for:

1. Commercially blended magnesium mono potassium phosphate packaged grouts,
2. Commercially available binders blended with inert fillers at SRNL,
3. Grouts prepared from technical grade MgO and KH_2PO_4 and inert fillers (quartz sands, Class F fly ash), and
4. Ceramicrete® magnesium mono potassium phosphate-based grouts[2] prepared at Argonne National Laboratory.

Boric acid was evaluated as a set retarder in the magnesium mono potassium phosphate mixes.

This work supports scope identified and authorized in TAR-SDD-2008-00133, TAR-SDD-2009-00231, and TT/QAP, SRNL-RP-2009-01248. This work supports the SRS Reactor In-Situ Decommission (ISD) Project.

1.2 P-Reactor Vessel In-Situ Decommissioning

1.2.1 P-Area Reactor Vessel Description

SRNS committed to the Department of Energy that it will 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 concrete. These features 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 current plan is to pull plugs in 3 to 8

[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 [Serrato, 2010 and Wiersma, 2010].
[2] Ceramicrete® is magnesium mono potassium phosphate cement and they are one and the same material.

permanent sleeves along the circumference of the vessel and to use these positions as grout entry and vent points in the vessel. The details of the connection between the grout hose and reactor vessel will be finalized after scale-up testing and final design of the grout placement.

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

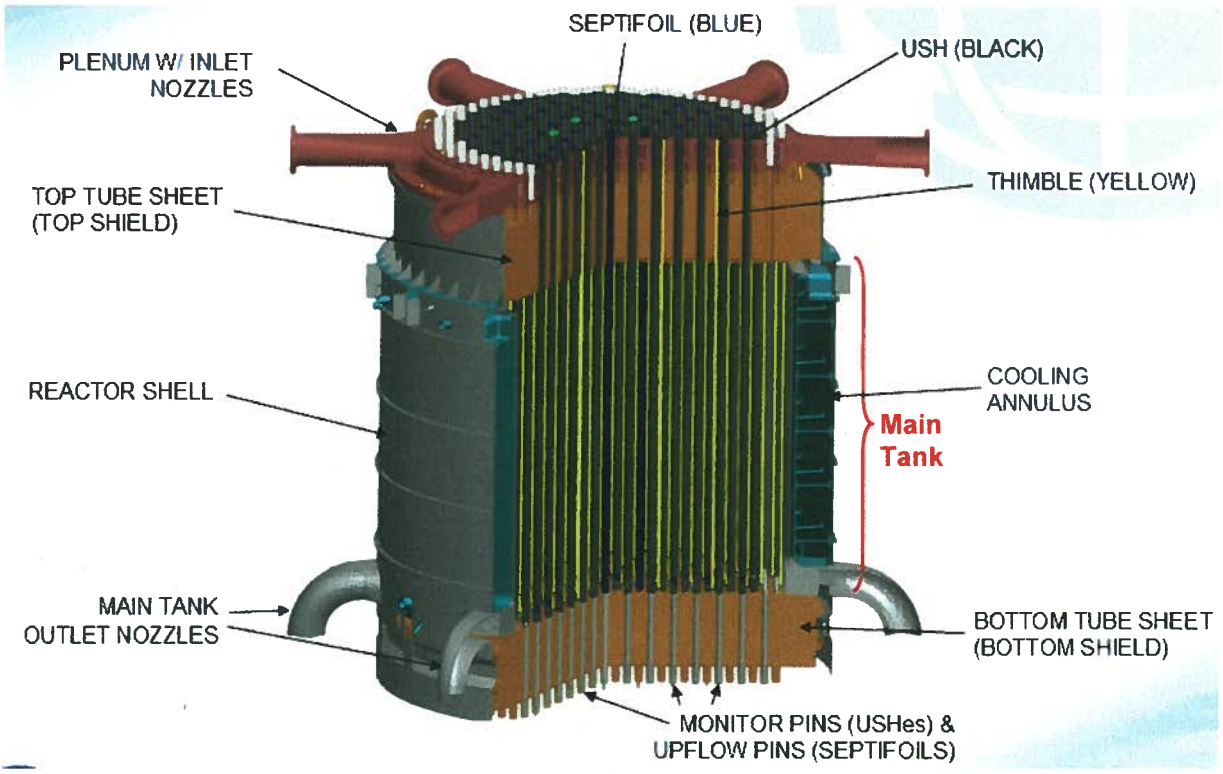

Figure 1-2. P-Reactor cross section [Vrettos, 2009].

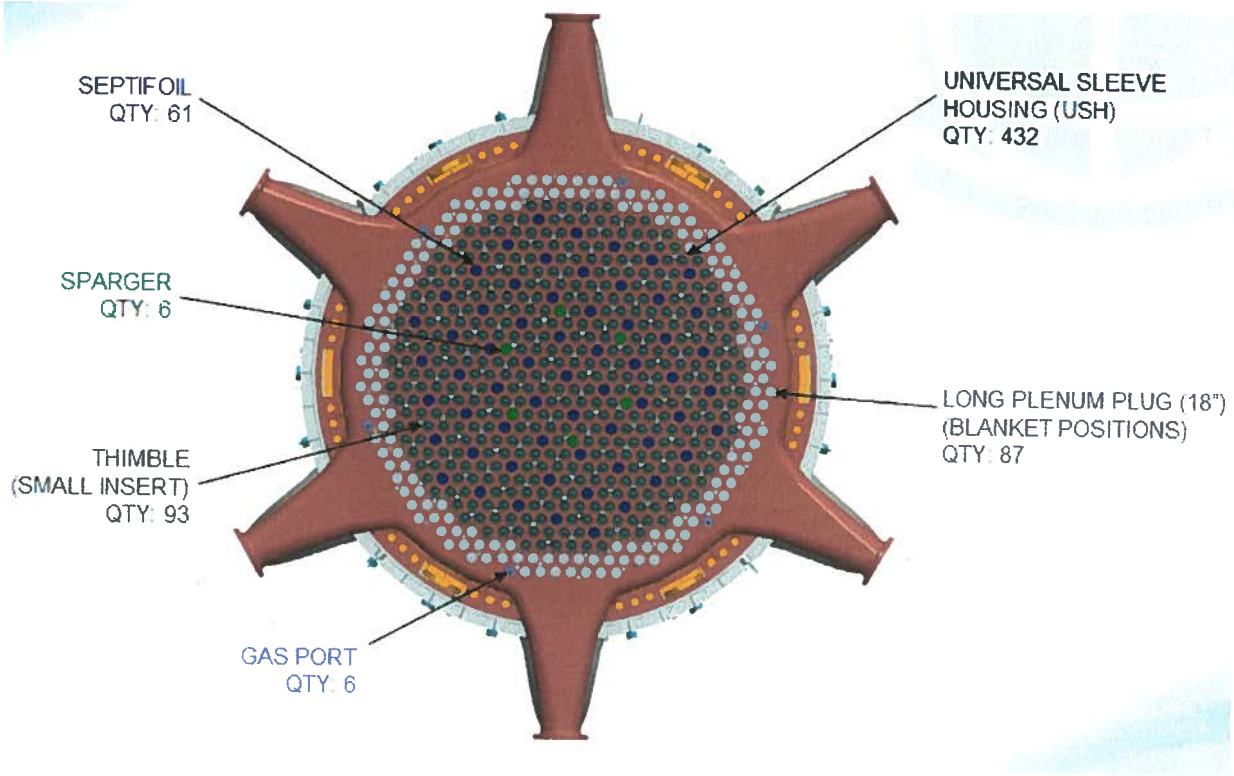

Figure 1-3. P-Reactor plan view [Vrettos, 2009].

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 operations (ALARA, cost, schedule, waste generation).

1.3 Magnesium Mono Potassium Phosphate Cement / Grout Description

Magnesium mono potassium phosphate-based cementitious materials are used in the construction industry for a variety of applications including rapid set road and airport runway repairs, structural applications, and anchor bolt cementing. Ceramicrete®, a magnesium mono potassium phosphate-based material patented by Argonne National Laboratory (ANL) was selected for testing because the pH of the fresh material is about 6, and phosphate chemistry is compatible with the steel vessel and stabilizes many of the radionuclides in the vessel. (Ceramicrete® also contains Class C fly ash as a functional filler that enhances the strength of the final product.)

A survey of the literature and industry practice indicated that formulating a pumpable, flowable, self-leveling, magnesium mono potassium phosphate slurry is not routine and may be a first time application of this technology. Techniques for reducing and managing reaction heat in a mass pour (more than 6 to 12 inch lifts) included dilution by incorporating inert aggregates (sand and Class F fly ash) and extreme set retardation.

Magnesium mono potassium phosphate cements were invented at ANL [Wagh, 1998, Patent 5,830,815 and Singh, 1998, Patent 5,846,894] and are composed of an acid, in this case, monopotassium phosphate (MKP), KH_2PO_4, and a base, MgO. When MgO and MKP are mixed with H_2O in the following proportions (1:1: 5 moles, respectively) the resulting reaction product is struvite, $MgKPO_4 \cdot 6H_2O$, a crystalline material that forms a dense cementitious ceramic.

Equation 1. $\mathbf{MgO + KH_2PO_4 + 5H_2O \longrightarrow MgKPO_4 6H_2O}$

In packaged magnesium mono potassium phosphate products based on MgO and MKP, the stoichiometric ratio is often not used because a portion of the dead / hard burned MgO is not reactive or has very low solubility. Consequently, the amount of MKP is reported to be reduced by up to 30 weight percent of the stoichiometric amount required in the case where all of the MgO were to be consumed in the reaction. This reduces the amount of excess potassium and phosphate leaching which causes an increase in porosity and efflorescence (G. M. Diken, 2010.)

The reaction in Equation 1 is an acid-base reaction and is exothermic. From the standpoint of managing reaction heat in the reactor vessel, the desire is to minimize the amount of reactive material, i.e., the binder phase but still produce a cementitious product. For the starting materials used in this study, a temperature between 60° and 65° C was required to produce a monolithic product. At lower temperatures, the reaction to struvite, $MgKPO_4 \cdot 6H_2O$, was incomplete and the resulting material was not cementitious. In other words, if the starting material is cooled too much or if the reactive components are overly diluted with inert ingredients; the resulting grout does not set to a monolithic material. Amorphous hydrated phosphate phase(s) which are less dense and less cementitious are formed instead.

Magnesium mono potassium phosphate cements typically exhibit a slight expansion, 1 to 2 volume percent, when prepared in stoichiometric proportions for commercial applications. The magnesium mono potassium phosphate cement-based materials also exhibited excellent bonding to metal substrates, including stainless steel and aluminum metal.

1.3.1 Magnesium Mono Potassium Phosphate Grout Material Sources

Magnesium mono potassium phosphate cement grout and concrete products based on mixtures of MgO and monopotassium phosphate (MKP), KH_2PO_4, are manufactured by several companies, e.g., Bindan Corporation, Chicago IL, Ceratec, MD, BASF, Inc., and Euclid Chemical Company, Cleveland OH. The Mono-Grout packaged product line, manufactured by Bindan Corporation, was selected for testing because it was marketed for self-leveling applications.

Blended magnesium mono potassium phosphate binder (no aggregates) was also obtained from Bindan Corporation for this study. These materials allowed SRNL to adjust the amount of

reactive material in test specimens. Other manufacturers were contacted but did not provide samples.

Further control of the binder and grout composition was achieved by using neat MgO and neat MKP in mixes designed by SRNL. The magnesium oxide used in these cements is typically manufactured at 1350 to 1550°C. The higher temperature materials are referred to as hard burned or dead burned depending on the calcining temperature. Samples of hard burned MgO, MagChem® 10CR and dead burned MgO, MagChem® P98-30 mesh and MagChem® P98 pulverized were obtained for testing. MgO P98 was also obtained from Bindan Corporation.

MKP is also produced / distributed by several companies, e.g., ICL Performance Products, LP, V. L. Clark Chemical Company, and is available in several grades (purity, particle size and manufacturing process). Two ICL products tested were: MKP 200 granular, MKP 771 (Rotem®), in addition to MKP provided by Bindan Corporation.

Inclusion of Kryton International Inc. KIM® 301, an integral waterproofing reagent, in the reactor fill grout was required by SDD / SRNS [Blankenship, 2009].

1.4 Approach

Because ANL researchers have considerable experience with magnesium mono potassium phosphate grouts, D. Singh, ANL, was funded by EM 30/44 to provide consultation and to modify the Ceramicrete® material for the SRS reactor vessel application.[3]

The testing performed at ANL was independent of the testing performed at SRNL. The formulations evaluated at ANL used Class C fly ash and also mixtures of Class C fly ash and general purpose quartz sand as inert fillers. Class C fly ash does react with water and possibly with phosphate so this material is not completely inert in the magnesium mono potassium phosphate system. However, Class C fly ash does provide certain benefits to the grout properties, such as longer working time and continued strength gain over weeks. A summary of the results of the test program conducted at ANL are included in this report.

The testing performed at SRNL focused on evaluating commercially available magnesium mono potassium phosphate packaged products (Bindan Corporation Mono-Grout SR products), modifying these products (modified Mono-Grout SR mixes), and formulating magnesium mono potassium phosphate grouts from customized blends of reactive and inert materials. Modifications of the Mono-Grout SR products focused on mixtures of the Mono-Grout SR binder and inert fillers. Inert fillers were added to dilute the reactive reagents and thereby reduce the temperature rise resulting from exothermic reactions, to improve the flow and reduce segregation. Special graded sands, glass beads, bauxite beads, and locally available masonry sand in addition to inert Class F fly ash[4] were added to the modified SRNL mixes.

---

[3] An Inter-Entity Work Order from DOE-SR was issued to ANL to perform the Statement of Work [Work Order Number M5Z0703, 2009 and Statement of Work 0S0202 G-SOW-A-00086, Rev. 0, respectively]. DOE-EM 30/44 is funding the feasibility study, Option 1 of this SOW.

[4] Class F fly ash is not pozzolanic (reactive) in the magnesium mono potassium phosphate system.

The laboratory testing described in this report is the first part of a phased program for evaluating magnesium mono potassium phosphate grouts for reactor vessel ISD. Because industry does not have experience with pumping magnesium mono potassium phosphate cementitious grouts or concretes or in mass pours, scale up testing is required.[5] Details of the proposed scale up testing are provided elsewhere, G-SOW-G-00121 [Griffin, 2010].

[5] Relevant properties of the commercially available materials are provided in the test plan. Approaches to improving working time, set time, rheology, and maximum temperature resulting from exothermic reactions are provided in the test plan [Stefanko, 2009].

2.0 EXPERIMENTAL METHOD

2.1 Test Methods

The initial SRNL scoping tests are listed below:

Table 2-1. Issues and tests for evaluating magnesium mono potassium phosphate cements for flowable mass pour grout applications.

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 (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 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

Researchers at ANL performed ASTM C-939 to measure flow, ASTM C-942, to prepare and measure compressive strength, and the SRNL calorimeter method for determining reaction heat.

Figure 2-1. Hobart planetary mixer used for preparing samples.

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

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

Figure 2-4. Static gel time test samples. Modified after ASTM D-6103 by performing after selected time intervals.

Figure 2-5. Compressive strength cubes prepared per ASTM C-942 prior to stripping molds.

Figure 2-6. ASTM C-39 Compression Test Apparatus.

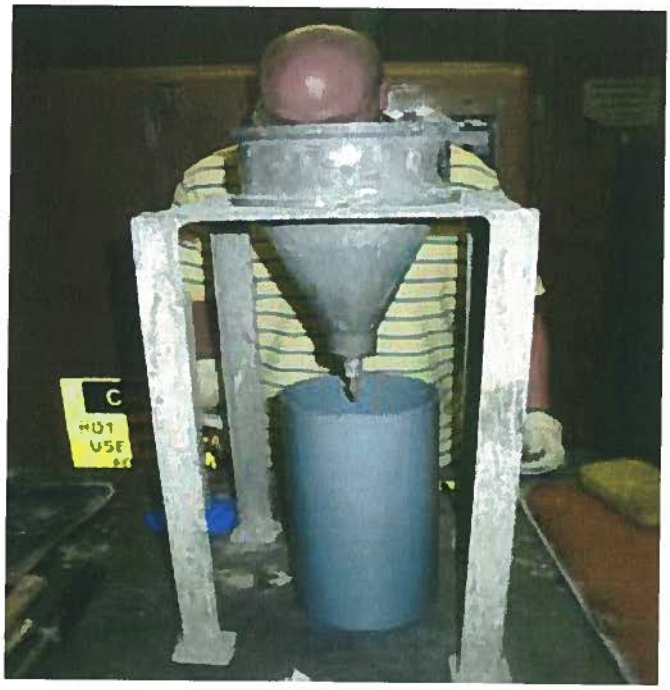

Figure 2-7. ASTM C-939 flow cone test.

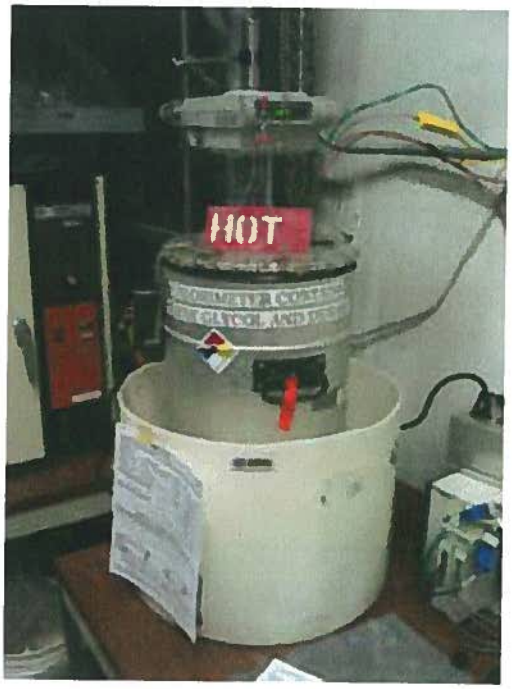

Figure 2-8. SRNL adiabatic calorimeter.

2.2 Starting Materials

Starting materials and suppliers are provided in Table 2-2.

Table 2-2. Materials used in laboratory testing.

Material	Supplier
Packaged Grout Products	Bindan Corp. Tom. Lally, Oak Brook IL, 630-734-0277 lally@bindancorp.com
Mono-Grout SR 1.0	Bindan Corp. 630-734-0277
Mono-Grout SR 2.0	Bindan Corp. 630-734-0277
Mono-Grout SR 3.0	Bindan Corp. 630-734-0277
Mono-Grout SR 3.10	Bindan Corp. 630-734-0277
SR 3.10 Binder (only)	Bindan Corp. 630-734-0277
MgO	
Hard Burned MagChem® 10CR Manistee MI Plant	Martin Marietta Magnesia Specialties, Daryl Stafford 865-377-4086 865-640-5743 (mobile) Daryl.stafford@martinmarietta.com
Dead Burned MagChem® P98 Pulverized Manistee MI Plant	Martin Marietta Magnesia Specialties, 865-377-4086
Dead Burned MagChem® P98 (-30 Mesh) Manistee MI Plant	Martin Marietta Magnesia Specialties, 865-377-4086
MgO P98 (believed to be MagChem® 10CR)	Bindan Corp. 630-734-0277
MKP	
MKP-200 (monopotassium phosphate, KH_2PO_4) granular	ICL Performance Products, LP, John K. Hager, 305-668-9159 800-244-6169 john.hager@icl-performanceproductslp.com
MKP 771 Rotem®	ICL Performance Products, LP, 800-244-6169
MKP	Bindan Corp. 630-734-0277
Powder Filler	
Class F Fly Ash (< 3 wt. % carbon) Wateree Plant, SC	SEFA. 803-520-9000
Sand Fillers	
Graded Quartz Sands	AGSCO 847-520-4454, US Silica 304-258-2500
Glass Beads	AGSCO 847-520-4454,
Bauxite Beads	AGSCO 847-520-4454,
Masonry Sand ASTM C-404	SCMI (South Carolina Mineral Industry) South Carolina Highway 125 Quarry
Additives	
KIM® 301	Kryton International Inc. www.kryton.com 800-267-8280
Boric Acid Technical grade, H_3BO_3	Reagents Inc. Charlotte, NC 704-554-74774
Water	SRS Process Water SRS Chilled Process Water (< 10°C)

Limited characterization of the SR 3.10 Binder material was performed. Based on x-ray diffraction results, the Bindan Binder contained mono-potassium phosphate, KH_2PO_4 and MgO in addition to other minor ingredients. Based on SEM imaging, the MKP particles had a rod-shaped morphology. The MgO was ground to a fine powder which appeared as a "dusting" on the MKP rods.

Boron (presumably from boric acid or a borate compound set retarder) and calcium (possibly from a calcium phosphate compound) were also identified in the Bindan 3.10 binder material. (No boron compounds were detected in the SEM / EDX analysis.)

The aggregate fraction sieved from the Bindan Mono-Grout SR 3.10 material consisted of a silicon containing compound (silica flour) and a sand size fraction consisting primarily of limestone or a dolomitic limestone (calcium, magnesium carbonate).

Table 2-3. Characterization of SR 3.10 Binder and Mono-Grout 3.10 aggregate.

Material	Wet chemical Analysis*	SEM / EDX	X-Ray Diffraction	No detected
SR 3.10 Binder	Major: K, Mg, P, Minor: Ca, Trace: B, Si, S	Powder: Mg, O Rod crystals: P, K, O Powder, Ca, P, O	MKP (Archenite), MgO (Periclase) Numerous unidentified peaks	Boric acid crystals or particles, Organic compounds
Mono-Grout SR 3.10 (aggregate)	Major: Si, Minor: Al, P. K, Ca, Mg Trace: Na, Fe,	Aggregates coated with MgO and MKP	Quartz (SiO_2), Dolomite ($CaMg(CO_3)_2$), Albite Feldspar ($NaAlSi_3O_8$)	

* For this tabulation the following designations were applied: Major > 5 wt. %, Minor 5- 1 wt. %. Trace 1-0.1 wt. %. Other trace components < 0.1 wt. % are not listed.

3.0 RESULTS: SRNL MAGNESIUM MONO POTASSIUM PHOSPHATE GROUT

3.1 Bindan Mono-Grout SR Packaged Products

SRNL testing was limited to screening tests to determine feasibility of several commercial products and blends of MgO and MKP reagents plus inert fillers to produce a suitable grout for filling the 105-P reactor vessel.

The first product tested was Bindan Mono-Grout SR 1.0. It contained binder ingredients and fine quartz. When mixed according to the manufacturer's directions, the grout had excellent flow, 45 minutes of static working time, more than 1 hour dynamic working time but it segregated. Consequently, Class F fly ash was added to Bindan Mono-Grout SR 1.0 to reduce segregation. This effort also resulted in a mix with acceptable flow properties but a lower strength because the modified mix had a high water demand to maintain flow properties. The adiabatic temperature rise was also too high for the SRS reactor application (63.5°C). Additional calorimeter testing was planned with higher fly ash additions. However, testing of Mono-Grout SR 1.0 was terminated because Bindan Corporation could not reproduce the initial packaged product.

The second product tested was Bindan Mono-Grout SR 2.0, which had less binder than SR 1.0. However, the reaction rate was faster than SR 1.0 and unacceptable. According to the supplier, this product was not properly formulated by the blending subcontractor. The third product tested was Bindan Mono-Grout SR 3.0. This material did not perform as well as the Mono-Grout SR 1.0 with respect to flow and rapid gelation but was better than the SR 2.0 product.

The fourth product tested was Bindan Mono-Grout SR 3.10. This material contained inert material with some particles > 3 mm and had a temperature rise of 51°C [Guerrero, 2010]. In an attempt to reduce the temperature rise and control the particle size of the inert filler, all further testing was performed with the binder portion of Mono-Grout SR 3.10 grout. This binder only material is referred to as Bindan SR 3.10 Binder.

A summary of the test results for the Bindan Mono-Grout SR packaged products is provided in Table 3-1.

Table 3-1. Summary of grout properties using Mono-Grout SR packaged products.

Mix	Proportions (wt. %)		Flow (inches)	Strength (psi)	Adiabatic Temperature Rise (°C)
Mono-Grout SR 1.0 Mix MG-5	SR 1.0 F Fly Ash Water	78.1 7.8 14.1	7.5 at 5, 10, and 30 min	864 at 5 days 810 at 32 days	63.5°C (Mix 1H) peak temp. = 80°C = 16.5°C initial + 63.5°C temp rise
Mono-Grout SR 2.0 Mix MG-11	SR 2.0 Water	85.5 14.5	8 at 5 min 0 at 30 min	Not measured because of rapid set	
Mono-Grout SR 3.0 Mix MG-16	SR 3.0 F Fly Ash Water	78.1 7.8 14.1	6.5 at 10 min 5 at 30 min	590 at 7 days	No calorimetry Bindan offered to reformulate
Mono-Grout SR 3.10 Assumed 20 wt% binder 80 wt% filler	SR3.10 Water KIM	85.4 14.5 0.1	7.5 at 5min 6 at 30 min 0 at 45 min (Mix 46)	693 at 3 days 869 at 6 days (Mix 19)	51 (Mix 2H) peak temp. = 74°C = 23°C initial + 51°C temp rise

3.2 Bindan SR 3.10 Binder –Inert AGSCO Aggregate Blends

In order to better control the amount of binder in the grout mixes, the binder (reagent) portion of Mono-Grout SR 3.10 was obtained from Bindan Corporation and inert fillers were added by SRNL. (This material is referred to as SR 3.10 binder.) Two size fractions of filler were used: powder (fly ash) and sand-size aggregate.

Class F fly ash was used as an inert powder (< 44 μm or -325 mesh) to serve the functions of reagent dilution and slurry property enhancement (reduce segregation and facilitate flow). Class F fly ash was the only inert powder tested. All SRNL modified mixes contained between 10 and 20 wt% fly ash.

In addition several types of inert aggregates (about 0.1 to 2 mm) were evaluated to determine whether they improved flow properties and controlled reaction heat. Several size gradations of rounded AGSCO, Inc. quartz (Ottawa sand), silica glass beads, and bauxite beads and locally available masonry sand were screened.

None of the special AGSCO inert fillers had a significant advantage over locally available masonry sand for the application of filling the reactor vessel tank (with or without obstructions).[6] Strength and temperature rise were not impacted by substituting bauxite beads or glass beads for a portion of the quartz sand. Consequently further testing of these materials not was conducted.

The amount of binder required to form a monolithic product (SR 3.10 binder – Class F fly ash – AGSCO sand sample) was determined to be greater than 14 weight percent of the total grout material. Samples prepared with 14 wt. % binder set but remained granular, crumbly and diggable. They had low compressive strengths. Calorimeter results confirmed that these mixes did not reach 63 to 65°C which is the approximate temperature for amorphous to poorly crystallized struvite (not cementitious) to convert to the stable, crystalline form which is cementitious. For example, Mixes 12 and 13 had strengths of only 162 and 168 psi, respectively, after 15 days. The adiabatic temperature rises for these 14 wt. % binder samples made with room temperature materials were 35 and 36° C, respectively and the maximum temperatures were less than 60°C.

Samples prepared with 16 wt. % SR 3.10 binder (Class F fly ash, and AGSCO sand) had higher compressive strengths of 630 to 1058 psi after curing for up to 5 days. Selected mix results are presented in Table 3-2 and Figure 3-1.

Amount of binder impacts strength and heat. Consequently at least 15 wt. % binder (of the total mix) is required for mixes containing the SR 3.10 binder and AGSCO 35 to 50 mesh gradation sand and Class F fly ash for reliable strength.

[6] The 40-70 gradation of the AGSCO, Inc. round quartz and the glass beads produced grouts with better self-leveling properties but the added cost did not warrant the added expense and was not pursed per SDD Eng request.

Table 3-2. Summary of grouts prepared with SR 3.10 binder plus SRNL added fillers.

Mix	Proportions (wt. %)	Flow (inches)	Strength (psi)	Adiabatic Temperature Rise (°C)
AGSCO 35-50 gradation sand + Class F fly ash				
MIX 15	SR 3.10 Binder 17.4 35-50 quartz sand 55.7 F fly ash 13.9 Water 13.0	7.9 (Mix 15)	799 at 5 days (Mix 15)	Not Measured
MIX 14	SR 3.10 Binder 15.7 35-50 quartz sand 55.6 F fly ash 15.7 Water 13.0	7.9 (Mix 14)	630 at 4 days (Mix 14)	Not Measured
AGSCO 35-50 gradation sand + Class F fly ash + KIM				
MIX 12	SR 3.10 Binder 13.9 35-50 quartz sand 55.6 F fly ash 17.4 KIM 0.16 Water 13.0	7.25	162 at 15 days	35.2 final temperature = 56.2°C = 21.0°C (initial) + 35.2°C (Mix 12H)
MIX 18	SR 3.10 Binder 17.4 35-50 quartz sand 55.6 F fly ash 13.9 KIM 0.17 Water 13.0	8	1058 at 3 days	Not Measured
MIX 16	SR 3.10 Binder 17.4 35-50 quartz sand 55.6 F fly ash 13.9 KIM 0.09 Water 13.0	7.9	624 at 4 days	Not Measured
AGSCO Bauxite Beads 60 -100 gradation + AGSCO 35-50 gradation sand + Class F fly ash + KIM				
MIX 13	SR 3.10 Binder 13.9 35-50 quartz sand 27.8 Bauxite beads 27.8 F fly ash 17.4 KIM 0.14 Water 13.0	8	168 at 15 days	36.0 final temperature = 58.4°C = 22.4°C (initial) + 36.0°C (Mix 13H)

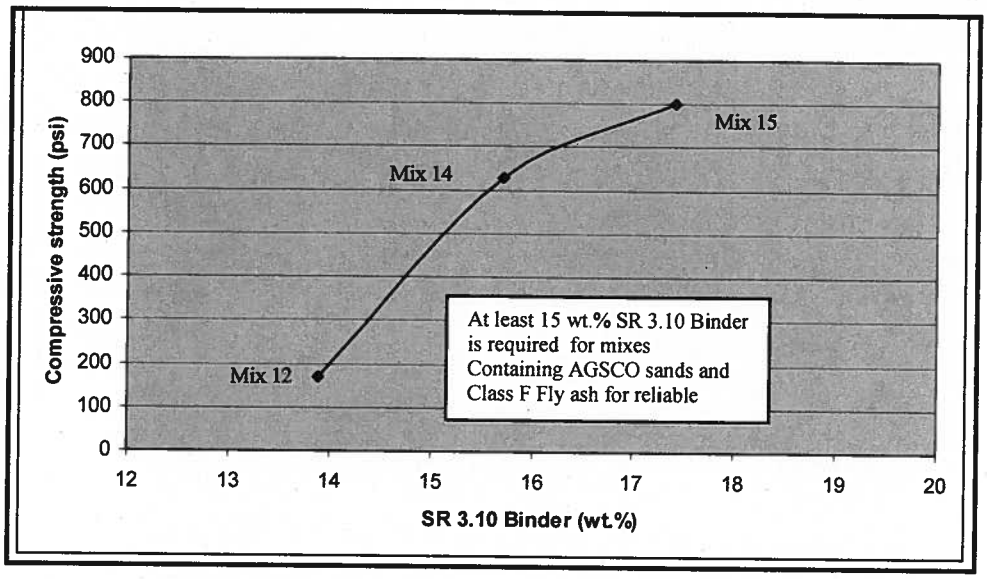

Figure 3-1. Compressive strength versus amount of SR 3.10 binder for mixes containing AGSCO 35 – 50 sand.

3.3 Bindan 3.10 Binder –Inert Masonry Sand and Class F Fly Ash Blends

Locally available masonry sand from the SCMI quarry on SC Highway 125 in Beach Island was selected and tested as a less expensive aggregate than the AGSCO quartz sands. This material meets the ASTM C-33 specifications for masonry sand (finer than concrete sand). One issue to be addressed is that low cost masonry sand acquired from the SCMI quarry is wet and can not be pre-blended with the reactive reagents unless it is dried.

Results of selected mixes containing masonry sand are presented in Table 3-3. Class F fly ash was used as the inert powder filler in all of the masonry sand mixes. Mixes were prepared with and without KIM (an integral waterproofing reagent). Mixes containing masonry sand, Class F fly ash plus 14 and 15.8 wt percents Bindan SR 3.10 binder (Mixes 34 and 29, respectively) met the temperature requirement.

For mixes containing between 14 and 17.5 wt. % SR 3.10 binder and 70 wt. % total inert filler, the compressive strength improved as the amount of fly ash relative to the amount of masonry sand increased. This is illustrated in Figure 3-2. However, as the amount of fly ash increased, the flow (measured by flow cone test ASTM C-939 and modified C-939 method) also increased. Extra boric acid and / or 1 to 4 wt. % more water should be tested to improve the viscosity.

Table 3-3. Summary of grouts prepared with SR 3.10 binder plus masonry sand and Class F fly ash.

Mix	Proportions (wt. %)		Flow (inches)	Strength (psi)	Adiabatic Temperature Rise (°C)
Masonry sand + Class F Fly Ash					
MIX 23 70 wt. % sand	SR 3.10 Binder Masonry sand Water	17.4 69.6 13.0	0	760 at 2 days	Not Measured
MIX 24 Replace 12.5 wt. % of the sand with fly ash	SR 3.10 Binder Masonry sand F fly ash Water	17.4 60.9 8.7 13.0	8.5	1010 at 2 days	Not Measured
MIX 25 Replace 25 wt. % of the sand with fly ash	SR 3.10 Binder Masonry sand F fly ash Water	17.4 52.2 17.4 13.0	8.25	1380 at 2 days	Not Measured
MIX 27 Replace 25 wt. % of the sand with fly ash + 2X KIM	SR 3.10 Binder Masonry sand F fly ash KIM Water	17.4 52.1 17.4 0.17 13.0	8.25	1100 at 2 days	Not Measured
MIX 28 Replace 25 wt. % of sand with fly ash + 1X KIM	SR 3.10 Binder Masonry sand F fly ash KIM Water	17.5 52.6 17.5 0.09 12.3	8.125	1108 at 5 days	51 (Mix 28H) final temperature = 73.2°C after 94 hours = 22.2°C (initial) + 51°C
MIX 29 Replace 27 wt. % of sand with fly ash + KIM	SR 3.10 Binder Masonry sand F fly ash KIM Water	15.8 52.6 19.3 0.16 12.3	7.25 7.37 @15 min 5.25 @45 min flow cone 153 sec after mixing for 15 min. 243 sec after mixing for 45 minutes (Mix 33)	1298 at 4 days	39.7 (Mix 29H) final temperature = 63.0°C after 39.7 hours = 22.0°C (initial) + 39.7°C
MIX 34 Replace 26 wt. % of sand with fly ash + KIM	SR 3.10 Binder Masonry sand F fly ash KIM Water	14.0 54.3 19.3 0.14 12.3	7.75	1096 at 1 days	42.9 (Mix 32H) final temperature = 67.9°C after 88.2 hours = 25.0°C (initial) + 42.9°C

Shading indicates recommended mixes.

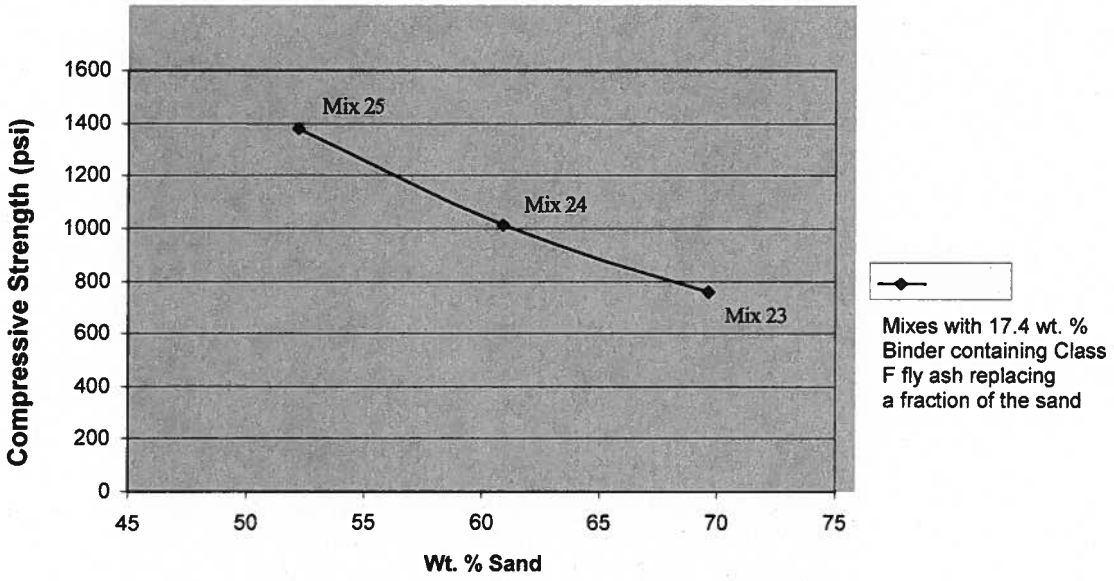

Figure 3-2. Strength for mixes containing masonry sand and 17.4 wt. % binder

3.4 Magnesium Mono Potassium Phosphate Grouts Prepared from Reagents

In addition to preparing magnesium mono potassium phosphate grouts from packaged products, mixes were prepared from the binder reagent ingredients in order to obtain a better understanding of the raw material characteristics and material reactions so quality control criteria can be developed for a procurement specification. Also given the limited number of magnesium mono potassium phosphate grout suppliers, options for multiple suppliers were investigated.

3.4.1 Magnesium Oxide Reagents

Mixes were prepared from each of the four MgO reagents listed in Table 2.2. The MagChem® 10CR material was selected for the magnesium mono potassium phosphate grout application. The MagChem® P98 material was somewhat coarser than 10CR. Grouts prepared with MagChem® P98 had excessive expansion and a disrupted structure when cast in the 2 inch cube molds. The addition of up to 2 wt. % boric acid controlled but did not completely eliminate the expansion in the MagChem® P98 formulations.

3.4.2 Mono Potassium Phosphate Reagents

The MKP 200 Granular material was initially selected as the type of mono potassium phosphate because it is coarser and thought to be easier to handle than the MKP 771 Rotem® product. However screening tests indicated that the dissolution was too slow for the grout application.

The MKP from Bindan Corp appeared to be similar or identical to the MKP 771 Rotem® product. Consequently, MKP 771 Rotem® and 10CR MgO were selected for evaluating the individual

reagents. Slight expansion was observed with the MKP 771 Rotem® – 10CR MgO grouts. Boric acid was evaluated to slow the reaction rate and thereby minimize the expansion and increase working time (static and dynamic working time).

3.4.3 Boric Acid Addition

Properties of the mixes prepared from MgO, MKP, Class F fly ash, masonry sand and boric acid are provided in Table 3-4. Boric acid additions of 1.5 and 2 wt. % of the binder weight resulted in mixes with acceptable flow and extended static and dynamic working times which were up to 40 minutes for mixes containing 14 wt. % binder. Adiabatic calorimeter data were collected for Mix 40-1 with boric acid (2 wt. % of the binder weight). The measured temperature rise was 40.4°C which meets the reactor vessel fill grout requirement of less than 60°C. This mix did not expand and the compressive strength after 3 days curing also met the requirement of > 200 psi.

Mixes with more boric acid did not result in increased flow or dynamic and static working times. In some cases they displayed slight expansion. Consequently, magnesium mono potassium phosphate grouts containing 14 wt. % binder, prepared from 10CR MgO and Rotem® 771 MKP reagents, plus Class F fly ash and masonry sand require 1.5 to 2 wt. % boric acid set retarder blended in with the reagents. The addition of more than 2 wt. % boric acid to mixes containing inert Class F-fly ash resulted in significantly lower compressive strengths compared to similar mixes containing reactive Class C fly ash. (More boric acid set retarder can be used in mixes containing more reactive ingredients without impacting the strength.) The dynamic working time also decreased for mixes containing more than 3 wt. % boric acid.

The amount of boric acid added in a scale-up test will depend on ambient conditions but should not exceed 2.5 weight percent of the binder weight based on the current laboratory results for mixes that contain very little additional sources of reactive compounds, such as CaO.

3.4.4 Expansion of Mixes Prepared from MgO and MKP Products

Samples prepared with the ingredients (MgO and MKP) in the packaged products showed a significant amount of unexpected expansion. Mixes prepared from MgO and MKP individual products that were blended at SRS and expanded are shown in Figure 3-3. Mixes prepared from Bindan SR3.10 prepackaged binder did not show disruptive expansion and are shown in Figure 3-4 for comparison. The expansion occurred within 24 hr of curing. Samples prepared with MagChem® 10CR expanded less than samples with identical proportions prepared with MagCem® P98. The difference in these two materials is particle size and calcining temperature. Addition of 1.5 to 2 wt. percent boric acid to mixes prepared with MagChem® 10CR prevented the expansion. More than 2 wt. % boric acid was less effective in controlling expansion. The KIM® 301 additive also had an effect on expansion. 2 wt. % KIM® 301 added to mixes containing MagChem® P98 and no boric acid did not expand.

Struvite was the only crystalline phase identified in x-ray diffraction patterns of samples from the expanded material. SEM microstructural analyses were not conclusive. Consequently, the cause of the expansion was not identified. Possible causes of the disruptive excessive expansion include: formation of a low density amorphous phase, reaction rate that was not compatible with

the MKP and MgO solubilities, impurities in the MgO reagent, or high temperature and off gassing however, small samples did not reach temperatures above about 60°C.

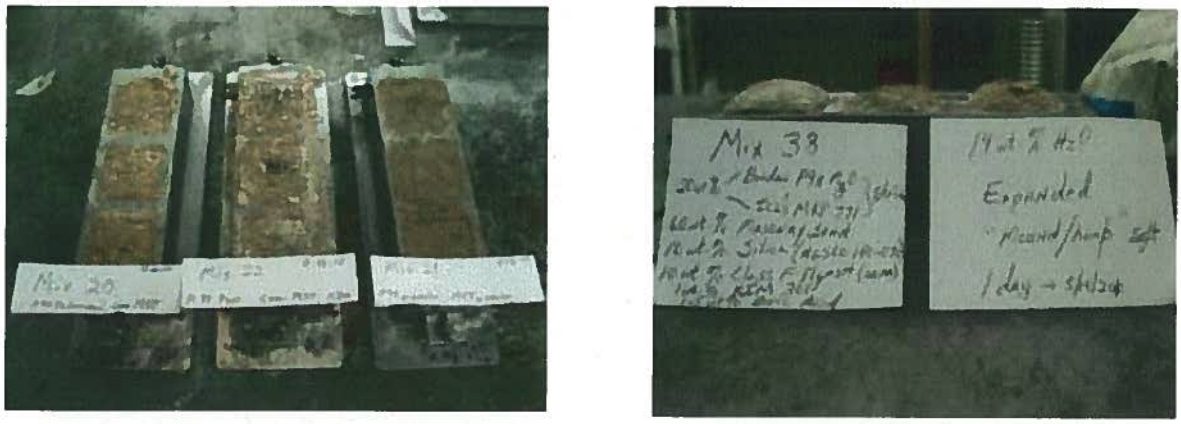

Figure 3-3. Examples of expansion observed in mixes prepared from MgO and MKP.

Figure 3-4. Examples of samples prepared from Bindan SR3.10 Binder that did not exhibit excessive expansion.

3.5 SRNL Mix Calorimeter Results

Adiabatic temperature rise was measured at SRNL in one of two adiabatic calorimeters. Data are presented in Figures 3.5 and 3.6 and in another report [Steimke, 2010]. The temperature rises were added to the temperature of the starting materials to obtain the maximum temperature resulting from the cementitious reactions.

Based on past experience with portland cement-based materials, a factor of 1.4 is applied to the adiabatic temperature rise measured in the calorimeter to account for reactions that occur after the calorimeter run is terminated. For portland cement systems, calorimeter runs typically do not extend beyond 14 days because the reaction heat is much less than that of system heat losses. However, it is well documented that portland cement based materials continue to react and gain strength over months. Continued strength gain over months has not been documented for

magnesium mono potassium phosphate-based materials. Consequently, applying the factor of 1.4 to the measured temperature rise may be overly conservative.

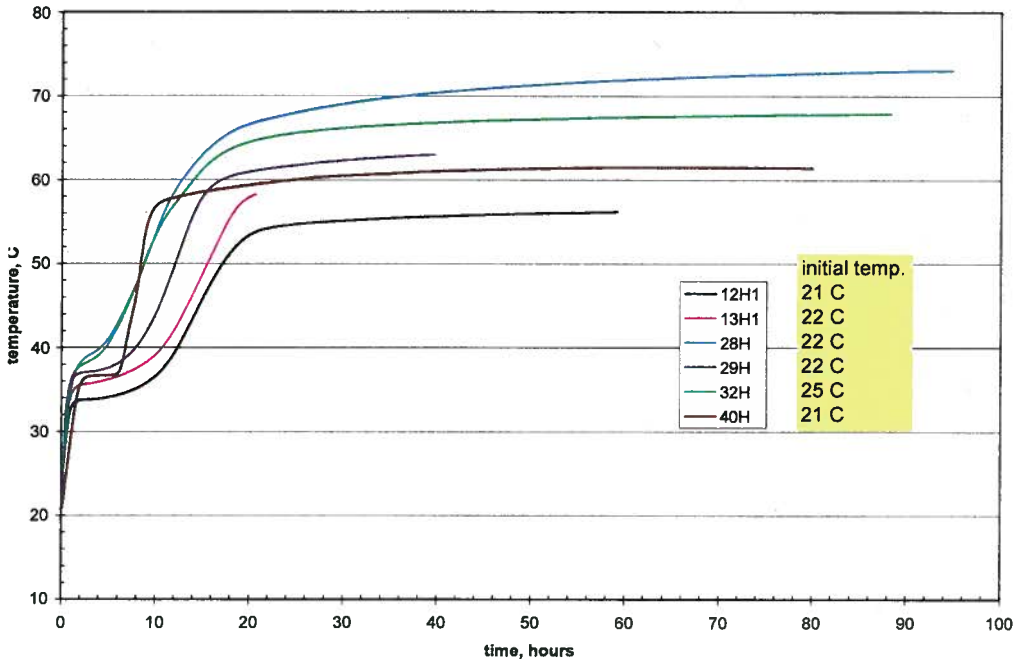

Figure 3-5. Adiabatic calorimeter results for mixes prepared from SR 3.10 Binder and inert fillers.

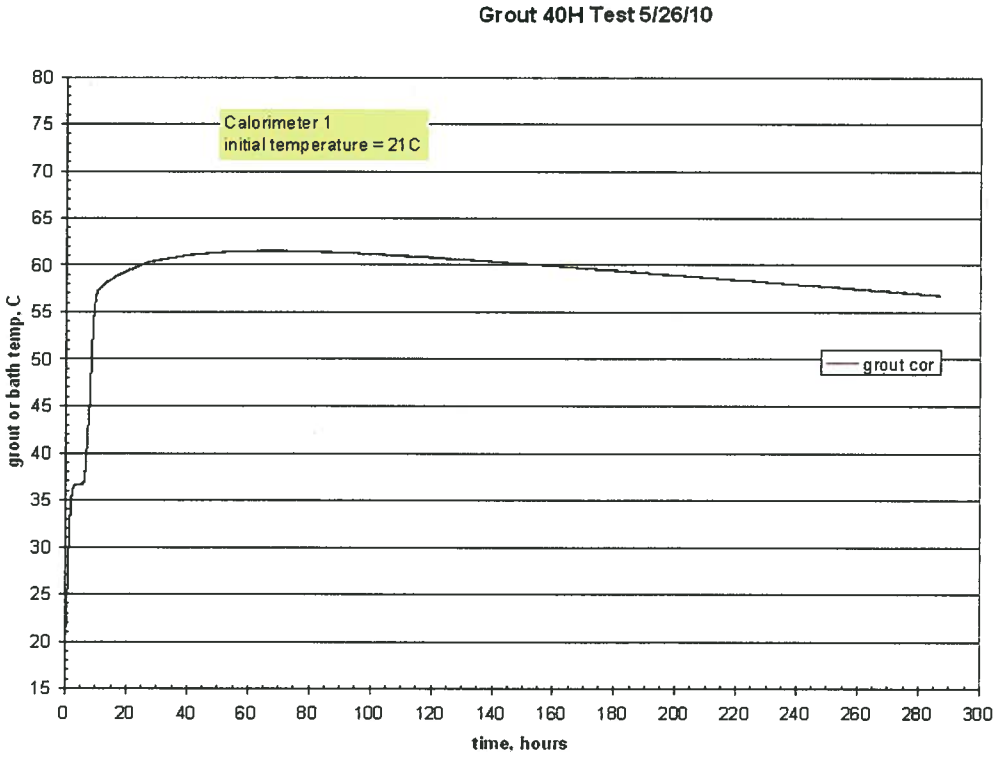

Figure 3-6. Adiabatic calorimeter result for Mix 40H (Mix 40) measured over 12 days.

Table 3-4. Magnesium mono potassium phosphate grouts made from reagents.

Mix	Proportions (wt. %)		Flow (inches)	Strength (psi)	Adiabatic Temperature Rise (°C)
Mag Chem 10 CR + MKP 771 + fly ash + masonry sand + boric acid					
MIX 35 13.9 wt. % Binder 0 wt. % boric acid	10 CR MgO Bindan MKP Masonry sand F fly ash KIM Water Boric acid	3.99 13.52 52.54 17.51 0.18 12.26 0	7.25 (initial) Static test 7.75 @ 15 min	983 at 8 days	Not Measured
MIX 45 13.9 wt. % Binder 1.5 wt. % boric acid	10 CR MgO MKP 771 Masonry sand F fly ash KIM Water Boric acid	3.17 10.73 53.8 19.1 0.14 13.0 1.5 wt. % of MgO + MKP	7.5 (initial) Static test 7.25 @ 15 min 6 @ 40 min 4.25@ 60 min Dynamic test 8.0 after mixing in Hobart for 60 min Flow Cone 5 min = 45 s 15 min = 45 s 30 min = 35 s 45 min = 48 s 60 min – 59 s 75 min = 74 s 105 min = 135 s	920 at 1 day no expansion	Not Measured
MIX 40 and 40-1 13.9 wt. % Binder 2 wt. % boric acid	10 CR MgO MKP 771 Masonry sand F fly ash KIM Water Boric acid	3.17 10.73 53.8 19.1 0.14 13.0 2 wt. % of MgO + MKP	7.5 (initial) Static test 6.75 @ 15 min 5.25 @ 30 min 4.75@ 45 min Dynamic test 7 in. after mixing by hand for 45 min Difficult to mix at 60 min (Mix 44)	670 at 1 day 710 at 1 day (Mix 44) no expansion	40.4 (Mix 40H) 21°C + 40.4°C = 61.4°C = max temperature

Shading indicates recommended mixes.

Table 3-4 (continued). Magnesium mono potassium phosphate grouts made from reagents.

Mix	Proportions (wt. %)		Flow (inches)	Strength (psi)	Adiabatic Temperature Rise (°C)
MIX 41 13.9 wt. % Binder 2.5 wt. % boric acid	10CR MgO MKP 771 Masonry sand F fly ash KIM Water Boric acid	3.17 10.73 53.8 19.1 0.14 13.0 2.5 wt. % of MgO + MKP	7.75 (initial) Static test 5.5 @ 15 min 3.75 @ 30 min 0@ 45 min Dynamic test 7.5 in. after mixing by hand for 40 min Difficult to mix at 60 min	300 at 1 days	Not Measured
MIX 41-1 13.9 wt. % Binder 3 wt. % boric acid	10CR MgO MKP 771 Masonry sand F fly ash KIM Water Boric acid	3.17 10.73 53.8 19.1 0.14 13.0 3 wt. % of MgO + MKP	7.75 (initial) Dynamic test 8 in. @ 10 min 6.5 @ 20 min 6 @ 40 min Difficult to mix at 60 min	300 at 1 days	Not Measured
MIX 42 13.9 wt. % Binder 5 wt. % boric acid	10CR MgO MKP 771 Masonry sand F fly ash KIM Water Boric acid	3.17 10.73 53.8 19.1 0.14 13.0 5 wt. % of MgO + MKP	7.5 (initial) Static test 6.25 @ 15 min 4.25 @ 30 min 0 @ 45 min	430 at 1 days Slight expansion	Not Measured
Mix 42-1 13.9 wt. % Binder 6.25 wt. % boric acid	10CR MgO MKP 771 Masonry sand F fly ash KIM Water Boric acid	3.17 10.73 53.8 19.1 0.14 13.0 6.25 wt. % of MgO + MKP	7.5 initial Static test 0 @ 30 min	300 psi at 4 days Slight expansion	Not Measured

3.6 Magnesium Mono Potassium Phosphate Grout pH Measurements

Magnesium mono potassium phosphate-based cementitious grouts were evaluated because the pH of water in equilibrium with these materials is in the range of 6 [Dileep Singh, 2009]. At this pH, aluminum components remaining in the reactor will not corrode quickly and therefore hydrogen generation during filling or long term is not a safety issue [Wiersma, 2010]. A pH of 6 was confirmed for water in equilibrium with Ceramicrete® and the Bindan SR 1.0 Mono-Grout by C. L. Crawford, 2009 [Crawford, 2009].

However, subsequent measurements performed on cured magnesium mono potassium phosphate grouts prepared at SRNL from numerous starting ingredients indicated that water in contact with cured samples had pHs of between 10 and 10.5 The experimental configuration was very simple and illustrated in Figure 3-7. The pH of the water was measured with pH paper.

Figure 3-7. pH Test for water in contact with SRNL magnesium mono potassium phosphate grout cured for 3 days.

Water in contact with crushed SRNL magnesium mono potassium phosphate grout samples cured in the adiabatic calorimeter had pHs between 7.9 and 9.8 which is slightly less than samples cured for three days at room temperature. See Table 3-5. The experimental set up for measuring the pH of the samples cured at elevated temperatures in the adiabatic calorimeter is shown in Figure 3-8. The water to solids ratio was 1:1 and the test was performed at room temperature.

Table 3-5. pH of water in contact with cured SRNL grout samples.

Contact Time	SRNL 40H	SRNL 32H	SRNL 29H
Days	pH	pH	pH
15 minutes	8.13	9.78	9.13
1	7.87	9.61	8.65
2	7.91	9.57	8.67
3	7.98	9.52	8.74

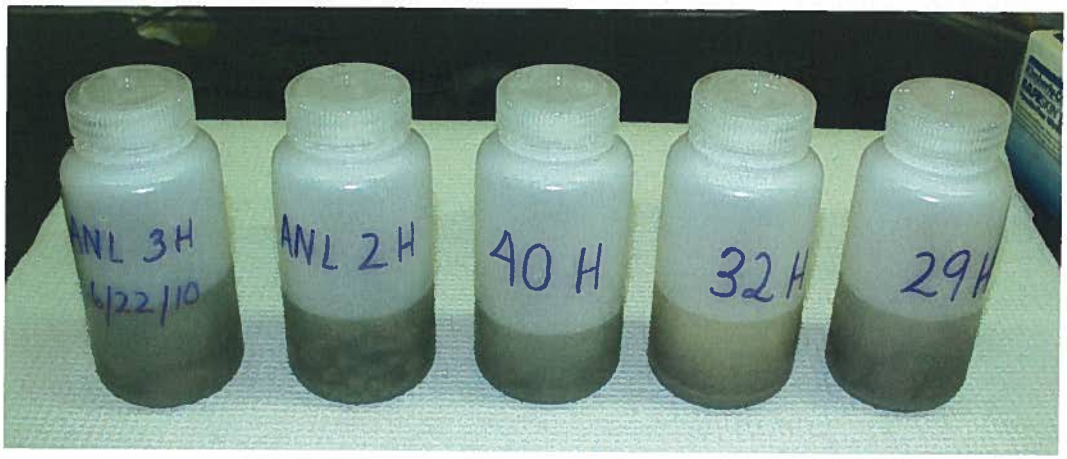

Figure 3-8. Crushed magnesium mono potassium phosphate grout samples in de-ionized water.

3.7 SRNL Bench Scale-Up Test for Magnesium Phosphate Grout

A small bench-scale test was conducted to determine mixing and flow properties of a 0.35 cubic foot batch of SRNL Mix 34 which was modified by increasing the water content from 14 to 15.5 wt. % based on the total solids weight. The mix ingredients and proportions are provided in Table 3-6.

The material was prepared in a Hobart mixer. All of the solid ingredients were pre-blended and gradually added to the water. Chilled water, 5.6°C (42°F), was used in these tests. Extra chilled water (11.7 wt. % of the initial amount) was added to the mix. (The mixing bowl and paddle were not wetted prior to the test.)

The mixing time was 6 minutes and the time measurement started when solids first contacted the water. See Figure 3-9.

Table 3-6. Mix proportions for modified SRNL Mix 34 used in the bench scale-up test.

Material	Pounds per Cubic Foot	Pounds per 0.35 Cubic Foot
Bindan SR 3.10 Binder	18.9	6.6
Class F Fly ash	26	9.1
Masonry Sand (oven dried)	73.2	25.6
KIM	0.19	0.03
Chilled Water (5.6°C)	16.5	5.8
Extra Chilled Water (extra 11.7 wt % of initial water)	1.93	0.68
Total Water	18.43	6.48

A 24 x 24 x 4 inch pan containing a steel ring and 2 x 4 inch cylinders as obstructions was used to quantitatively evaluate the grout flow and self-leveling properties. See Figure 3-10. The grout was discharged from an ASTM C-939 flow cone with a ½ inch opening. The flow cone was positioned 12 inches above a pan containing flow obstructions. See Figures 3-10 and 3-11.

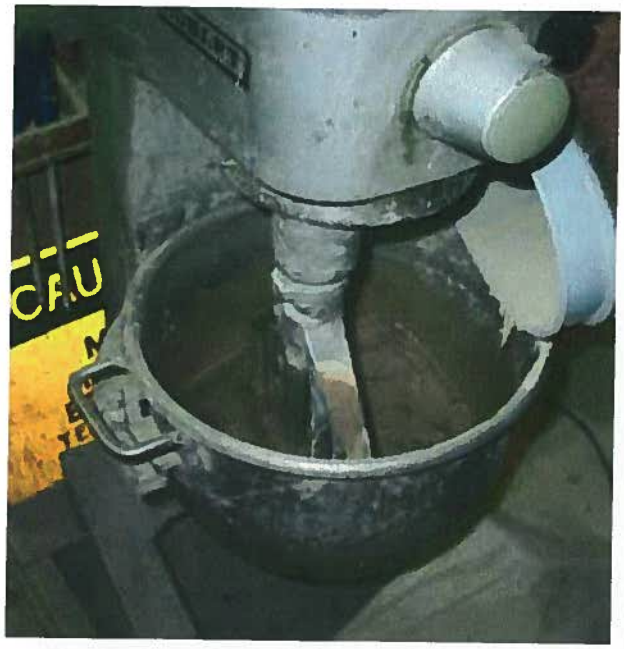

Figure 3-9. Bench scale-up test mixing.

Figure 3-10. Bench scale-up flow test.

Figure 3-11. Flow cone used to obtain flow data and to place grout in the bench scale-up test.

The flow cone was filled five times over an eight minute period. Flows were measured for each batch. The flow cone measurements are provided in Table 3-7. 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.

Table 3-7. Bench scale-up test flow cone measurements.

Sequential Flow Test	Seconds
1	31
2	34
3	36
4	42
5	50

SRNL Mix 34 with additional water flowed around the obstructions and through 1.0 inch gaps between obstructions in the bench scale-up test as illustrated in Figure 3-12. The mix was not quite self-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.

Figure 3-12. Bench scale-up test flow evaluation.

The static working time was estimated using a modified ASTM D-6103 method (2 x 4 inch cylinders) where a small open-ended cylinder is filled with grout and then lifted at selected time intervals. Results are shown in Figure 3-13. The static working time is between 15 and 20 minutes. At time 0 the sample had a 9 inch spread, where as after 5 minutes under static conditions the mix had a 5.5 inch spread. After 25 minutes the material is self supporting but can be remixed to a flowable paste with sufficient shear.

Material was recovered from the flow test and returned to the mixer for dynamic working time evaluation. The dynamic working time for SRNL Mix modified Mix 34 (bench scale-up mix) is about one hour. A 6 inch spread was obtained by the modified ASTM D 6103 test for material intermittently mixed for 50 minutes in the Hobart mixer at low speed. See Figure 3-14. Temperature has an effect on the dynamic working time.

Figure 3-13. Static working time for the bench scale-up mix.

Figure 3-14. Dynamic working time for the bench scale-up mix.

The temperature of the recovered sample (about 0.3 cubic feet of material) rose to 88°F in 1 hour. After 1 hour and 30 minutes the temperature reached 90.6 F as reaction began to accelerate and the material thickened quickly while it was being mixed. Figure 3-15 illustrates the appearance of the mix after 1 hour of intermittent mixing and after 1.5 hours of mixing. The addition of more water did not thin the material once the chemical reaction began to accelerate, but it did reduce adhesion to the mixing bowl and facilitate clean up.

Figure 3-15. Bench scale-up mix after 60 (left) and 90 (right) minutes of intermittent mixing.

The Compressive strength results for 2-inch cubes cast with material recovered from the bench scale-up pour test are provided in Table 3-8.

Table 3-8. Compressive strength results for material produced in the bench scale-up test.

Cure Time (days)	Compressive strength (psi)
4	262
7	388
38	973

4.0 RESULTS: ANL MAGNESIUM MONO POTASSIUM PHOSPHATE GROUT

4.1 Background

Magnesium mono potassium phosphate ceramic (Ceramicrete®) was developed at Argonne National Laboratory (ANL) to stabilize radioactive and hazardous waste streams [Wagh, 2001]. Ceramicrete® is a room temperature forming material and is based on magnesium mono potassium phosphate. Because of its superior mechanical properties, it is now finding applications in building and construction, and even as cement in dental and bone applications. Ceramicrete® is fabricated by acid/base reactions. The chemical reaction for the formation of Ceramicrete® is given below:

$$MgO + KH_2PO_4 + 5\,H_2O \rightarrow MgKPO_4 \cdot 6H_2O$$

Ceramicrete® is formed by mixing 1 mole of each of MgO and KH_2PO_4 powders with 5 moles of water. The slurry formed has a pH that is close to neutral.

4.2 ANL Objective

The objective of this work was to demonstrate mixing and placement of a neutral/low pH Ceramicrete® grout to fill reactor vessels at Savannah River Site (SRS). The reactor vessel has the highest concentrations of radionuclides in the reactor building including metal activation products, Co-60 and Ni-59. Rationale is that by filling the reactor vessel, contaminants will be immobilized. A neutral pH grout is required because the P-Reactor vessel contains a significant amount of aluminum metal components. Aluminum dissolves in high pH environments such as those generated by portland cement-based grouts. The void volume in each SRS reactor vessel is approximately 110 cubic yards and filling it requires a very fluid grout because the interior of the reactor is very congested with piping. Bench scale and pilot scale testing is required to confirm this material as a candidate for closing the SRS reactors.

SRS subcontracted a task to ANL to help in the development and placement of the phosphate-based grout. Overall project was divided into three phases. Phase 1 of the project started in early October 2009. Follow-on phases are currently under discussion.

4.2.1 Target Cement Properties

ANL's role was to develop formulations/variations of magnesium mono potassium phosphate-based cement or Ceramicrete® that meet the specific P-Reactor requirements. As part of phase 1, the goals were to develop optimized formulations of Ceramicrete® that fulfill the placement requirements. The grout requirements, identified by SRNL, were as follows:

a. slurry pH = 5-8
b. temperature rise under adiabatic conditions < 60 °C
c. dynamic working time ~ 2-3 hours
d. static gel time > 30 minutes
e. compressive strength > 500 psi after 28 days.

4.3 Materials Used

Various base binder phase materials such as MgO and KH_2PO_4 and fillers such as sand and Class C fly ash used in the study are listed in Table 4-1.

Table 4-1. Materials used and suppliers.

Material	Supplier
Magnesium oxide –10CR	Bindan (630-734-0277)
Mono potassium phosphate (believed to be MKP 771 Rotem®)	Bindan (630-734-0277)
Class C fly ash	Bindan (630-734-0277)
Sand medium – No. 1962	Home Depot, Commercial grade Quikcrete®
Boric acid – A73-1	Fischer Scientific
Daratard -17	W.G. Grace Construction Products

4.4 Baseline Ceramicrete Performance

As part of this activity, focus was to optimize the filler loading in the Ceramicrete® formulation to establish a base binder composition. Ceramicrete® reaction is exothermic so to control the heat generation and the effective temperature rise, filler materials can be added. Fly ash has been extensively used in Ceramicrete® as a filler material. For this optimization study, starting powder materials were obtained from Bindan Corporation. Bindan also supplied Class C fly ash for this study.

In the initial trials, several samples were prepared where fly ash loading was varied between 40-80 wt. % in the dry powder mix. All samples were prepared by adding water to the powders and slow mixing for about 20-25 minutes to form a pourable slurry. Slurry was poured into plastic molds for setting and curing. In about 1-2 hours the slurry would set up into a hard ceramic. Thus, further modifications were made to the mix design to attain the goals of flow and set properties desired for ISD reactor placement.

4.5 Role of Boric Acid and Additional Water

To address the issue of the setting time and the peak temperature rise, boric acid additions were made to the base formulations. A series of samples were prepared with varying amounts of boric acid. Ratio of binder phase (MgO + MKP) to fly ash C was kept at 30:70. Peak temperature rise was measured using a thermocouple. At least one formulation was sent to SRNL for the measurement of temperature rise using the calorimeter. Results of the various experimentations are listed in Table 4-2.

To ensure fluidity and viscosity of the slurry, additional water (over the stoichiometric amount) was investigated.

Characterizations performed were flow cone test, viscosity, temperature rise using thermocouple, adiabatic temperature rise using calorimeter, pipe test (gel time), and compressive strength.

4.5.1 Key Observations

- Boric acid helps in retarding the phosphate reaction

- For samples with 1.5 wt.% boric acid (of the total dry powders)
  - calorimeter test showed temperature rise of 43.6° after 14 days (Mix 102-009-1)
  - standard flow cone tests give flow time of 28 seconds up to 4.5 hours of mixing of slurry (Mix110509-1)
  - compressive strengths are 800 psi after 26 days and 1150 psi after 129 days; strength build-up occurs with time (Mix 102009-1).

- For samples with 1.5 wt.% boric acid (of the total dry powders) and additional water
  - calorimeter test showed a temperature rise of 48°C after 14 days (Mix 020310-1)
  - standard flow cone tests give flow time of 21 seconds up to 4.5 hours of mixing of slurry (Mix 030210-1)
  - initial viscosity is 325 cP and rises up to 1700 cP at approximately 60 minute mark, under static conditions (Mix 030510-1)
  - spread test showed 8.5 and 5.5 inch spreads at 10 and 30 minute marks, respectively (Mix 012810-1)
  - compressive strength >600 psi after 31 days (Mix 030210-1).

- For samples with 1.5 wt.% boric acid (of the total dry powders) and additional water
  - spread test showed 5.75 inch spread at 30 minute mark (Mix 011910-2)
  - compressive strength ~700 psi after 60 days (Mix 011910-2).

Table 4-2. Test results on boric acid additions and additional water on Ceramicrete® based formulations

Sample	Composition for 100 g sample	Peak Temp (°C) with thermo-couple	Adiabatic Temp. rise (°C) (SRNL)	Flow-cone Test and Viscosity Data	Spread test (Pipe test)	Strength (psi)
033110-1 (MgO+MKP)/Fly Ash = **30/70** No boric.acid (B.A.) Total = 2016 g (≈1000 mL)	MgO = 5.44 g MKP = 18.37 g F.Ash C = 55.56 g Water = 20.63 g	57 °C after 90 min.	-	-	-	-
121009-4 (MgO+MKP)/ Fly Ash = 20/80 No B.A. Total = 1488 g	MgO = 3.69 g MKP = 12.44 g F.Ash C = 64.52 g Water = 19.35 g	50 °C after 8 h	-	-	-	≈2150 psi @75 days
102009-1 (MgO+MKP)/Fly Ash = 30/70 1.5wt% B.A. (based on the dry powders) Total = 1020 g (≈580 mL)	MgO = 5.39 g MKP = 18.14 g F.Ash C = 54.90 g B.Acid = 1.18 g Water = 20.39 g	30.1 °C after 180 min.	43.6 °C after 14 days Maximum temp. = 22.9°C starting temp. + 43.6°C rise = 66.5°C (test terminated by SRNL) Corresponds to RG-18R and ANL 1	-	-	≈ 800 psi after 26 days ≈ 1150 psi after 129 days
102209-1 (MgO+MKP)/Fly Ash = 30/70 2 wt% B.A. (based on the dry powders) Total = 1024 g	MgO = 5.36 g MKP = 18.09 g F.Ash C = 54.69 g B.Acid = 1.59 g Water = 20.31 g	26.7 °C after 200 min.	-	-	-	-

Table 4-2 continued. Test results on boric acid additions and additional water on Ceramicrete® based formulations

Sample	Composition for 100 g sample	Peak Temp (°C) with thermo-couple	Adiabatic Temp. rise (°C) (SRNL)	Flow-cone Test and Viscosity Data	Spread test (Pipe test)	Strength (psi)
102909-1 (MgO+MKP)/Fly Ash =30/70 2 wt% B.A. (based on the dry powders) Total=4097 g (≈2100 mL)	MgO = 5.36 g MKP = 18.09 g F.Ash C = 54.69 g B.Acid = 1.59 g Water = 20.31g	-	-	Flow Cone: 15 min=14.5 s 45 min=14.4 s 90 min=15.2 s 135 min=16.4 s 165 min=17.6 s 195 min=18.1 s 225 min=19.5 s 270 min=21.6 s	-	-
110509-1 (MgO+MKP)/Fly Ash =30/70 1.5 wt% B.A. (based on the dry powders) Total = 4081 g (≈2100 mL)	MgO = 5.39 g MKP = 18.14 g F.Ash C = 54.90 g B.Acid = 1.18 g Water = 20.39 g	-	-	Flow Cone: 15 min=16.9 s 45 min=16.5 s 90 min=18.1 s 135 min=19.9 s 165 min=20.0 s 195 min=21.8 s 225 min=23.1 s 270 min=28.5 s	-	-
111809-1 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) Total = 2040 g (≈1000 mL)	MgO = 5.39 g MKP = 18.14 g F.Ash C = 54.90 g B.Acid = 1.18 g Water = 20.39 g	29 °C after 300 min.	-	-	-	-
012810-1 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B. A. (based on the dry powders) Total = 2103 g	MgO=5.22 g MKP=17.61 g F.Ash C=53.26 g B.Acid=1.16 g Water=22.75 g	-	-	-	8.5 in. @10 min. 7.25 in. @20 min. 5.5 in. @30 min.	-

Table 4-2 continued. Test results on boric acid additions and additional water on Ceramicrete® based formulations.

Sample	Composition for 100 g sample	Peak Temp (°C) with thermo-couple	Adiabatic Temp. rise (°C) (SRNL)	Flow-cone Test and Viscosity Data	Spread test (Pipe test)	Strength (psi)
020310-1 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) Total = 2103 g	MgO = 5.22 g MKP = 17.61 g F.Ash C = 53.26 g B.Acid = 1.16 g Water = 22.75 g	38 °C after 16 days	48 °C after 14 days (SRNL stopped the test). Corresponds to ANL 2	-	-	-
030210-1 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) Total = 4206 g	MgO = 5.22 g MKP = 17.61 g F.Ash C = 53.26 g B.Acid = 1.16 g Water = 22.75 g	-	-	Flow Cone: 15 min=11.1 s 45 min=11.5 s 90 min=12.6 s 135 min=14.4 s 165 min=16.1 s 195 min=17.1 s 225 min=19.4 s 270 min=21.6 s	-	≈ 600 psi @31 days ≈ 600 psi @41 days ≈ 650 psi @48 days
030510-1 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) Total = 1051 g	MgO = 5.22 g MKP = 17.61 g F.Ash C = 53.26 g B.Acid = 1.16 g Water = 22.75 g	-	-	Viscosity: 4 min=325 cP 16 min=340 cP 31 min=725 cP 55 min=1702cP 67 min=2402cP	-	-
011910-2 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) Total = 1858 g	MgO=5.17 g MKP=17.43 g F.Ash C=52.73 g B.Acid=1.15 g Water=23.52 g	-	-	-	9.0 in. @10 min. 8.5 in. @20 min. 5.75 in. @30 min.	≈ 690 psi @52 days ≈ 725 psi @60 days
121809-1 (MgO+MKP)/ Fly Ash = 20/80 1.5 wt% B.A. (based on the dry powders) Total = 2154 g	MgO = 3.64 g MKP = 12.29 g F.Ash C = 63.73 g B.Acid = 1.22 g Water = 19.12 g	32°C after 13 days	-	-	-	≈ 2060 psi @70 days

4.6 Enhance Fluidity Using Daratard-17

To further improve on the viscosity, flow characteristics, and gel times, a commercial water reducer / set retarder, such as, Daratard-17 was investigated. Various formulations were prepared in which Daratard-17 loading was varied, while keeping the ratio of binder phase to class C fly ash fixed at 30:70, and boric acid at 1.5 wt. % as in Section 4.5. The characterizations tests performed and results for this series of mixes are listed in Table 4-3.

4.6.1 Key Observations:

- Parametric study of Daratard loading (2-8 wt.%) was conducted on the baseline formulation of binder/class C fly ash 70:30 and 1.5 wt% boric acid
  - increasing Daratard content increases the static gel time; 4 wt.% Daratard shows 5.5 inch spread at 20 min mark
  - standard flow cone tests give flow time of 20 s up to 3.25 hours of mixing of slurry for 4 wt. % Daratard loading
  - viscosity of the slurry increased from 582 cP to 1462 cP over 1.6 hours
  - compressive strengths are 900 psi after 75 days for 4 wt. % Daratard loading; strength build-up occurs with time
  - no water bleeding observed

Table 4-3. Test results on Daratard-17 additions on Ceramicrete® based formulations

Sample	Composition for 100 g sample	Peak Temp(°C) with thermo-couple test	Adiabatic Temperature rise (°C) (SRNL)	Flow-cone Test and Viscosity Data	Spread test (Pipe test)	Strength (psi)
121009-1 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) 2.0 wt% Daratard (based on the dry powders) Total = 2073g	MgO=5.29 g MKP=17.86 g F.Ash C=54.03 g Daratard=1.57g B.Acid=1.18 g Water=20.07 g	26.5°C after 4 h	-	-	6.6 in. @ 10 min. 4 in. @ 20 min. Takes the shape of the pipe at 40 min.	≈ 1300 psi @ 75 days
121009-2 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) 4.0 wt% Daratard (based on the dry powders) Total = 2107g	MgO=5.21 g MKP=17.58 g F.Ash C=53.16 g Daratard=3.16g B.Acid=1.16 g Water=19.74 g	-	-	-	8.5 in. @ 10 min. 5.5 in. @ 20 min. Takes the shape of the pipe at 40 min.	≈ 900 psi @ 75 days
121409-1 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) 6.0 wt% Daratard (based on the dry powders) Total = 2143g	MgO=5.12 g MKP=17.28 g F.Ash C=52.27 g Daratard=4.77g B.Acid=1.14 g Water=19.42 g	26.5°C after 6 h	-	-	6 in. @ 20 min. Takes the shape of the pipe at 40 min.	≈ 950psi @ 70 days

Table 4-3 continued. Test results on Daratard-17 additions on Ceramicrete® based formulations.

Sample	Composition for 100 g sample	Peak Temp (°C) with thermo-couple test	Adiabatic Temperature rise (°C) (SRNL)	Flow-cone Test and Viscosity Data	Spread test (Pipe test)	Strength (psi)
121409-2 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) 8.0 wt% Daratard (based on the dry powders) Total = 2179g	MgO=5.03 g MKP=16.99 g F.Ash C=51.39 g Daratard=6.38g B.Acid=1.12 g Water=19.09 g	-	-	-	7.5 in. @ 20 min. Takes the shape of the pipe at 50 min.	≈ 900 psi @ 70 days
010410-1 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B. A. (based on the dry powders) 4.0 wt% Daratard (based on the dry powders) Total = 4214g	MgO=5.21 g MKP=17.58 g F.Ash C=53.16 g Daratard=3.16g B.Acid=1.16 g Water=19.74 g	-	-	Flow Cone: 15 min=12.8 s 45 min=13.3 s 90 min=15.0 s 135 min=16.9 s 165min=18.2 s 195min=19.9 s	-	-
011810-1 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) 4.0 wt% Daratard (based on the dry powders) Total = 1053g	MgO=5.21 g MKP=17.58 g F.Ash C=53.16 g Daratard=3.16g B.Acid=1.16 g Water=19.74 g	-	-	Viscosity: 4min=582 cP 16min=606 cP 31min=769 cP 55min=977 cP 67min=1159cP 82min=1316cP 97min=1462cP	-	-

Table 4-3 continued. Test results on Daratard-17 additions on Ceramicrete® based formulations.

Sample	Composition for 100 g sample	Peak Temp(°C) with thermo-couple test	Adiabatic Temperature rise (°C) (SRNL)	Flow-cone Test and Viscosity Data	Spread test (Pipe test)	Strength (psi)
010410-2 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) 4.0 wt% Daratard (based on the dry powders) Total = 2107g	MgO=5.21 g MKP=17.58 g F.Ash C=53.16 g Daratard=3.16g B.Acid=1.16 g Water=19.74 g	28 °C after 7 h	-	-	-	-
010510-1 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) 4.0 wt% Daratard (based on the dry powders) Total = 2128g	MgO=5.16 g MKP=17.40 g F.Ash C=52.64 g Daratard=3.12g B.Acid=1.15 g Water=20.53 g	-	-	-	8 in. @ 10 min. 6.25 in. @ 20 min. 5.50 in. @ 30 min. 3.75 in. @ 40 min. Takes the shape of the pipe at 50 min.	-
010710-1 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) 4.0 wt% Daratard (based on the dry powders) Total = 2149g	MgO=5.11 g MKP=17.24 g F.Ash C=52.13 g Daratard=3.10g B.Acid=1.13 g Water=21.30 g	-	-	-	8 in. @ 10 min. 7 in. @ 20 min. 5.75 in. @ 30 min. 4 in. @ 40 min. Takes the shape of the pipe at 50 min.	-

Table 4-3 continued. Test results on Daratard-17 additions on Ceramicrete® based formulations.

Sample	Composition for 100 g sample	Peak Temp(°C) with thermo-couple test	Adiabatic Temperature rise (°C) (SRNL)	Flow-cone Test and Viscosity Data	Spread test (Pipe test)	Strength (psi)
010810-1 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) 4.0 wt% Daratard (based on the dry powders) Total = 2169g	MgO=5.06 g MKP=17.07 g F.AshC=51.63 g Daratard=3.07g B.Acid=1.12 g Water=22.05 g	-	-	-	8.75 in. @ 10 min. 7.75 in. @ 20 min. 6.75 in. @ 30 min. 5.75 in. @ 40 min. 4.50 in. @ 50 min.	-
011110-1 (MgO+MKP)/ Fly Ash = 30/70 1.5 wt% B.A. (based on the dry powders) 4.0 wt% Daratard (based on the dry powders) Total = 2190g	MgO=5.01 g MKP=16.91 g F.AshC=51.14 g Daratard=3.04g B.Acid=1.11 g Water=22.80 g	-	-	-	9 in. @ 10 min. 8 in. @ 20 min. 7 in. @ 30 min. 5.75 in. @ 40 min. 4.50 in. @ 50 min.	-

4.7 Temperature and Fluidity Control (using Class C fly ash and Sand)

It was next decided to improve the flow characteristic and minimize temperature rise by substituting Class C fly ash filler with non-reactive sand filler. Various ratios of binder phase (MgO+MKP) and filler materials (Class C fly ash + sand) and ratios of Class C fly ash and sand were investigated. Property characterizations are listed in Table 4-4.

4.7.1 Key Observations

- Optimum results obtained were for formulation that had binder phase to filler ratio of 20:80 and filler (class C fly ash : sand) as 50:50 and with 5% additional water
  - Spread tests showed 8.5 inches at 10 min and 4.25 inch spread at 30 min mark (Mix 042010-1)
  - Calorimeter temperature rise stabilized at 59°C after 27 days (Mix 042010-1)
  - Temperature rise is gradual
  - Flow cone test showed 18 s flow time after 4.25 hours of mixing (Mix 031810-1)
  - Viscosity varied from 385 cP to 952 cP after 1.7 hour for static slurry (Mix 032210-1)
  - Compressive strength was 1500 psi after 60 days (Mix 031810-1).

- The above formulation meets all the criteria. However, if required, to further improve on the net temperature rise, it may be prudent to reduce the Class C fly ash content and replace it with sand.

- Thus, formulation 071510 was prepared to minimize the adiabatic temperature rise and optimize the flow and setting properties.
  - Flow time is 66 s after 4 hours
  - Gel time > 30 minutes
  - Adiabatic temperature rise for the equivalent mix, ANL 4, was 57°C after 33 days.

Table 4-4. Test results on using combination of Class C fly ash and sand as filler.

Sample	Composition for 100 g Sample	Peak Temp (°C) with Thermocouple Test	Adiabatic Temperature Rise (°C)	Flow-cone Test and Viscosity Data	Spread Test (Pipe test)	Strength (psi)
020510-1 (MgO+MKP)/ Filler (Sand and Fly Ash) = 30/70 Sand:FlyAsh = 60:40 Total = 192 g	MgO = 5.73 g MKP = 19.27 g Sand = 35.00 g F.Ash = 23.33g Water = 16.67 g	The first peak was seen at 48.5°C after 60 min. We started to see a temperature increase after 255 min.	-	-	-	-
020510-2 (MgO+MKP)/ Filler (Sand and Fly Ash) = 30/70 Sand:FlyAsh = 70:30 Total = 192 g	MgO = 5.73 g MKP = 19.27 g Sand = 40.83 g F.Ash C = 17.5g Water = 16.67 g	The first peak was seen at 49.5°C after 63 min. We started to see a temperature increase after 150 min.	-	-	-	-
020810-2 (MgO+MKP)/ Filler (Sand and Fly Ash) = 20/80 Sand:FlyAsh = 80:20 Total = 283 g	MgO = 3.89 g MKP = 13.10 g Sand = 54.37 g F.Ash C = 13.59g Water = 15.04 g	44.4°C after 6 h.	-	-	-	-
020910-1 (MgO+MKP)/ Filler (Sand and Fly Ash) = 20/80 Sand:FlyAsh = 60:40 Total = 283 g	MgO = 3.89 g MKP = 13.10 g Sand = 40.78 g F.Ash C = 27.19g Water = 15.04 g	42.4°C after 73 min.	-	-	-	-

Table 4-4 continued. Test results on using combination of Class C fly ash and sand as filler.

Sample	Composition for 100 g sample	Peak Temp (°C) with thermocouple test	Adiabatic Temperature rise (°C) (SRNL)	Flow-cone Test and Viscosity Data	Spread test (Pipe test)	Strength (psi)
020910-2 (MgO + MKP)/Filler (Sand and Fly Ash) = 20/80 Sand:FlyAsh = 50:50 Total = 283 g	MgO = 3.89 g MKP = 13.10 g Sand = 33.98 g F.Ash C = 33.98g Water = 15.04 g	42.5°C after 70 min	-	-	-	-
020910-3 (MgO + MKP)/Filler (Sand and Fly Ash) = 20/80 Sand:FlyAsh = 70:30 Total = 283 g	MgO = 3.89 g MKP = 13.10 g Sand = 47.58 g F.Ash C = 20.39g Water = 15.04 g	42.5°C after 70 min	-	-	-	-
021010-1 (MgO + MKP)/Filler (Sand and Fly Ash) = 20/80 No sand Total = 303 g	MgO = 3.64 g MKP = 12.23 g F.Ash C = 63.47g Water = 20.66 g	42.9°C after 70 min	-	-	-	-

Table 4-4 continued. Test results on using combination of Class C fly ash and sand as filler.

Sample	Composition for 100 g sample	Peak Temp (°C) with thermocouple test	Adiabatic Temperature rise (°C (SRNL)	Flow-cone Test and Viscosity Data	Spread test (Pipe test)	Strength (psi)
042010-1 (MgO+MKP)/ Filler (Sand and Fly Ash) = 20/80 Sand:FlyAsh = 50:50 1.5 wt% B.acid (based on the dry powders) Total = 2250 g (≈1000 mL)	MgO = 3.81 g MKP = 12.85 g Sand = 33.29 g F.Ash C = 33.29 g B.Acid = 1.28 g Water = 15.50 g	22 °C after 21 days	59°C after 27 days ANL 3 Final temp. = 20°C (initial) + 59°C (temp rise) = 79°C	-	8.5 in @ 10 min 7.25 in @ 20 min 4.50 in @ 30 min Takes the shape of the pipe at 40 min	-
031810-1 (MgO+MKP)/ Filler (Sand and Fly Ash) = 20/80 Sand:FlyAsh = 50:50 1.5 wt% B.A. (based on the dry powders) Total = 4501 g	MgO = 3.81 g MKP = 12.85 g Sand = 33.29 g F.Ash C = 33.29 g B.Acid = 1.28 g Water = 15.50 g	-	-	Flow Cone: 15min=12.9 s 45min=13.1 s 90min=13.6 s 135min=14.1 s 165min=14.6 s 195min=15.3 s 225min=16.9 s 255min=18.0 s	-	≈1500 psi after 60 days
032210-1 (MgO+MKP)/ Filler (Sand and Fly Ash) = 20/80 Sand:FlyAsh = 50:50 1.5 wt% B.A. (based on the dry powders) Total = 1052 g	MgO = 3.81 g MKP = 12.85 g Sand = 33.29 g F.Ash C = 33.29 g B.Acid = 1.28 g Water = 15.50 g	-	-	Viscosity: 4min=385 cP 16min=283 cP 31min=416 cP 55min=630 cP 67min=692 cP 82min=730 cP 97min=813 cP 106min=952cP	-	-

Table 4-4 continued. Test results on using combination of Class C fly ash and sand as filler.

Sample	Composition for 100 g sample	Peak Temp (°C) with thermocouple test	Adiabatic Temperature rise (°C) (SRNL)	Flow-cone Test and Viscosity Data	Spread test (Pipe test)	Strength (psi)
030810-1 (MgO+MKP)/ Filler (Sand and Fly Ash) = 20/80 Sand:FlyAsh = 50:50 Total = 565 g	MgO=3.89 g MKP=13.10 g Sand=33.98 g F.Ash C=33.98g Water=15.04 g	-	-	-	-	≈970 psi after 18 days
062510-1 (MgO+MKP)/ Filler (Sand and Fly Ash) = 20/80 Sand:FlyAsh = 70:30 0.5 wt% B.A. (based on the dry powders) Total = 1138 g	MgO=4.02 g MKP=13.55 g Sand=49.14 g F.Ash C=21.06 g B.Acid=0.45 g Water=11.78 g	-	-	Viscosity: 4min=451 cP 16min=592 cP 31min=866 cP 55min=1518cP 64min=2451cP	-	≈2060 psi after 7 days
062410-1 (MgO+MKP)/ Filler (Sand and Fly Ash) = 20/80 Sand:FlyAsh= 60:40 0.5 wt% B.A. (based on the dry powders) Total = 356 g	MgO=4.02 g MKP=13.55 g Sand=42.11 g F.Ash C=28.09 g B.Acid=0.45 g Water=11.78 g	-	-	-	-	1980 psi after 7 days

Table 4-4 continued. Test results on using combination of Class C fly ash and sand as filler.

Sample	Composition for 100 g sample	Peak Temp (°C) with thermocouple test	Adiabatic Temperature rise (°C)	Flow-cone Test and Viscosity Data	Spread test (Pipe test)	Strength (psi)
062410-2 (MgO+MKP)/ Filler (Sand and Fly Ash) = 20/80 Sand:FlyAsh = 70:30 0.5 wt% B.A. (based on the dry powders) Total = 5008 g	MgO=4.02 g MKP=13.55 g Sand=49.14 g F.Ash C=21.06 g B.Acid=0.45 g Water=11.78 g	-	-	Flow Cone: 15min=43.6 s 45min=45.4 s 90min=52.0 s 135min=122 s	-	2059 psi after 7 days
062810-1 (MgO+MKP)/ Filler (Sand and Fly Ash) = 20/80 Sand:FlyAsh = 70:30 0.5 wt%B.acid (based on dry powders) Total = 5008 g	MgO=4.02 g MKP=13.55 g Sand=49.14 g F.Ash C=21.06 g B.Acid=0.45 g Water=11.78 g	-	-	Flow Cone: 15min=43.6 s 45min=45.4 s 90min=52.0 s 135min=122 s	-	-
071510-1 (MgO+MKP)/ Filler (Sand and Fly Ash) = 20/80 Sand:FlyAsh= 70:30 1.0 wt%B.acid (based on dry powders) Total = 5060.83 g	MgO=4 g MKP=13.4 g Sand=48.4 g F.Ash C=20.8 g B.Acid=0.9 g Water=12.5 g	-	57°C after 33 days ANL 4 Final temp. = 23°C (initial) + 57°C (temp. rise) = 80°C	Flow Cone: 15min=25.85 s 45min=26.22 s 90min=28.45 s 135min=33.75 s 165min=38.99 s 195min=44.54 s 225min=55.92 s 240min=65.55 s	5.5 in @ 10 min 4.0 in @20 min 2.75 in @ 30 min	-

4.8 Phase Analysis

X-ray diffraction was conducted on set and cured mixes 010410-1 (Table 4-3) and 012810-1 (Table 4-2) to ensure the right binder phases are formed. As shown in the diffraction pattern in Figure 4-1, sharp peaks of binding phase magnesium mono potassium phosphate hexahydrate are formed. In addition, some residual magnesium oxide remains encapsulated in the magnesium phosphate phase.

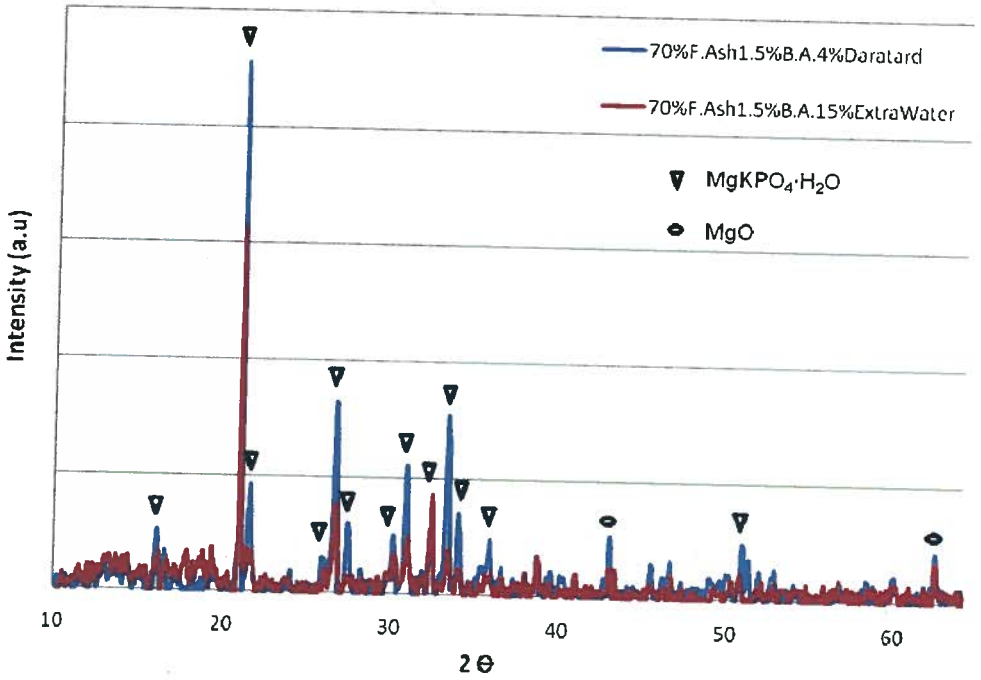

Figure 4-1. X-ray diffraction analysis of cured Ceramicrete®

4.9 Alkalinity of Water in Contact With Cured ANL Grouts

The pH of water in contact with unset ANL grout slurries had pHs between 6 and 8 [Singh, 2009]. However, the pH of water in contact with two ANL grouts cured in the SRNL calorimeter was between 11 and 11.2 after contact for 1 to 3 days. See Table 4-5.

Table 4-5. pH of water in contact with cured ANL grout samples.

Contact Time	ANL 042010-1 (ANL 3H calorimeter)	ANL 020310-1 (ANL 2H calorimeter)
Days	pH	pH
15 minutes	10.8	10.94
1	11.02	11.08
2	11.1	11.15
3	11.16	11.2

4.10 Bench Scale-Up Test

At ANL, it was decided to do a test in which the slurry was put in an aluminum pipe. This evaluation was done to see how the slurry sets in the aluminum pipe, shrinkage, and any bleed water.

The composition of the slurry prepared was similar to the sample 010410-1 as indicated in Table 4-3. The slurry was poured into a 4-inch diameter aluminum tube. Figure 4-2 (a) shows the photographs of the poured slurry in the tube. As can be observed, there is no separation or bleeding of water. Figure 4-2 (b) and 4-2 (c) show the cut sections of the tube after complete setting. Again, the cut section shows uniform material along the length of the sample. Material is uniform and dense. There is no segregation or trapped porosity or bubbles. Post setting, cement did not pull away from the tube wall. Based on these preliminary tests in aluminum pipe, the cement behavior for placement is encouraging.

(a) (b) (c)

Figure 4-2. Photographs of the slurry prepared in lab and placed in an aluminum tube.

One half of the sample shown above was examined at SRNL several months after it was cast. The inside surface of aluminum tube in which the sample was cast was covered with numerous small pits (white spots indicating aluminum hydroxide). The sample was stored in an unsealed plastic bag at room temperature. Although this observation is qualitative, it does illustrate

localized corrosion for aluminum metal in contact with alkaline grout. (Small white spots on the aluminum tube are just visible in Figure 4-2 (c).)

4.11 ANL Adiabatic Calorimeter Results

Adiabatic calorimeter results for three ANL mixes are shown in Figures 4-3 to 4-6. These grout samples continued to react and generate heat over at least 2 weeks (13 to 33 days, i.e., length of the experiment). Differences in the shape of the time versus temperature curves may be due to different set retarders and / or to the proportions of the ingredients used in the mixes.

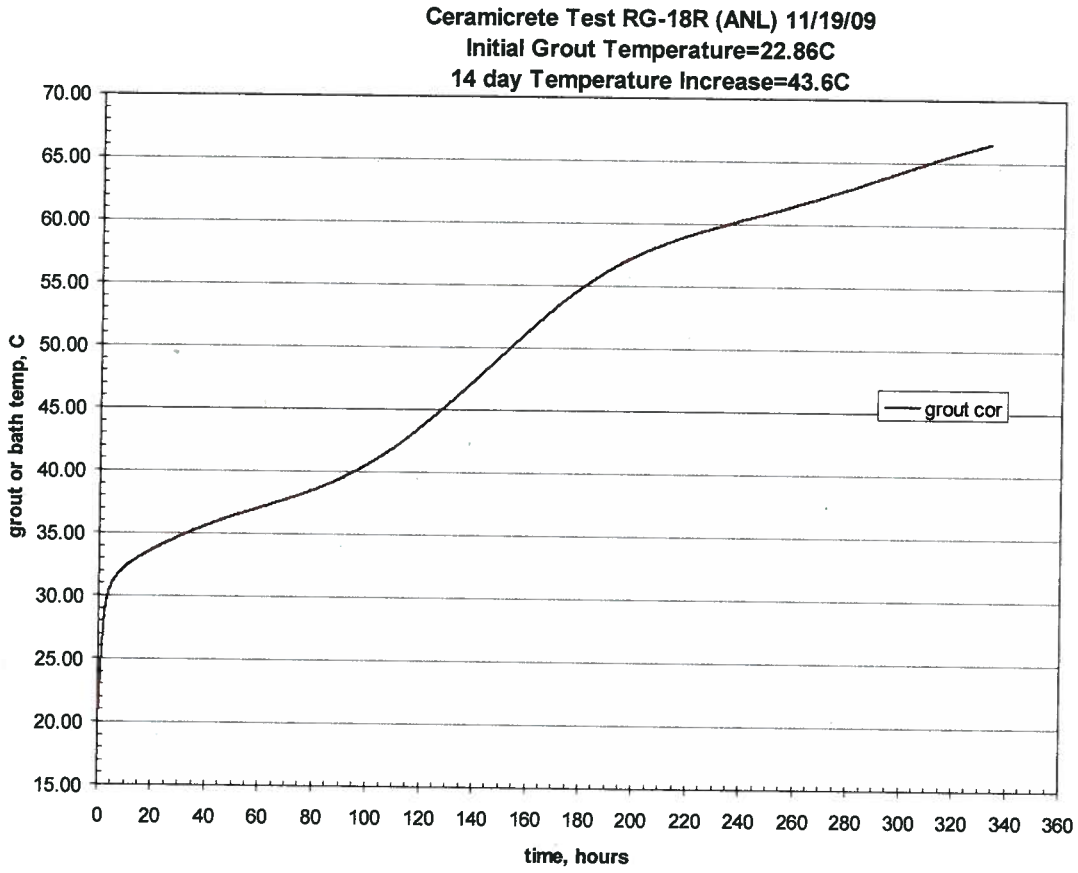

Figure 4-3. Adiabatic calorimeter time versus temperature plot for Mix RG-18R which is ANL 102009-1 in Table 4-2.

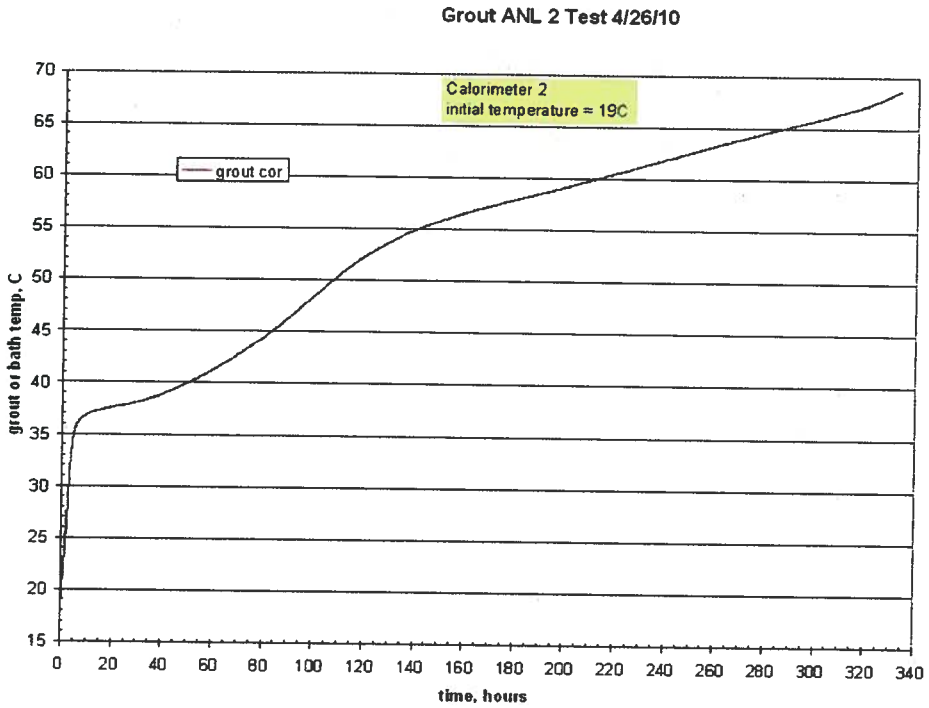

Figure 4-4. Adiabatic calorimeter time versus temperature plot for ANL Mix 2 which is Mix 020310-1 in Table 4-2.

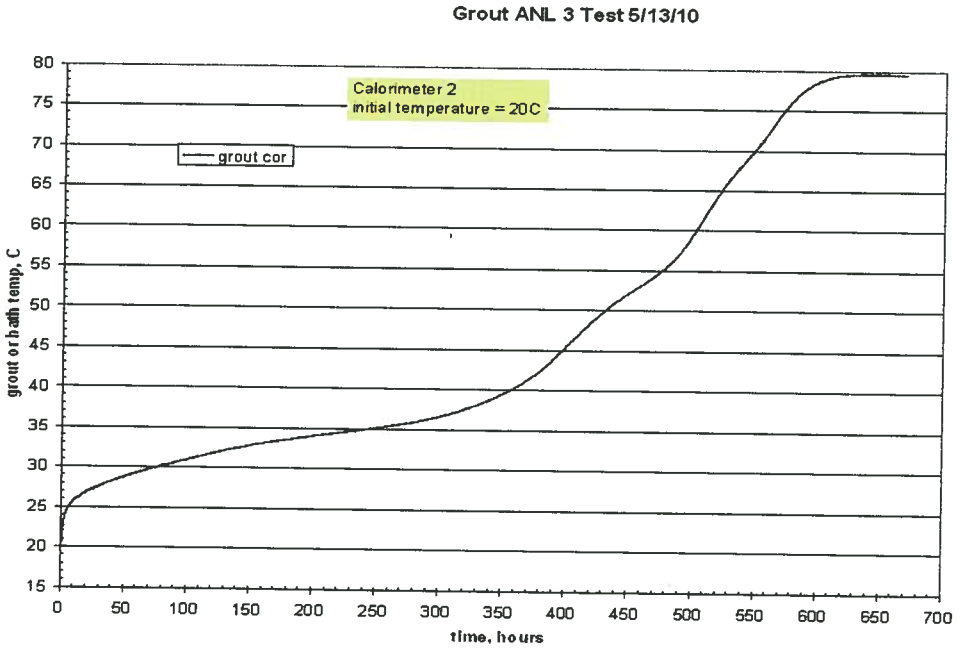

Figure 4-5. Adiabatic calorimeter time versus temperature plot for Mix ANL 3 which is ANL Mix 042010-1 in Table 4-4.

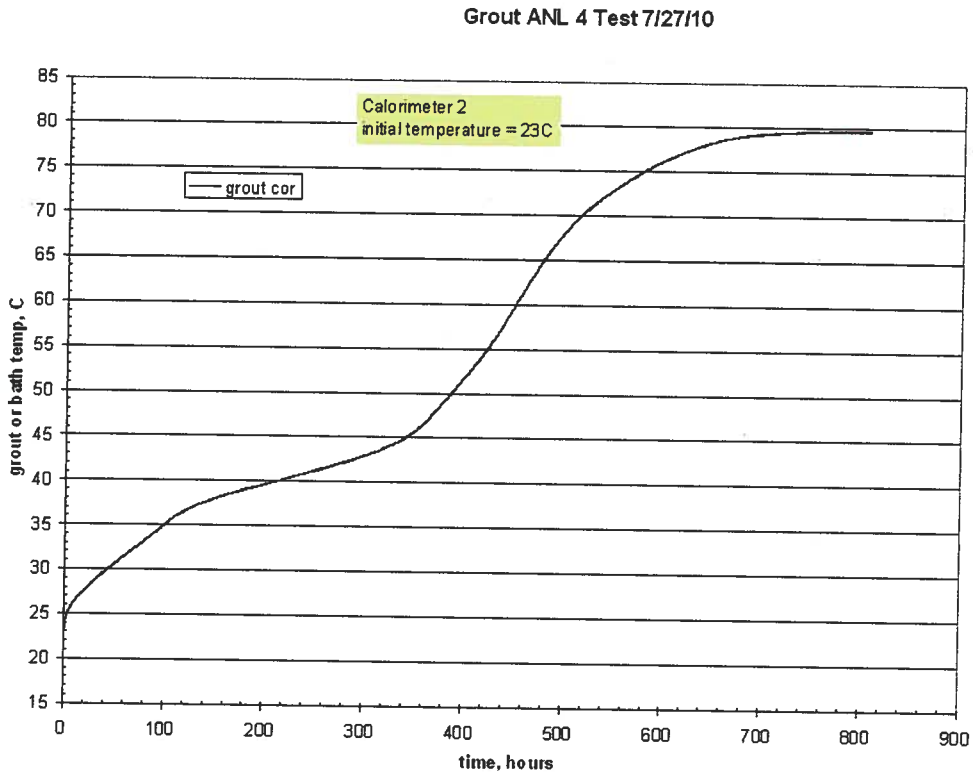

Figure 4-6. Adiabatic calorimeter time versus temperature plot for Mix ANL 4 which is ANL Mix 071510-1 in Table 4-4.

5.0 DISCUSSION and CONCLUSIONS

Magnesium mono potassium phosphate grouts were evaluated as reactor fill materials. Magnesium mono potassium phosphate based grouts can be formulated that meet the requirements for SRS Reactor Vessel ISD. Two approaches to formulating a magnesium mono potassium phosphate grout for the SRS reactor vessel ISD were investigated. SRNL concentrated on using a Class F fly ash and quartz sand (bimodal size distribution) for the inert filler portion of the mix. ANL concentrated on using a fine powder, Class C fly ash, which is reactive as the filler and quartz sand as an inert filler.

Although magnesium mono potassium phosphate cements are used in the construction industry for rapid set applications, the commercial materials are not suitable for large pours and have not been formulated as flowable grouts. Consequently the commercial products need to be modified or completely reformulated. Reformulation focused on reducing the reaction heat, extending the working times, and producing a physically stable, flowable grout that spread upon placement. Multiple approaches were initiated and several resulted in potential formulations.

A literature review and a product search were performed to identify commercial suppliers of magnesium mono potassium phosphate cement products. Magnesium mono potassium phosphate grouts can be prepared from:

- Packaged grout product (binder plus inert fillers) mixed with water
- Packaged binder mixed with water, sand aggregate and inert powder and set retarded as needed
- Individual binder reagents mixed with water, sand aggregate and inert powder and set retarder as needed.

The SRNL approach resulted in lower temperature rises for reactions that were completed within a few days (complete reaction resulted in 40.4°C over 48 hours) The ANL approach resulted in mixes with more gradual temperature rises that continued to increase over the length of the longest test which was 33 days (ANL 4 had a temperature rise of 57°C.)

Mixes prepared with the Bindan SR 3.10 binder and masonry sand met the requirements for filling the reactor vessel and are recommended for the P-Reactor fill grout. Mix 34 contains 14 wt. % binder, 12.3 wt. % water, 19.3. % Class F fly ash and 54.3 % inert sand-size aggregate and is recommended for scale-up testing. Field conditions may require set adjustment of Mix 34. Boric acid set retarder can be added up to 2 wt. % of the binder to achieve longer working times.

Some of the magnesium mono potassium phosphate grouts tested in the laboratory displayed expansion. The cause of this expansion is not fully understood and although the recommended mix did not expand, understanding of these phenomena is important.

In summary, both the ANL and SRNL mixes meet most of the SRS reactor vessel fill material requirements. The properties of the recommended mixes are tabulated in Table 5-1 along with selected requirements.

Table 5-1. Summary of properties of magnesium phosphate grout mixes recommended for filling the SRS P-Reactor Vessel.

Property	Requirement	ANL Mix 071510-1 (ANL 4)	SRNL Mix 34 With Chilled Water
pH Slurry	< 10.5	6 to 8	6
pH Cured Material in Contact with Water	< 10.5	11 to 11.2	7.9 to 9.8
Adiabatic Temperature Rise (°C)	< 60	57	42.9
Maximum Temperature (°C)	< 95	80	68
Flow (flow cone) ASTM C-939 (s)	< 100	~ 26	31 to 50 over 8 minutes
Static Working Time (min.)	~ 30	~15	~ 15 minutes without boric acid ~ 30 with boric acid at 1.5 wt. % of binder
Dynamic Working Time (min.)	> 60	> 180	~ 60 minutes with and without boric acid
Compressive Strength	> 200	Not measured	1096 @ 1 day w/o boric acid 705 @ 1 day w/ 1.5 wt.% boric acid
Maximum Particle Size (mm)	< 3	If general purpose sand does not meet this requirement another quartz sand can be used.	If general purpose sand does not meet this requirement another quartz sand can be used.

5.1 SRNL Mixes

5.1.1 Packaged Grout Products

Commercially available magnesium mono potassium phosphate grout products were obtained and tested. Several packaged Bindan Mono-Grouts products (SR 1.0, SR 2.0, SR 3.0 and 3.10) were acquired and tested at SRNL, but these materials did not meet the RV requirements. Mix 2H, Bindan Corporation, Mono-Grout SR 3.10, is an example of one of the lowest temperature (least reactive) mixes. However, the temperature rise for this mix was still too high (51°C) for the SRS reactor vessel application since multiple pours / lifts and time between lifts for heat dissipation could be required.

5.1.2 Packaged Binder Plus Specialty Inert Fillers

Since efforts to acquire a complete packaged grout product were considered unsuccessful, SRNL personnel requested Bindan Corporation to supply only the binder portion of the packaged grout product. The commercial Bindan SR 3.10 binder was used by SRNL researchers to formulate grouts with inert aggregates in proportions that resulted in lower temperature (less reactive) mixes. Special graded inert fillers in addition to locally available inert fillers were tested. The special graded sands did not have any significant advantage over the locally available masonry sand, except that they were finer and possibly capable of filling the septifoils. The special graded sand mixes were not pursued because they required more binder relative to the amount of aggregate to achieve a monolithic material. The additional binder resulted in a higher temperature rise and additional cost.

5.1.3 Packaged Binder Plus SRS Inert Fillers (Masonry and Class F Fly Ash)

Mixes prepared with the Bindan SR 3.10 binder and masonry sand met the requirements for a reactor fill material. The coarser masonry sand enabled mixes to be formulated with less binder and consequently lower adiabatic temperature rises. Mix 29 is an example of these mixes. This mix contains 15.8 wt. % binder, 12.3 wt. % water (boric acid is in the packaged product), 19.3 wt. % Class F fly ash, and 55.6 wt. % inert sand-size aggregate.

One issue that arises from using masonry sand obtained from a local quarry is that the sand contains moisture and cannot be premixed with the binder. This needs to be taken into account in designing the production process for the scale-up test and for full-scale production.

5.1.4 Cementitious Reagents Plus Local Masonry Sand and Class F Fly Ash

Ingredients in the SRNL magnesium mono potassium phosphate grouts included: magnesium mono potassium phosphate binder (mixture of MgO and MKP), inert powder (Class F fly ash) and inert aggregate (quartz sand). Several MgO and MKP reagent products were evaluated. MagChem® 10CR MgO and MKP 771 performed best. Other products produced mixes that displayed excessive expansion. The cause of the expansion is related to the reaction rate (rate of temperature rise and maximum temperature) and the phases formed. Boric acid additions were partially successful in controlling the reaction rate and expansion.

Grouts with 14 to 16 weight percent binder meet the compressive strength and adiabatic temperature rise requirements. Flow and working times (dynamic and static) require adjustments with boric acid and / or water. The reagents, (MagChem® 10CR, and MKP 771), fillers (Class F fly ash and masonry sand), KIM, and boric acid and proportions in Mix 40 are recommended for scale-up testing, if the desire is to prepare a magnesium mono potassium phosphate binder from individual ingredients.

5.2 ANL Formulations

Slurry properties and cured properties of the ANL magnesium mono potassium phosphate grouts designed for the SRS reactor vessel ISD requirements are provided in this report. All of the mixes submitted for consideration contained Class C fly ash which is a reactive filler. These

mixes continued to react and generate heat over at least 3 to 4 weeks and the cumulative heat generated under adiabatic conditions resulted in temperatures above the limit set for the reactor vessel grout. Attempts to reduce the total reaction heat were partially successful but did not lower the reaction heat enough. In order to account for heat produced by exothermic reactions that occur beyond the test time, a factor of 1.4 is applied to the measured adiabatic temperature rise [Guerrero, 2010].[7] Consequently, the ANL magnesium mono potassium phosphate cementitious system was the second rather than first choice for the scale-up testing. See Figure 4-6.

[7] The factor of 1.4 was established for portland cement- and slag-based materials and is probably too high for the magnesium phosphate based materials. Because the ANL mixes had higher temperature rises than the SRNL mixes, they were not chosen for the reactor application. However other ISD applications are being investigated for these materials.

6.0 RECOMMENDATIONS

SRNL Mix 34 (Bindan SR 3.10 binder, 14 wt. %; water, 12.3 wt. %; Class F fly ash, 19.3 wt. %; inert masonry sand, 54.3 wt. %; and KIM, 1.0 wt.% of the binder) is recommended for scale-up testing. A bimodal distribution of inert fillers (powder and sand) is recommended to achieve a low heat, stable slurry.

Ingredient	Proportions* (lbs / cubic foot)	Proportions* (lbs / cubic yard)
Bindan SR 3.10 Binder (contains boric acid)	18.9	510.2
Class F Fly Ash	26.0	701
Masonry Sand	73.2	1976.4
KIM 301 Integral Waterproofing reagent	0.19	5.1
Chilled Potable Water (0 to 10°C)	16.5	446.2
Total	134.8	3639.9
Boric Acid and or organic set retarder	As Needed Up to 2 wt. % of the SR 3.10 binder	

* Proportions per unit volume are approximate and were determined on laboratory scale samples. Proportions per unit volume need to be confirmed on larger size batches.

Commercially available packaged binders are recommended instead of preparing the binder from MgO and MKP because these materials, especially the MgO is variable and the responsibility of obtaining suitable material is best assumed by producers who have experience in obtaining and formulating the magnesium mono potassium phosphate cements. Bindan Corporation SR 3.10 Binder is the packaged product recommended for scale-up testing. This material was tested along with several other Bindan products and was used to formulate SRNL Mix 34 for the bench scale-up test.

Chilled water 0 to 10°C is recommended for scale up testing and for full-scale production. Cooling the mixer and transfer hose should also be considered for the scale-up testing which was scheduled for August and September 2010 in Atlanta, GA, and for the full-scale production if work is performed during hot weather. The need to clean the mixer and transfer line every 60 minutes should be evaluated. The need will depend in part on the configuration of the mixer, hold tank and pump hopper used in the scale-up testing. The material thickens quickly once it reaches 88 to 90°F. The ability to control chemical reactions by controlling temperature requires further investigation. Addition of more water is not adequate to recover slurry properties (pumpability) once the material reaches 88 to 90°F.

The ability to make field adjustments in the amount of water is required to account for the sand moisture sorption and ambient conditions. The ability to make minor adjustments in the proportions of the binder, sand and fly ash is recommended because of reported minor variability in the properties of the binder ingredients. The need for such adjustments should be made on the basis of quality control performance testing and should be accomplished prior to delivery of the material to the job site.

Performance testing of the blended material will determine whether an organic and/or inorganic set retarding admixture is required for scale-up and full scale production. The capability to add a set retarding admixture in addition to that which may be supplied in the pre-blended binder material should also be provided for the job site.

An alternative low pH grout system should be developed in case the scale-up testing of the magnesium mono potassium phosphate system is found to present problems that cannot be overcome in time to meet the project schedule. Calcium sulfo-aluminate-based cement which hydrates to form ettringite as a primary phase and aluminum hydroxide as a minor phase is a potential candidate for meeting the reactor vessel fill requirements.

Mix 40 (MagChem® 10CR, 3.2 wt. % ; MKP 771, 10.7 wt.% ; Class F fly ash, 19.1 wt. %; masonry sand, 53.8 wt. %; KIM, 1.0 wt. % of the binder; boric acid, up to 2 wt.%; and water, 13.0 wt.% is also recommended as an alternative to Mix 34.

Ceramicrete® based grouts, i.e., mono potassium phosphate mixes containing Class C fly ash, were not selected for the SRS Reactor Vessel ISD project but are being investigated for other applications. These materials are slightly expansive, have excellent metal adhesion and multivalent ion stabilization characteristics. The testing performed in this study demonstrates that flowable fills can be formulated with the Ceramicrete® binder. Significant set retardation can be achieved with boric acid and a gradual strength gain over several weeks is possible. Another feature of this material is that surface preparation is not required to eliminate cold joints.

Research on mixing, selecting raw materials, and hydration reactions in the magnesium potassium phosphate system could expand the applications of this material if the working time of the fresh material can be further lengthened, the temperature rise lowered, and the formation of struvite (cementitious phase) can be achieved at a lower temperature.

7.0 QUALITY ASSURANCE

The work performed at SRNLwas done 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) and WSRC-2004-NB-0064, and SRNL-NB-2009-00162 (calorimeter data).

8.0 ACKNOWLEDGEMENTS

DOE-EM-44 provided funding for the magnesium mono potassium phosphate grout screening studies performed at ANL. ARRA funded the development work at SRNL.

Support and technical expertise from the following researchers was much appreciated and essential to this effort. Justin Waymer and David Matheny, SRNL summer interns, prepared most of the samples generated for this study under the supervision of W. B. Mhyre, and A. G. Isherwood, and W. Pope Jr., URS Washington Group, Quality and Testing Division, provided technical expertise, testing, and use of the SRS Civil Engineering Laboratory for conducting this study. H. N. Guerrero, J. L. Steimke, Q. H. Zafar, and M. L. Restivo, SRNL, performed the calorimeter testing. N. J. Vrettos, J. T. Bobbitt III, SRNL, provided drawings and models of the P-Reactor Vessel, which were essential for visualizing flow paths and for designing the placement strategy. M. M. Reigel and A. J. Duncan, SRNL, provided characterization of the materials. M. G. Serrato, SRNL, managed this project and served as liaison between D&D and the SRNL technical resources. J. K. Blankenship and W. B. Griffin, provided much appreciated project review and support for this effort. Y. Yusufoglu and R. Ganga provided much appreciated laboratory assistance at the ANL.

9.0 REFERENCES

Blankenship, J. K. 2009. Personal communication with C. A. Langton and M. S. Serrato.

Bobbitt, J. and N. Vertos, 2010. P-Reactor Vessel Scale Model, SRNL-L3100-2010-00093, Savannah River National Laboratory, Savannah River Nuclear Solutions, Aiken SC 29801.

Crawford, C. L., 2009. Personal Communication of Data to C. A. Langton, Savannah River National Laboratory, Aiken, SC 29808.

Diken, G. M. 2010. ICL Performance Products LP, Technical Support, Personal Communication with D. Stefanko and C. Langton.

Griffin, W. B., 2010. "Reactor Vessel Grout Scale-up Testing and Material Mixing / Pumping for Placement (U)," G-SOW-G-00121, Savannah River Nuclear Solutions, Aiken, SC 29808.

Guerrero, H. N., 2009. Thermo-Physical Characterization of Reactor Vessel Fill Materials for P- and R- Reactor In-Situ Decommissioning," SRNL-RP-2009-01185, September, 2009, Savannah River National Laboratory, Aiken, SC 29808.

Guerrero, H. N., 2010. Personal Communication of Data to D. B. Stefanko, Savannah River National Laboratory, Aiken, SC 29808.

Guerrero, H. N., et al, 2009. "Measurement of Thermo-Physical Parameters of Base Portland Cement and Ceramicrete® Grout," SRNL-L3100-2009-00266, October 29, 2009, Savannah River National Laboratory, Savannah River Nuclear Solutions, Aiken SC 29801.

Musall, J. C. 2009. SDD Engineering, Technical Assistance Request, "Grout/Concrete (Cementitious Materials) related Engineering Activities Needed to Support PAOU Remedial Actin Final design," TAR-SDD-2008-00133, Savannah River Nuclear Solutions, Aiken, SC 29808.

Odler, I., 2000. Special Inorganic Cements, E&FN SPON, NY, NY.

PAOU Final Action Reactor Building Complex, 2008. Q-MT-P-00003, October 21, 2008, Savannah River Site, Aiken, SC 29808.

Serrato, M. G., et. al., 2010. "105-R Reactor Vessel Filling Using Cementitious Grout," SRNL-L6100-2010-00008, Memorandum to J. C. Musall and J.K. Blankenship, May 24, 2010, Savannah River National Laboratory, Savannah River Nuclear Solutions, Aiken, SC 29801.

Singh. D. 1998. U. S. Patent 5,846,894, Phosphate Bonded Structural Products from High Volume Waste, Argonne National Laboratory, Argonne, IL.

Singh, D., 2009. Personal Communication with C. A. Langton and M. S. Serrato, Savannah River National Laboratory, Aiken, SC 29808.

SRS-MPO, 2009. Memorandum Purchase Order, (MPO), Argonne National Laboratory – Chemical Grout Analysis and Technical Consultation, Statement of Work 0S0202 G-SOW-A-00086, Rev. 0, Savannah River Nuclear Solutions, Aiken, SC 29808.

Stefanko, D. B., 2009. "Design, Testing and Recommendations for SRS Reactor Vessel Fill Materials, Task Technical and Quality Assurance Plan," SRNL-RP-2009-01248, Rev. 0, October 5, 2009, Savannah River National Laboratory, Savannah River Nuclear Solutions, Aiken, SC 29801.

Stefanko, D. B., 2009. "Reactor Vessel Fill feasibility Study: Magnesium potassium phosphate Cement Grout, Laboratory Test Plan, SRNL-RP-2009-01501," Savannah River National Laboratory, Savannah River Nuclear Solutions, Aiken, SC 29801.

Steimke, J. L., A. H. Qureshi, M. L. Restivo, and H. N. Guerrero, 2010. "Reactor Grout Thermal Properties," SRNL-STI-2010-00806 DRAFT (not reviewed), January 2011, Savannah River National Laboratory, Savannah River Nuclear Solutions, Aiken, SC 29801.

Vrettos, N. J., 2009. Personal Communication / PowerPoint Presentation, November 2009, Savannah River National Laboratory, Savannah River Nuclear Solutions, Aiken, SC 29801.

Wagh, A. S., et al., 1998. U.S. Patent 5,830,815, Method of Waste Stabilization via Chemically Bonded Phosphate Ceramics, Argonne National Laboratory, Argonne, IL.

Wagh, A. S., 2001. "Chemically Bonded Phosphate Ceramics for Stabilization and Solidification of Mixed Waste," Chapter 6.3 in Hazardous and Radioactive Waste Treatment Technologies Handbook, ed. Oh, C. H., CRC Press, NY, NY.

Wagh, A. S., 2004. Chemically Bonded Phosphate Ceramics, Elsevier, NY, NY.

Wiersma, B. J., 2009. "Reactive Metal (Al) Interactions During Grouting Operations of the R- and R-Reactor Vessel," SRNL-RP-2009-01198, Rev. 0, September 2009, Savannah River National Laboratory, Aiken, SC 29808.

Wiersma, B. J., 2009. "Assessment of the Potential for Hydrogen Generation During Grouting Operations in the R- and P- Reactor Vessels," SRNL-STI-2009-00639, Rev. 0, October 2009, Savannah River National Laboratory, Savannah River Nuclear Solutions, Aiken, SC 29801.

Wilson, A. D. and J. W. Nicholson, 1993. Acid-Base Cements, Cambridge University Press, Cambridge, UK.

BLANK PAGE

DISTRIBUTION:

R. J. Abitz, 773-43A
A. B. Barnes, 999-W
J. K. Blankenship, 707-25B
B. J. Giddings, 786-5A
J. C. Griffin, 773-A
W. B. Griffin, 707-25B
H. N. Guerrero, 786-5A
A. G. Isherwood, 717-5N
H. Khalil, ANL
C. A. Langton, 773-43A
J. T. Long, 730-4B
S. L. Marra, 773-A
J. J. Mayer II, 773-42A
W. L. Mhyre, 717-5N
J. C. Musall, 707-25B
A. C. Raptis, ANL
F. M. Pennebaker, 773-42A
M. G. Serrato, 773-42A
D. Singh, ANL
D. B. Stefanko, 773-43A
J. L. Steimke, 786-5A
STI