

Final Scientific/Technical Report

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Executive Summary

After an oil, gas, or geothermal production well has been drilled, the well must be stabilized with a casing (sections of steel pipe that are joined together) in order to prevent the walls of the well from collapsing. The gap between the casing and the walls of the well is filled with cement, which locks the casing into place. The casing and cementing of geothermal wells is complicated by the harsh conditions of high temperature, high pressure, and a chemical environment (brines with high concentrations of carbon dioxide and sulfuric acid) that degrades conventional Portland cement.¹

During the 1990s and early 2000s, the U.S. Department of Energy's Geothermal Technologies Office (GTO) provided support for the development of fly-ash-modified calcium aluminate phosphate (CaP) cement, which offers improved resistance to degradation compared with conventional cement. However, the use of CaP cements involves some operational constraints that can increase the cost and complexity of well cementing. In some cases, CaP cements are incompatible with chemical additives that are commonly used to adjust cement setting time. Care must also be taken to ensure that CaP cements do not become contaminated with leftover conventional cement in pumping equipment used in conventional well cementing.

With assistance from GTO, Trabits Group, LLC has developed a zeolite-containing cement that performs well in harsh geothermal conditions (thermal stability at temperatures of up to 300°C and resistance to carbonation) and is easy to use (can be easily adjusted with additives and eliminates the need to "sterilize" pumping equipment as with CaP cements). This combination of properties reduces the complexity/cost of well cementing, which will help enable the widespread development of geothermal energy in the United States.

¹*Advanced Cements for Geothermal Wells*, Brookhaven National Laboratory (2006), <http://www.bnl.gov/isd/documents/35393.pdf>

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Comparison of Goals and Accomplishments

Project Objective

Develop a novel, zeolite-containing lightweight, high temperature, high pressure geothermal cement, with the following characteristics:

- Zero percent free water
- Rheological properties of less than 200 reading at 300 rpm
- 24 Hour compressive strength greater than 500 psi
- Thickening time and consistency, end thickening under 70 Bc
- Slurry density less than 13.5 lbs/gal

The development of such a cement would provide operators with an easy to use, flexible cementing system that saves time and simplifies logistics.

Technical Approach

The project was based on technology developed for low temperature, weak formation applications that has had limited commercialization. There existed a sound scientific knowledge base using the technology in actual well completions but not the harsh high temperature, high pressure, corrosive environments posed in geothermal well completions. Performance characteristics of the technology however, indicated that the technology could be amended or modified to be effective in harsh geothermal environments.

The research and development was conducted in five overlapping Tasks. These were:

TASK 1 – RESEARCH

Literature Search

A comprehensive literature search was performed to fully review the current technology in cementing of HTHP oil, gas, and geothermal wells. Since most of the information related to these cement compositions and additives are proprietary, a careful literature search is necessary to establish a starting point for this project. The literature search involved reviewing information in the public domain as well as acquiring documents with fee payments.

Geothermal Cementing Practices and Constraints

A comprehensive review of current cementing materials and placement methods was performed to identify operational constraints that could be reduced or eliminated with the development of improved geothermal cement. This review included U.S. geothermal development and information requests to the International Partnership for Geothermal Technology member countries Australia and Iceland.

Mechanisms of Geothermal Well Failure

A review was completed to understand the processes of geothermal well failure resulting from cement breakdown. The primary design of the well cement was to reduce or eliminate the risk of the well failing to function as a long-term conduit between the surface and the deep geothermal resource. The unique EGS well conditions of long casing strings, temperature drops during stimulation and the mechanical stresses of through-casing stimulation was examined for cement design.

TASK 2 – DESIGN

Compile Research Findings

The knowledge base gained during the completion of Task 1 was compiled noting existing technology, current practices as well as cost and logistical constraints that influence cement development.

Modification of Project Tasks 3 and 4

Under this Task, Tasks 3 and 4 were modified to take advantage of any improvements in additives, methods and testing procedures. Additionally, refinement of the Development and Testing Tasks continued throughout the project as research results were factored into cement formulations.

TASK 3 – DEVELOP

Zeolite Sample Acquisition

It was noted at the beginning of the project that there are more than 40 naturally occurring zeolite types or “species”. For this project four types were used. These were, Clinoptilolite, Chabazite, Ferrierite and Analcime. Because these are naturally occurring minerals there was variability in the zeolite composition for each type. Therefore, it was necessary to acquire sufficient sample for each type to supply the testing needs for the entire project. This ensured that natural variability was eliminated as a factor in different permutations of cement development.

Approximately 1,000 pounds of each zeolite type was required for the project. Samples for two of the types came from operating mines while the other two were acquired as bulk exploration samples. For each sample type the material was crushed and sized to a uniform minus US 8 Mesh product.

Zeolite Type Confirmation

Representative samples were taken from each of the four zeolite type bulk 8 Mesh samples. These representative samples were submitted for X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) studies to confirm zeolite percentage and type.

Zeolite Particle Size Preparation

For this project each zeolite type was prepared to three different particle sizes. These particle sizes were: 5 micron, 10 micron and 44 micron. Preparation was accomplished using a 15 inch, ceramic lined, jet mill with dry oil free compressed injection air. Milling requirements were for 80% particle distribution in the target size. Particle size distribution was confirmed by Coulter Multisizer tests. Between runs of each zeolite type the mill was brushed down and bags changed to minimize cross contamination of zeolite types.

Initial Screening of Cement Formulations

Development work completed by Halliburton on the technology licensed to Trabits Group provided a starting point in the development of high temperature geothermal cement. This previous work indicates that not all natural zeolites are effective. For example the zeolite species Mordenite was not effective while Chabizite and Clinoptilolite appear to have qualities that improve lightweight cement at low temperatures. This previous work also identified a number of variables that affect the cement characteristics. Among these are; particle size of zeolite, percent of zeolite by weight of cement, the API Class of cement used and of course the zeolite type. No work had been completed on using multiple types of zeolite in the same blend.

A large number of cement samples were prepared for initial screening using permutations of zeolite species, particle size, percent zeolite by weight of cement and certain additives. Some cement samples contained more than one zeolite species and particle size in a test blend to take advantage of the properties of each. Sample preparation was be a heuristic process as the sample composition needed to be fine-tuned based on the feedback from sample testing. API Class G and Class H cements were used as the base for making the zeolite test samples.

The following properties were the primary criteria for initial screening:

- Percent free water
- Rheological properties
- 24 Hour compressive strength
- Thickening time and consistency
- Slurry density

TASK 4 – TEST

Second Stage Cement Development

In the second stage of development, comprehensive testing of cement samples that met the minimum criteria of the initial screening were performed. However, in view of multiple variables presented in initial screening a blend that failed to meet minimums in one variable did not necessarily eliminate it from second stage development. Cement property trends were

established as a function of cement composition. This provided the necessary feedback to adjust cement compositions. During the second stage of development the following tests were performed:

- Rheological properties of cement slurry (shear stress versus shear rate)
- Slurry density measurement
- Slurry consistency and thickening time
- Compressive strength at 12 hour and 24 hour
- Tensile strength of set cement
- Percent free water measurement
- Response to retarders at high pressure and high temperature
- Quality of cement to casing bond
- Resistance to geothermal brines (long term stability)
- Compressive strength retrogression over a three to six month period
- Determination of the optimum blend ratio of silica flour and other additives to zeolite for thermal stability
- Permeability of set cement
- Poisson's ratio and Young's modulus of set cement
- Thermal conductivity of set cement

Final Stage Cement Development

Two cement blends were presented for final stage development. One of the primary objectives of the project is the development of geothermal cement with qualities that resist destruction due to the effects of carbonation. During Final Stage Cement Development samples were subjected to a test cell bath of steam and formation fluid from Ormat's Brawley, California field which has high CO₂ and minerals content. Samples were tested at 1 week and 3 week time periods.

TASK 5 – DEMONSTRATE

Laboratory Scale Demonstration

Cement samples for laboratory scale demonstration were subjected to conditions of heat and brine for 3 month and 6 month exposures. Curing was done at 300°C at high pressure and then tested for Young's modules and Poisson's ratio for ultimate strength and retrogression from high temperature. Some test cylinders were examined by SEM for the occurrence of microscopic degradation.

Logistics and Ease of Use Field Demonstration – Chena Hot Springs Resort

One of the intended qualities of the developed cement is to “provide operators with an easy to use, flexible cementing system that saves time and simplifies logistics”. Although the geothermal resource at Chena Hot Springs in Alaska is low temperature it is somewhat remote and drilling work has been done by local contractors. It was the intent of this task to place the cement using Chena Hot Springs’ local contractor with their normal and customary methods and equipment. However, Chena Hot Springs did not have a well completed during the Period of Performance of the project. As a substitute for the “ease of use” concept six low temperature wells were completed near Bakersfield, California during final months of the project.

High Temperature EGS Well Demonstration – Ormat Technologies

It was the intent of this demonstration to test the cement in one of Ormat’s wells under development in a “real world” situation. Ormat had agreed to provide data from their geothermal wells, both hydrothermal and EGS, to guide the development of the cement. Ormat had and still has interest in the proposed cement development as a way to reduce costs and extend the life of geothermal wells. Unfortunately, a suitable well did not become available after the final cement formulation was determined. A significant volume of well cement suitable for high temperature use was manufactured and silo stored at Tehachapi, California six months prior to the end of the Period of Performance but an Ormat well did not become available.

Project Timeline

Modification 001 issued March 27, 2010 allowed for work to begin under Task 1 (Research) and Task 2 (Design) of the Project with an authorized spending limitation of \$215,423. Modification 002 issued April 29, 2010 with the Prime Award Contact provided full funding and allowed work to proceed. Accordingly, actual work on the Project did not begin until April 29, 2010.

The University of Alaska Fairbanks (UAF) entered into a Sub Award for the project on August 20, 2010. Proposal industry partner, ThermaSource Cementing, failed to negotiate a Sub Award agreement in a timely manner. Following more than a year of unsuccessful negotiation Sub Award efforts were terminated with ThermaSource on March 2, 2011.

The Project Budget was revised resulting from the withdrawal of ThermaSource. Under the revisions the UAF budget was increased by \$543,651 and the Trabits Group budget was increased by \$371,456. The total of these increases is the amount that was budgeted for ThermaSource being \$915,107.

UAF and Trabits Group reviewed the project schedule and work remaining to be completed. Work under Task 3, Element 4 had been delayed pending delivery of specialized cement testing equipment ordered from Chandler Engineering. Accordingly a request for a NCTE was submitted to extend the Period of Performance to September 30, 2013.

Modification 005 was issued on November 21, 2012 to extend the Period of Performance to September 30, 2013.

Trabits Group received notification from Baker Hughes that Ormat had experienced a delay in drilling the well at Brawley, California intended to be cemented using the developed high temperature/high pressure cement. This well offered by Ormat with the developed cement to be pumped by Baker Hughes is under Task 5 of the Project. Ormat advised Baker Hughes that completion was expected in the first quarter of 2014. Accordingly a request for a NCTE was submitted to extend the Period of Performance to March 31, 2014.

Modification 006 was issued on August 28, 2013 to extend the Period of Performance to March 31, 2014.

Trabits Group received notification from Baker Hughes on February 24, 2014 that Ormat had experienced further delay in drilling the well at Brawley, California intended to be cemented using the developed high temperature/high pressure cement. Given this additional delay Ormat offered a well scheduled for June 2014 in their Steamboat field located near Reno, Nevada. Accordingly a request for a NCTE was submitted to extend the Period of Performance beyond March 31, 2014.

Modification 007 was issued on March 19, 2014 to extend the Period of Performance to October 31, 2014.

Modification 008 was issued on November 7, 2014 to extend the Period of Performance to January 29, 2015.

Goals

Development of a zeolite-containing lightweight, high temperature, high pressure geothermal cement will provide operators with an easy to use, flexible cementing system that saves time and simplifies logistics. The requirement to “sterilize” pumping equipment before use, as with the CaP cement, will be eliminated.

- Thermal stability with little strength retrogression to 300° C.
- Tensile strength to withstand temperature and pressure changes.
- Low-density, low-viscosity slurries with low equivalent circulating densities (ECD) without the need for air or nitrogen foaming.
- A single cement blend allowing density adjustments without adversely affecting slurry properties to eliminate the need for separate blends for lead and tail slurries.
- Resistance to carbonation.
- Accurate downhole densities throughout cement placement without significant changes in viscosity.
- Water absorption capacity without retaining free water.
- Good bonding to casing and formation.
- Adequate compressive strength.

Accomplishments

Task 1 – Research

Literature Review:

- Zeolite:

Zeolites are highly porous materials found naturally as well as manufactured synthetically. When added to Portland cement, zeolites act as a pozzolan during the hydration reaction. The cured cement is much denser after using zeolites (Perraki et al). Addition of zeolite to cement increases resistance to chloride permeability, acid/sulfate attacks and alkali silicate reactions. Due to zeolite being highly porous in nature, it can be used to make lightweight slurry.

- Causes for cement failure:

High pressures and high temperatures (HPHT) are encountered in deep geothermal wells. The stress fields in the vicinity of the HPHT wells puts structural stability of the cement sheath into question. To ensure integrity of high temperature and high pressure wells novel cement design is important. For rigorous designing of cement it is necessary to study the failure mechanism of the cement sheath and the factors that affect it such as the composition of cement, rheology of the slurry, its strength, various loads the cement is subjected to during the life of the well, mechanical properties of the cement and the strength of the cement. The work of Ravi et al showed that cement failure mainly occurs due to the following mechanisms;

- Radial cracking: This kind of failure occurs due to gradual increase of cracks when cement is subjected to loading. Failure will take place under the condition of increasing load that is perpendicular to the loading axis in tension and inclined to the loading axis in compression. Shrinkage of cement could crack the entire sheath. The increase in temperature and pressure inside the casing could cause cracks to develop in part of a cement sheath.
- Shear Failure/de-bonding: De-bonding may occur either between the casing and cement sheath or between the formation and cement sheath. It may be a result of shear failure or due to cement shrinkage
- Plastic deformation: Differences in principal stresses causes compressive shear failure. This may take place during cement shrinkage that results in decrease of tangential compressive stress and/or due to expansion of casing against the cement sheath that result in increase of radial compressive stress.
- Tensile failure: Cements, being weak in tension can crack under tension due to cement shrinkage or if the casing expands (Petty et al).

The type of failure is a function of the down-hole condition variations. According to Goodwin and Crook the failure of cement sheath would usually occur in the bottom one half to three-quarters of the casing string due to excessive pressures and in the upper one fourth to two-thirds due to high temperatures.

- Benefits of adding zeolite in geothermal well cement:

Since geothermal well can contain high amounts of CO₂, NaCl, formation of carbonic acid and chlorides is likely. In such cases, addition of zeolite to cement can help reduce the problems related to corrosion and other related problems on the cements. Also since the cured cement is denser, possibilities of micro fractures are highly reduced, hence reducing the permeability of the cement to gases or liquids. Zeolite being highly porous and water absorbent, it can help in hydration of cement even at high temperature as water loss from the slurry would be much slower and also increase of workability with the slurry.

Scanning Electron Microscopy (SEM):

SEM images of a representative zeolite sample were taken at the Advanced Instrumentation Lab at the University of Alaska Fairbanks. A sample image is shown in Figure 1 below. The images were overall inconclusive of the amount of zeolite present as the crystal structures in the zeolites were not clearly visible. This might have been caused because of improper preparation of samples and/or impurities present in the sample.

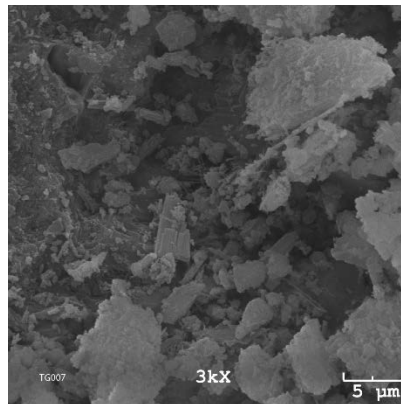


Figure 1. SEM image of Ferrierite (TG007), magnified 3000X

An X-ray Diffraction (XRD) analysis of zeolite samples is being planned to find out the amount and type of zeolites present. The XRD analysis will be conducted in the fourth quarter of 2010.

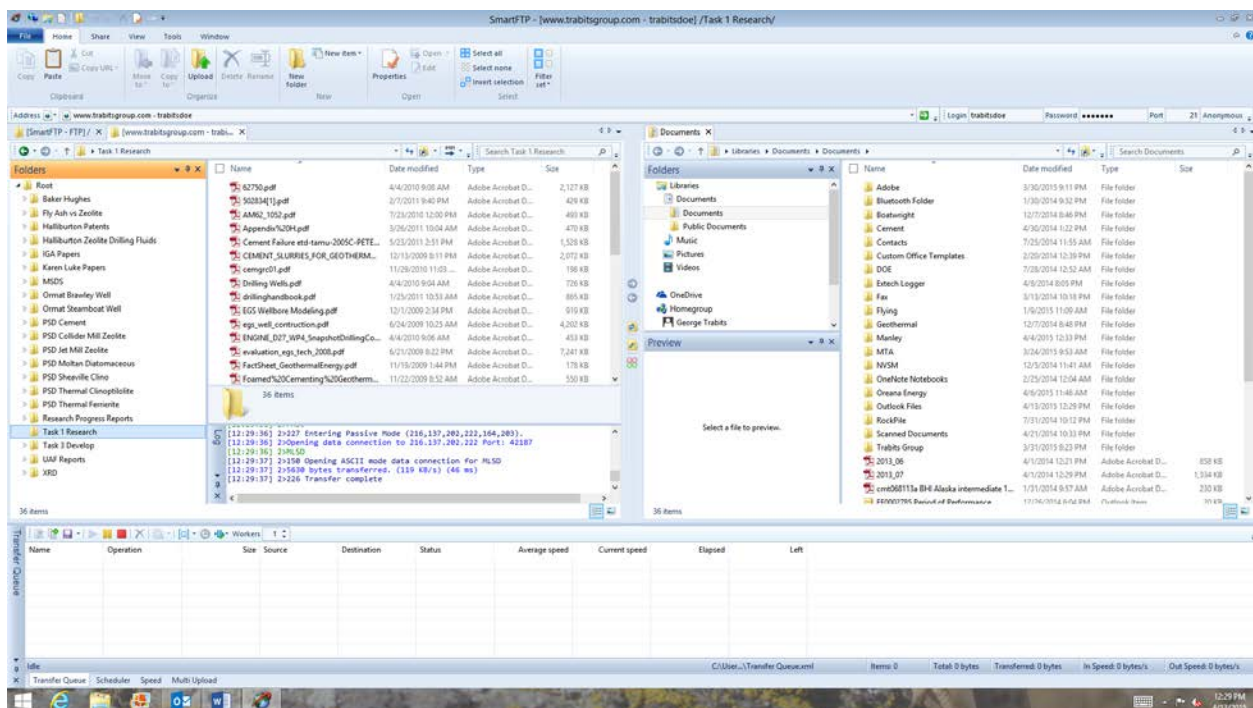
References:

- Perraki, Th., Kakali, G., Kontoleon, F. " The effect of natural zeolites on the early hydration of Portland Cement" Microporous and Mesoporous Materials (October 2002)
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- Goodwin, K. J., Crook, R. J. "Cement sheath stress failure" SPE 20453 (1992).

- Ravi, K., Bosma, M., Gastbled, O., “Safe and economic gas wells through cement design for life of the well” SPE 75700 (May 2002).
- Petty, S., Gastineau, J., Bour, D., Ravi, K., “Life cycle modeling of wellbore cement systems used for enhanced geothermal system development” 28th Workshop on Geothermal Reservoir Engineering, Stanford, California (January 2003).

FTP Site:

In order to share large literature search files the project established a FTP site that could be accessed by team members. Below is a screen capture of the FTP site.



Task 1 was completed as planned.

Task 2 – Design

The purpose of Task 2 was to serve to refine the development and testing of cement formulations to meet the Project Objectives. Under this Task, Tasks 3 and 4 were modified to take advantage of trial cement blend test results. Task 2 continued throughout the project as research results were factored into cement formulations.

Task 2 was completed as planned.

Task 3 – Develop

Element One – Zeolite Sample Acquisition:

Four types of zeolite were identified for testing. These are: clinoptilolite, analcime, chabazite, and ferrierite. The clinoptilolite used in the study came from Steelhead Specialty Minerals mine located near Barstow, California. The analcime came from a site near Wikieup, Arizona. The chabazite was purchased from Zeox Minerals from their mine near Bowie, Arizona. The ferrierite came from an undeveloped resource controlled by Nevada Specialty Minerals which is located near Lovelock, Nevada.



Zeolite Sample Location Map



Barstow, California Clinoptilolite Stockpiled for Processing

Element Two – Zeolite Type Confirmation:

From each bulk zeolite sample a small representative “split” was taken for XRD and SEM analysis by UAF when the bulk samples were field prepared. For example, UAF found that the Bowie Chabazite is actually a mixture of the zeolites Chabazite and Offertite. Additionally, the reported Analcime deposit was actually a clay mixture and contained little Analcime. The Barstow Clinoptilolite was confirmed as well as the Nevada Ferrierite as being the zeolite type as reported. The project selected a second Clinoptilolite from New Mexico which replaced the “Analcime” in later screening tests.

Element Three – Zeolite Particle Size Preparation:

After sizing to US Mesh 8 was completed the samples were truck transported to CCE Technologies at Cottage Grove, Minnesota for jet milling. For this step in the process Trabits Group reviewed five different jet milling operations and found CCE to be the best at custom processing applications. CCE has the internal controls to reliably process small quantities of material that is repeatable without risk of cross contamination. CCE can also process to ensure that the zeolite particle sizes are 80% being within the target size which is important for the research on effect of particle size in the cement blends. All test zeolites were jet milled in three particle sizes being 5 micron, 10 micron and 44 micron.



CCE Technologies Jet Mill Apparatus

Element Four – Initial Screening of Cement Formulations:

A large number of cement samples were prepared for initial screening using permutations of zeolite species, particle size, percent zeolite by weight of cement and certain additives. Some cement samples did contain more than one zeolite species and particle size in a test blend to take advantage of the properties of each. Sample preparation was a heuristic process as the sample composition needed to be fine-tuned based on the feedback from sample testing. API Class G and Class H cements were used as the base for making the zeolite test samples.

The following properties were the primary criteria for initial screening:

- Zero Percent free water
- Rheological properties of less than 200 reading at 300 rpm
- 24 Hour compressive strength greater than 500 psi
- Thickening time and consistency, end thickening under 70 Bc
- Slurry density less than 13.5 lbs/gal”

		Class G						Class H						Total Samples
		11.5ppg slurry (Light)			13.5ppg slurry (Medium)			11.5ppg slurry (Light)			13.5ppg slurry (Medium)			
	Size	% Zeolite, replacement of cement						% Zeolite, replacement of cement						
Ferrierite	5	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	Total Samples 180
	10	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	44	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Clinoptilolite Mud Hills	5	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	10	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	44	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Chabazite	5	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	10	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	44	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Clinoptilolite NM Mine 1	5	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	10	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	44	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Clinoptilolite NM Mine 2	5	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	10	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	44	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
					Initial Screening Criteria						Initial Screening Criteria			

Initial Screening Test Matrix

Task 3 was completed as planned.

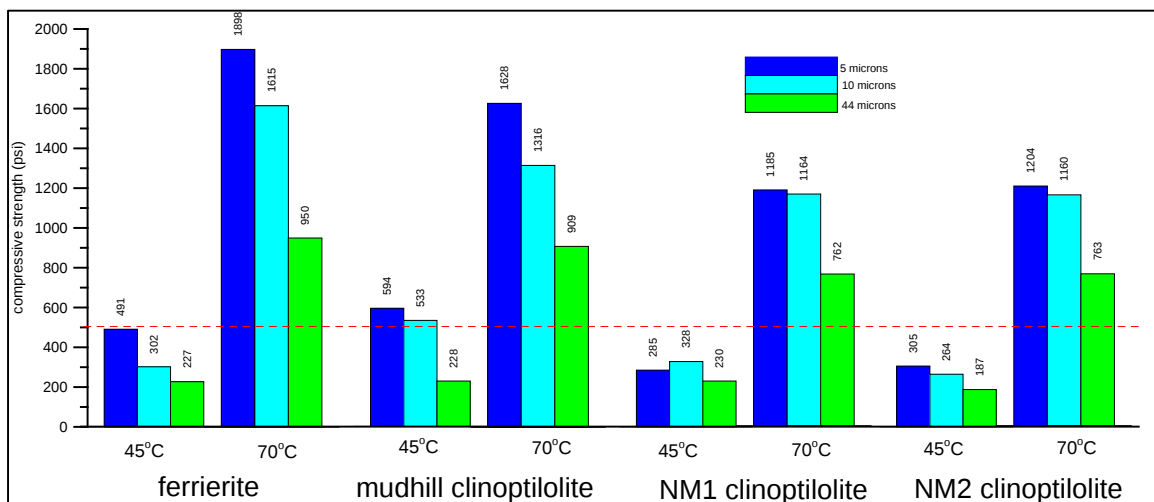
Task 4 – Test

Element One – Second Stage Cement Development

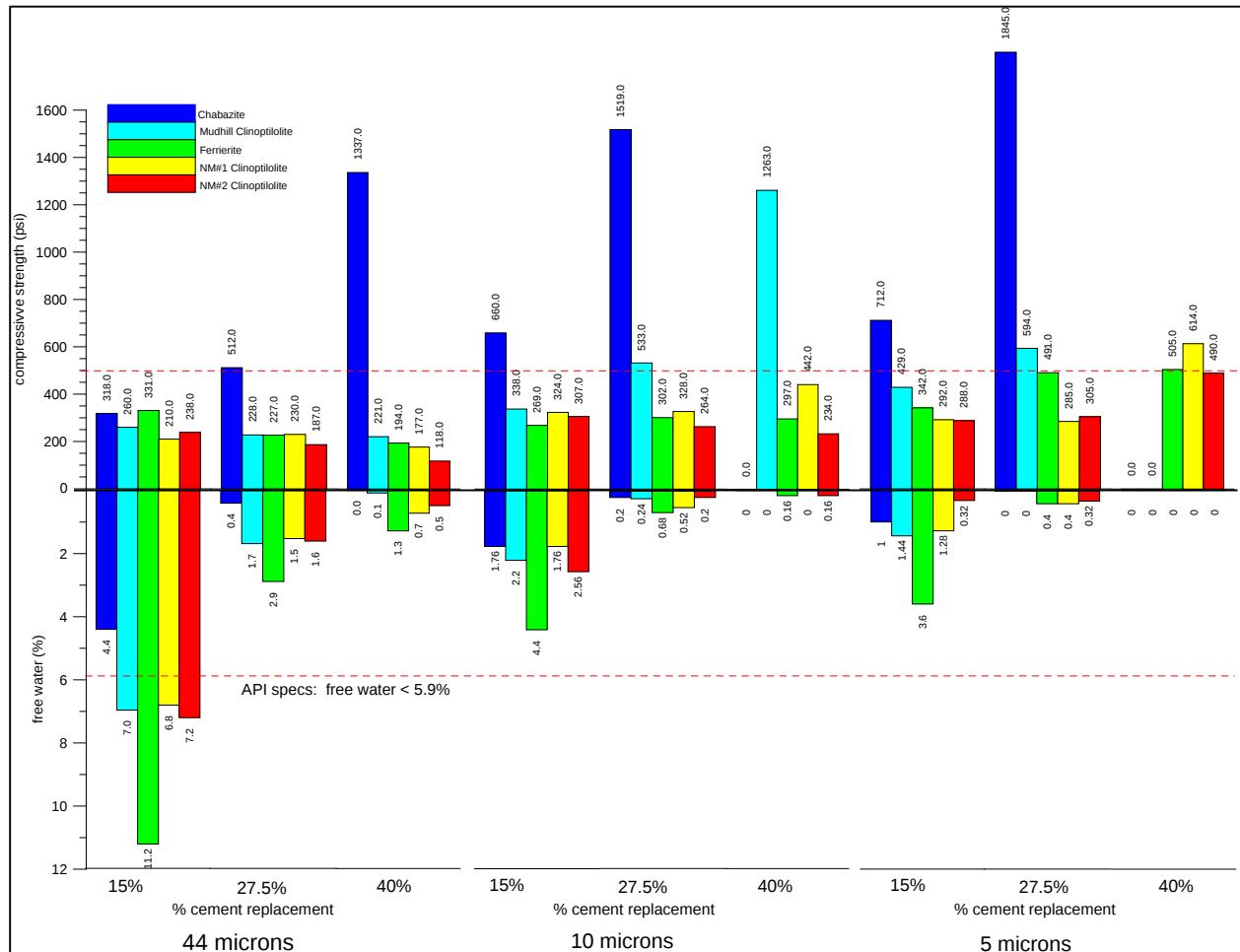
In the second stage of development, comprehensive testing of cement samples that met the minimum criteria of the initial screening were performed. Second Stage comprehensive testing included the following:

- Rheological properties of cement slurry (shear stress versus shear rate)
- Slurry density measurement
- Slurry consistency and thickening time
- Compressive strength at 12 hour and 24 hour
- Tensile strength of set cement
- Percent free water measurement
- Response to retarders at high pressure and high temperature
- Quality of cement to casing bond
- Resistance to geothermal brines (long term stability)
- Compressive strength retrogression over a three to six month period
- Determination of the optimum blend ratio of silica flour and other additives to zeolite for thermal stability
- Permeability of set cement
- Poisson's ratio and Young's modulus of set cement
- Thermal conductivity of set cement

Second Stage testing results were compared between various combinations of zeolite type, percentage of cement replacement and particle size. The below graphic illustrates a comparison based on zeolite type, particle size and curing temperature.



As an additional example of Second Stage testing the below graphic illustrates a comparison based on zeolite type, particle size and the percent of replacement.



Element Two – Final Stage Cement Development

Two cement blends were presented for final stage development. One of the primary objectives of the project is the development of geothermal cement with qualities that resist destruction due to the effects of carbonation. During Final Stage Cement Development samples were subjected to a test cell bath of steam and formation fluid from Ormat's Brawley, California field which has high CO₂ and minerals content.

The first round of tests at 550°F using the base mixes of 5 µm ferrierite and NM2 clinoptilolite at the 27.5% and 40% replacement levels were conducted. The results are summarized in Table 1, on the following page, along with test data for 300°F and 400°F for comparison. From the results, it is apparent that at 550°F, the samples show very low strength characteristics without the addition of silica.

Table 1. Summary of data for base ferrierite and NM2 clinoptilolite mixes at the 27.5% and 40% replacement level without the addition of silica for strength retrogression.

	Ferrierite_5μm_27.5%		Ferrierite_5μm_40%			NM2_5μm_27.5%		NM2_5μm_40%	
	300°F	550°F	300°F	400°F	550°F	300°F	550°F	300°F	550°F
q_u (psi)	1997	173	3181	1340	304	1470	403	1447	353
E (ksi)	949	91	1500	766	157	850	268	1000	197
ρ (g/cm³)	1.64	1.64	1.64	1.65	1.64	1.62	1.64	1.61	1.63
K (mD)	--	--	--	--	--	--	--	--	0.54

notes: q_u is compressive strength at 7 days. E is the Young's Modulus, ρ is the sample density, and K is the permeability.

* All samples at 550°F contained 0.8%BWOB tartaric acid

Table 2. Various silica added to base mixes. Temperature 550°F. Cure time 6 days

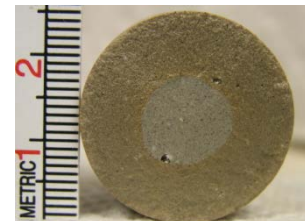
	% BWOC							
Sample	MDE	SF	MINUSIL 40	SIL 325	TA (%BWOB)	W/C	q _u (psi)	E (ksi)
base mix: ferrierite_5μm_30%_44μm_10%.								
S1	0	20	0	0	0.8	1.21	1622	624
S2	0	40	0	0	0.8	1.33	2208	749
S3	0	60	0	0	0.8	1.46	1973	661
S4	20	0	0	0	0.8	1.18	685	326
S5	40	0	0	0	0.8	1.27	1501	541
S6	20	20	0	0	0.8	1.30	2035	783
S7	20	40	0	0	0.8	1.43	2115	544
S8	30	30	0	0	0.8	1.41	2279	525
S9	20	0	20	0	0.8	1.30	2627	504
S10	20	0	40	0	0.8	1.42	2798	529
S11	20	20	20	0	0.8	1.42	2734	558

S12	0	0	20	0	0.8	1.21	2209	742
S13	0	0	40	0	0.8	1.33	3416	611
S14	20	0	0	20	0.8	1.30	2439	550
base mix: NM2_5µm_27.5%.								
S15	0	40	0	0	0.8	1.24	1808	685
S16	40	0	0	0	0.8	1.17	484	216

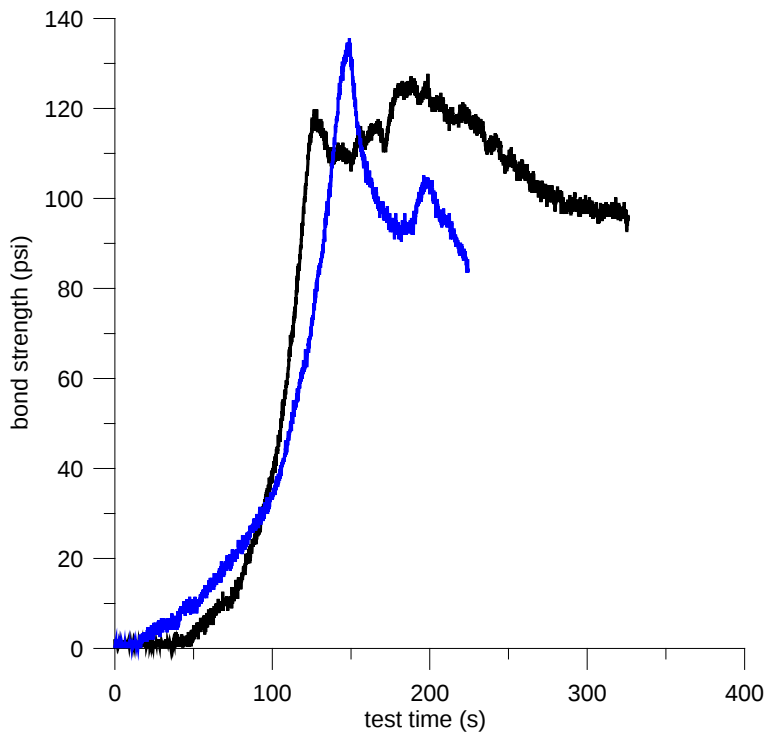
The effects of carbonation of cement samples in geothermal brine were tested as illustrated in the below Table. More extensive testing for the effects of carbonation were conducted under Task 5.

Carbonation characteristics for ferrierite and NM2 using
5µm_27.5%_MINUSIL20%_lime20%_H_13.5ppg

	Ferrierite		NM2	
	Initial	1 week	Initial	1 week
Permeability (mD)	0.0031	0.010	0.003	0.012
% alteration (area)	--	57.7%	--	63.0%
% alteration (linear)	--	37.0%	--	38.6%
mass gain	--	7.1%	--	7.4%



The quality of the cement bond to casing was tested using apparatus designed to represent casing normally used. A typical test profile for pipe to cement bond is shown below.



Typical test profile for pipe-cement bond test for Fmix1.

Task 4 was completed as planned.

Task 5 – Demonstrate

Element One – Laboratory Scale Demonstration:

Cement samples for laboratory scale demonstration were subjected to conditions of heat and brine for up to 3 months. Curing was done at 300°C at high pressure and then tested for Young's modules and Poisson's ratio for ultimate strength and retrogression from high temperature. Some test cylinders were examined by SEM for the occurrence of microscopic degradation.

Sample were tested in actual geothermal brine supplied by Ormat from Brawley, California. The image on the following page shows the testing apparatus.



Carbonation Test Apparatus

Summary of mechanical properties of Fmix1 cured at 300°F

Cure medium/time	q_u (psi)	E (ksi)	ν
Initial cure; 2 days (medium water)	6484	1243	0.33-0.38
1 week; Ormat Brawley Brine/CO ₂	3968	831	~0.28
1 week; control	5091	933	~0.38
3 week; Ormat Brawley Brine/CO ₂	3233	828	~0.40
3 week; control	3652	556	0.27
3 month; Ormat Brawley Brine/CO ₂	3696	654	0.29
3 month; water/CO ₂	3494	642	0.24
3 month; control	4817	1553	? (data high, structural control on results)

Element Two – Logistics and Ease of Use Field Demonstration:

One of the intended qualities of the developed cement is to “provide operators with an easy to use, flexible cementing system that saves time and simplifies logistics”. The method used during development of the cement was dry blending micronized zeolite and finished API Classed well cement. While this blended cement met all the cement performance goals, micronizing zeolite by jet milling methods is expensive. To be a practical new geothermal cement the method of manufacture needed to be cost competitive to existing well cements. Additionally, dry blending presented an added step prior to placement which limited application in remote areas. Accordingly, attention was turned late in the project for a cost effective method of cement manufacture. Trabits Group developed a method of intergrinding cement clinker and zeolite at the cement point of manufacture at the cement plant. Under this method the clinker and zeolite are interground at the cement plant finish mill. Zeolite being softer than cement clinker preferentially grinds to a smaller particle size which is desirable for the final down hole performance.

Trabits Group contacted for a 1,000 ton full scale production run using the intergrinding method at the Lehigh Hanson Tehachapi, California cement plant. Following testing conducted by Dr. Karen Luke at

Trican Well Services in Calgary to characterize the physical qualities six wells were completed using the Tehachapi interground cement.

Element Three – High Temperature EGS Well Demonstration:

Prior to the end of the Period of Performance a high temperature well did not become available for a demonstration of the developed cement.

Elements One and Two of Task 5 were completed as planned. Element Three of Task 5 was not completed.

Chronological Summary of Project Activities

FY2010 Q2

Because the project had not officially started during the reporting period specific project goals identified by Task were not advanced. However, in order to make use of project team availability a Project Kick Off Meeting was held on March 15, 2010. The Kick Off meeting was hosted by ThermaSource Cementing and held at ThermaSource's facility at Arbuckle, California. In attendance were:

George Trabits – Trabits Group
Shirish Patil – University of Alaska Fairbanks
Santanu Khataniar - University of Alaska Fairbanks
Abhijit Dandekar - University of Alaska Fairbanks
Lou Capuano, Jr. – ThermaSource
Andy Frei – ThermaSource
Jenn Capuano – ThermaSource
Hamid Najafi – ThermaSource
Vicki Klein – ThermaSource
Matt Ryan – ThermaSource
Marc Brennen – ThermaSource

Topics discussed at the meeting were:

1. Review of Project Tasks
2. Task Assignments
3. Record keeping / time sheets
4. Zeolite sample acquisition and size of bulk samples
5. Preparation of laboratory testing sample size
6. Establishing an ftp site for data collection and transfer to team members
7. Discussion of purchase and location of HTHP Chandler test cell

During the meeting a teleconference was held between the meeting participants and DOE representatives to discuss reporting requirements under ARRA, intellectual property guidelines and the Project Objectives.

FY2010 Q3

Task 1

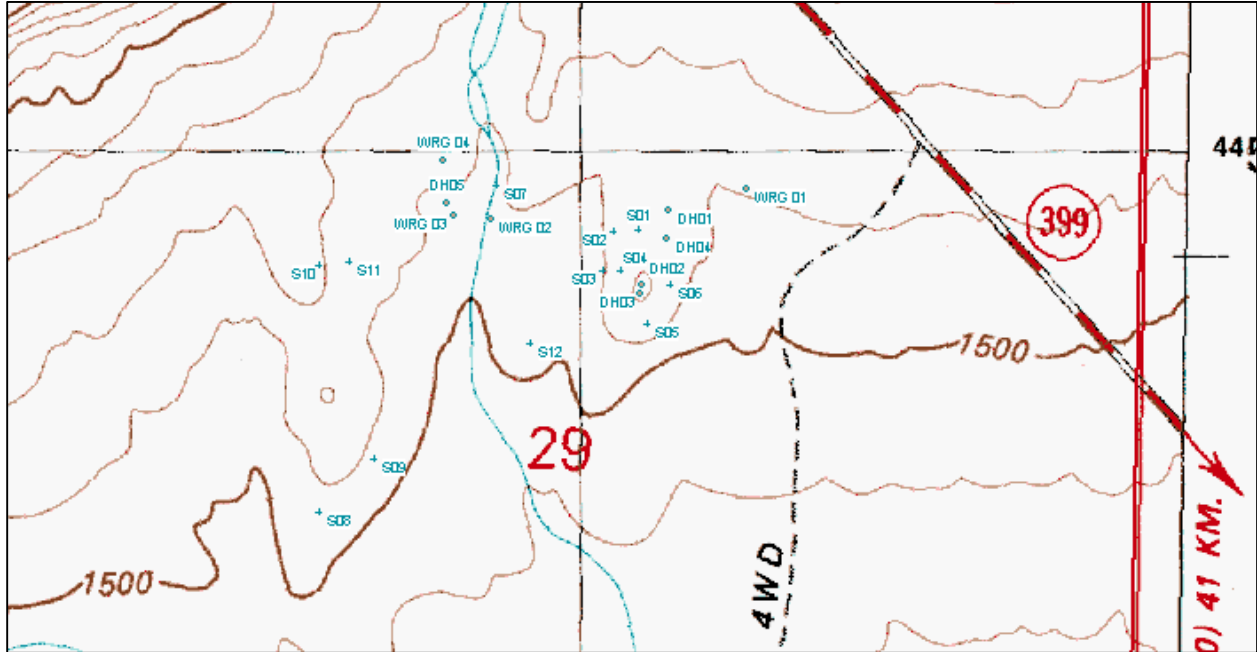
Under Element 2 of Task 1 Trabits Group began research and inquiry on current cementing practices and constraints. Discussions were held with the U.S. representative to the International Partnership for Geothermal Technology for contact references for member countries Australia and Iceland.

Task 2

Under Element 2 of Task 2 Trabits Group recalculated the number of screening cement samples and zeolite required for each screening test to ensure that 1,000 pounds of each zeolite type would be sufficient for the testing program. A request for modification of the Sample Protocol was previously submitted concerning the preparation of all bulk zeolite samples to 5, 10 and 44 micron sizes. Additionally, Trabits Group evaluated a small trailer mounted two stage crusher that could be field deployed to prepare rock sized zeolite to 8 Mesh size required for jet milling. Using this portable crusher would eliminate the need for toll processing of the bulk zeolites and remove any chance of sample contamination by “other” residual minerals.

Task 3

Under Element 1 of Task 3 Trabits Group began planning the logistics necessary for the collection, preparation and storage of the four zeolite types to be used in the cement test blends. Four types of zeolite have been identified for testing. These are: clinoptilolite, analcime, chabazite, and ferrierite. The clinoptilolite used in the study will come from Steelhead Specialty Minerals mine located near Barstow, California. The analcime will come from a site near Wikieup, Arizona. The chabazite will be purchased from Zeox Minerals from their mine near Bowie, Arizona. The ferrierite will come from an undeveloped resource controlled by Nevada Specialty Minerals which is located near Lovelock, Nevada. Given the undeveloped nature of the ferrierite site it was necessary to determine the best sample location. Nevada Specialty Minerals core drilled the property in 2008 and submitted the cores for x-ray diffraction studies. This 2008 drilling program was reviewed along with corresponding x-ray diffraction scans to pick the most likely location for ferrierite concentration.



Lovelock Drill Hole and Surface Sample Locations

FY2010 Q4

University of Alaska Fairbanks

On August 19, 2010 Trabits Group received email confirmation from DOE Procurement that the "Subcontract Approvals" provision for UAF had been lifted allowing Trabits Group to proceed with the UAF Sub Award. On August 20, 2010 Trabits Group met with Maren Boyack at Fairbanks and signed the UAF Sub Award. Executing for the University was G. Maggie Griscavage, Director Office of Grants and Contracts Administration. Executing for Trabits Group was George Trabits, President and Managing Member.

ThermaSource Cementing, Inc.

The Draft Final ThermaSource subcontract was in review at the end of the reporting period. DOE Procurement has completed review and is expected to issue approval to allow completion of the subcontract to ThermaSource.

FY2011 Q1

Task 1 and Task 2

Trabits Group worked with UAF and ThermaSource on the protocols to be used in the testing for free water in cement blends. ThermaSource uses a method for cement slurry testing that is in accordance with API SPEC 10B under section 15.4. Briefly, the testing apparatus must be a graduated cylinder with

an height to inside diameter ration of 6:1 – 8:1. Volume must be visually determined within plus or minus 2 mL. The test volume must be between 100 and 250 mL. Test provisions are made for vertical wells and deviated wells. Additionally, provisions are made to simulate bottom hole circulating temperatures of less than 176° F and greater than 176° F. The ThermaSource approach is good and will be used for free water performance criteria.

Task 3 / Element Two (Zeolite Type)

It is critical for the research to be certain that the type of zeolite is confirmed. Natural zeolites will have variability within deposits and be referred to as a specific type just by physical characteristics. In actuality natural zeolites are rarely “pure” and more often made up of several types of zeolite with the dominate type being used to identify the deposit.

From each bulk zeolite sample a small representative “split” was taken for XRD and SEM analysis by UAF when the bulk samples were field prepared in July. UAF found that the Bowie Chabazite is actually a mixture of the zeolites Chabazite and Offertite. Offretite is a rare natural zeolite and in combination with the Chabazite would have similar properties to synthetic zeolite Phi. Zeolite Phi exhibits increased adsorption capacity which may be why the Bowie Chabazite worked so well in the Halliburton technology. The Bowie Chabazite is important to the project research in that it was the base zeolite used in development of the Halliburton technology. Although it performed very well the Bowie Chabazite is a very small deposit, thinly bedded and expensive. There are not sufficient reserves of the mineral to support any large scale use as a geothermal well cement additive

During the reporting period UAF also completed the XRD on the Ferrierite and Analcime representative samples from the field bulk samples. The results were good for Ferrierite but showed no Analcime in the Analcime sample. Therefore the sample designated as Analcime is not and will be removed from the testing program. The Project Team is considering whether or not to try for another Analcime sample or to replace this one with a second Clinoptilolite to compare performance that could be specific to deposit. Trabits Group located a high quality Clinoptilolite in New Mexico that has tested 92% pure and is listed by the International Committee on Natural Zeolites. A bulk sample from this deposit is available. Trabits Group contacted CCE Technologies and was able to stop preparation of the Analcime sample.

Task 3 / Element Three (Preparation)

Under Task 3 / Element Three the zeolites to be used in the cement screening blends were prepared and transported to CCE Technologies at Cottage Grove, Minnesota.

Trabits Group traveled to Lovelock, Nevada where the crushed bulk zeolite samples are in storage. For the cement blend screening tests we will be using Ferrierite, Chabazite, Clinoptilolite and perhaps a second Clinoptilolite prepared in 5, 10 and 44 micron sizes. Trabits Group has been working on a new zeolite processing method which may greatly enhance the water uptake of zeolite as well as other interesting properties. For this new method we need a larger initial size to be treated and then micronized as usual for the technology. The jet mill feed for the micronized samples requires a small particle so that is why we crushed all the bulk samples to a generally uniform size. In any crushing operation there are always larger particles so we needed to “save” the bigger pieces for the treatment

step of the new method. Accordingly, Trabits Group made a hand operated screening device that allowed us to hand screen more than 4,000 pounds of bulk sample in just under four hours. The hand screen is show in Figure 1 below.



Figure 1

Figure 2 shows the operation of the screening device where sizes smaller than 1/4 inch fall through while the larger sizes are retained and then dumped into the separate tray on the right.



Figure 2

After sizing was completed the samples were truck transported to CCE Technologies for jet milling. For this step in the process Trabits Group reviewed five different jet milling operations and found CCE to be the best at custom processing applications. CCE has the internal controls to reliably process small quantities of material that is repeatable without risk of cross contamination. CCE can also process to ensure that the zeolite particle sizes are 80% being within the target size which is important for the research on effect of particle size in the cement blends. The following Figure 3 is an image of the CCE particle size lab. Figure 4 shows one of the jet mills at CCE Technologies.



Figure 3



Figure 4

Task 3 / Element Four (Initial Screening)

During the reporting period Trabits Group completed arrangements with Texas Lehigh Cement for the supply of Class G and Class H cement for Task 3 Element Four (Initial Screening). Critical to the testing integrity is to ensure that base cement, and zeolites as well, are identical for both UAF and ThermaSource testing. Texas Lehigh provided identical batch runs split into (5) five gallon buckets each for UAF and ThermaSource. Additionally, Trabits Group made arrangements with Dyckerhoff AG in Germany for 52 kg of Dyckerhoff Class G which was used to compare performance with US Class G cement. As a note, Halliburton recommended Dyckerhoff Class G for superior performance in high temperature / high pressure applications.

Also during the period Geoff Trabits met with Jim Jarl of Texas Lehigh Cement at Buda, Texas to review the Buda operation and get information on the preparation of well cements. Texas Lehigh has been very helpful and made several suggestions during Geoff's onsite visit for additives that could improve thermal stability. Texas Lehigh is a major oil field cement supplier.

FY2011 Q2

After extensive delays Trabits Group set March 2nd at 6:00 pm Pacific Time for ThermaSource to enter into the Sub Award Agreement. On March 1st Mr. Marc Brennen of ThermaSource called and emailed that ThermaSource could not find their updated budget which would become Schedule J of the Agreement. Mr. Brennen provided the ThermaSource budget that was prepared in July, 2009 as the only budget he had. This July, 2009 budget was rejected because ThermaSource had only provided broad categories without specific detail on cement test costs or the number of tests anticipated. On

Tuesday March 2nd Ms. Jenn Capuano of ThermaSource asked for an extension to March 18th to prepare a new Schedule J budget. Additionally, ThermaSource attorney David Goldenberg reported that ThermaSource still had questions on the application of the Davis Bacon Act as it could apply to ThermaSource. Given the foregoing, it was unreasonable to accept another delay with no guarantee of a final agreement. Accordingly an extension was not granted and negotiations were ended.

Trabits Group was holding the micronized zeolite intended for ThermaSource at CCE pending ThermaSource entering into the Sub Award. Given that there is no Sub Award to ThermaSource Trabits Group consulted with UAF on whether or not to ship this held zeolite to Fairbanks. The consensus was to continue to hold the zeolite at CCE until it was determined which zeolite types would be of interest based on first stage screening to save on shipping costs. CCE was contacted and agreed to hold the zeolite in their warehouse at no charge to the project.

UAF and Trabits Group held discussions on the scope of work vacated by ThermaSource. UAF has the capabilities for testing but lacks some of the specialized equipment that will be required.

Task 2 / Element Two (Modification)

Cement production economics will be a significant factor in the development of a new high temperature / high pressure geothermal cement. Accordingly, Trabits Group initiated bench scale testing on the preparation of the zeolite by a rotary collider milling method. The particle size distributions from the collider mill run on Ferrierite were determined by CCE Technology. The current method of zeolite preparation is by a controlled jet mill. As testing progresses it is intended to compare cement performance between micronization methods to achieve a favorable cost/performance ratio.

Figure 1 below shows the particle size distribution for Ferrierite as prepared using a collider mill. Figure 2 shows the particle size distribution for Ferrierite at a 10 μm mean using a jet mill.

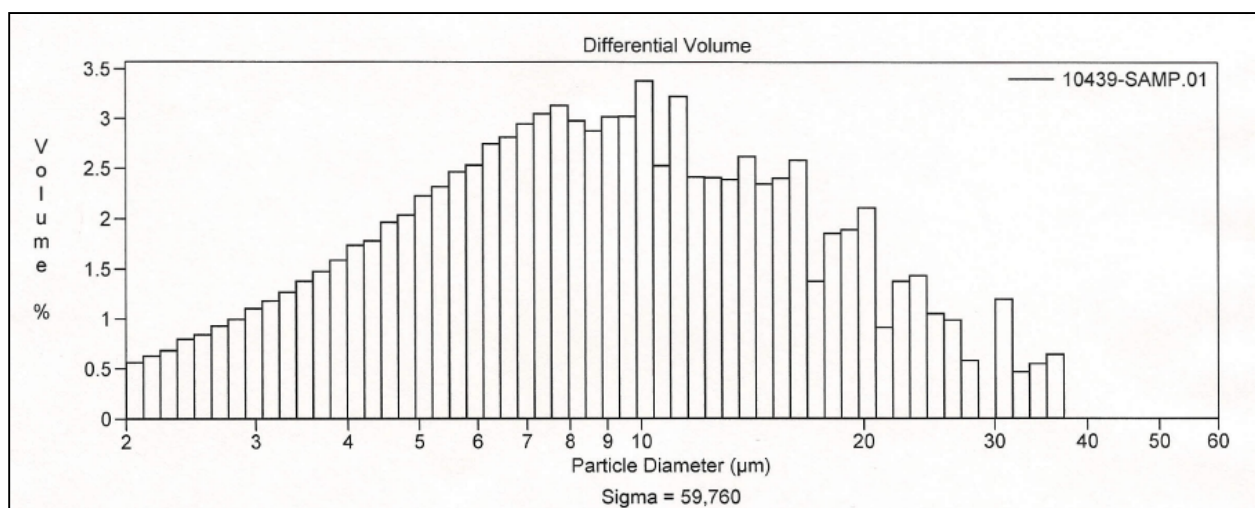


Figure 5

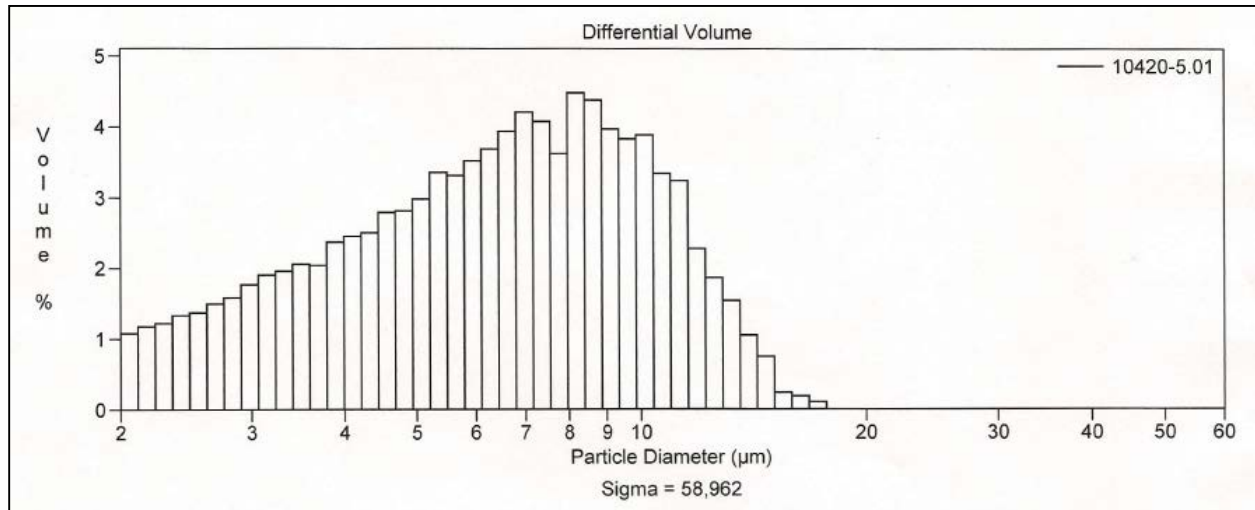


Figure 6

Task 3 / Element Two (Zeolite Type)

The XRD and XRF tests on two zeolite samples, TG014 (Analcime) and TG015 (Calcined Analcime) gave some unexpected results. Analysis of TG014 showed that it did not contain any Analcime, and contained only 11% Zeolite (Celadonite). The rest of it was mostly Feldspar.

XRD and XRF tests and data analysis were completed on the Calcined Analcime sample (TG015). This sample was very complicated to analyze due to the presence of multiple minerals. The minerals were identified using a trial and error procedure.

Figure 3 shows the plots for the analysis. The red line on the upper plot is the reference data and the blue line is the match to that data. The lower plot is the difference plot between the reference data and the match.

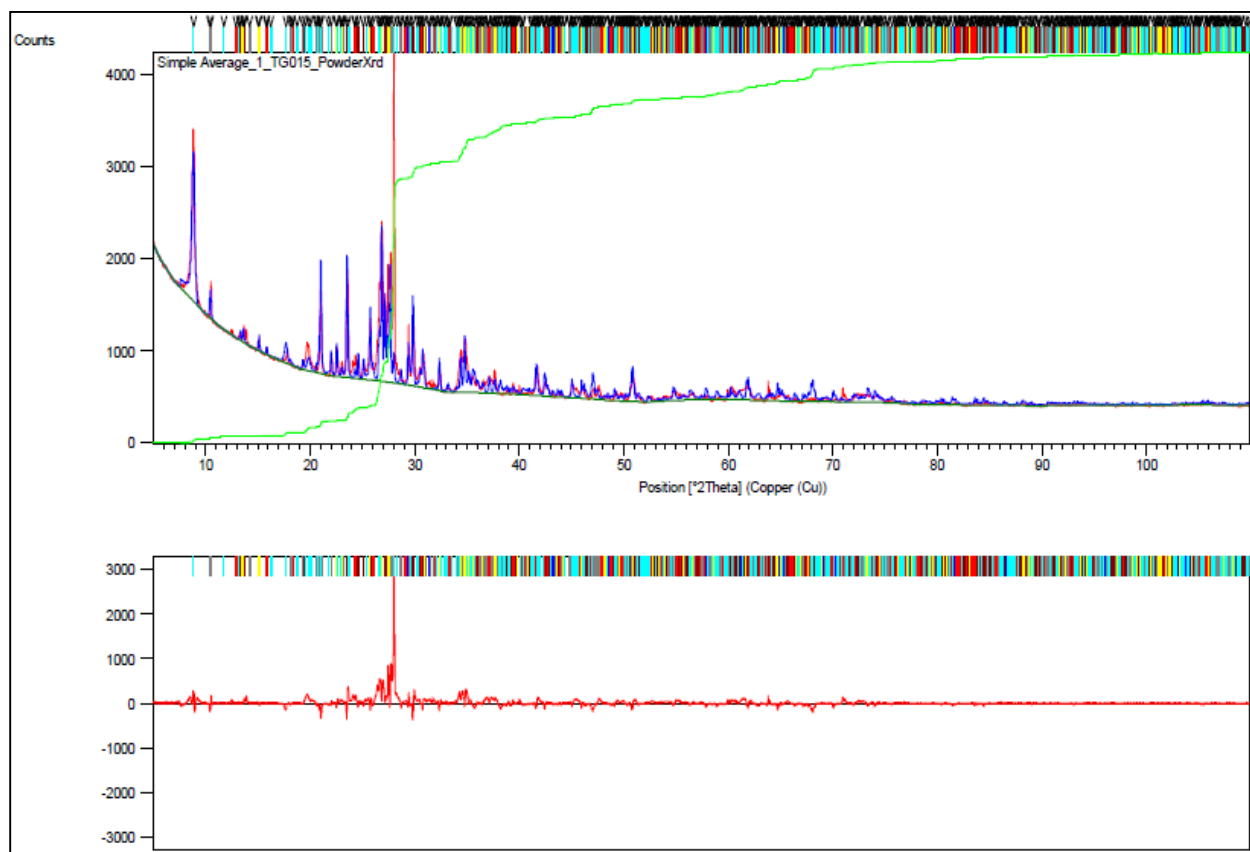


Figure 7

According to the analysis, TG015 contains Analcime (1%), Feldspar (61%), Quartz (4%), Calcite (3%), Montmorillonite (12%), Kyanite (12%), Cordierite (6%). The remaining 1% was labeled as undeterminable as it would have required unreasonable analyzing effort. All the percentages mentioned are based on weight. The results are consistent with the result for TG014 (Analcime), which had no Analcime present. Based on this analysis it is concluded that Analcime present in TG015 is a mere impurity in a sample containing mostly Feldspar.

Given the above it was decided to replace the Analcime with a second Clinoptilolite from a different geographic area. After review, Trabits Group selected a Clinoptilolite from New Mexico. This second Clinoptilolite is actually from two deposits situated one mile apart. One is on state lands and the other on federal lands. The deposits are very similar but we elected to take bulk 300 pound samples from each. These bulk samples are being processed by CCE Technologies. The samples are designated Coyote Cliff Type S and Coyote Cliff Type F.

Task 3 / Element Three (Particle Size Preparation)

Trabits Group received the particle size distributions on the Chabazite, Clinoptilolite and Ferrierite bulk samples prepared by CCE Technologies. The required quality control standard set by Trabits Group for the processing is 80% at the target size range. CCE reported as follows:

Chabazite

5 micron 80% at 4.803 microns

10 micron 80% at 9.696 microns

44 micron 80% at 44.30 microns

Clinoptilolite

5 micron 80% at 5.384 microns

10 micron 80% at 10.02 microns

44 micron 80% at 42.59 microns

Ferrierite

5 micron 80% at 4.788 microns

10 micron 80% at 9.658 microns

44 micron 80% at 42.92 microns

Figure 4 below is a Coulter Multisizer plot of the particle size distribution for the 5 μm Ferrierite.

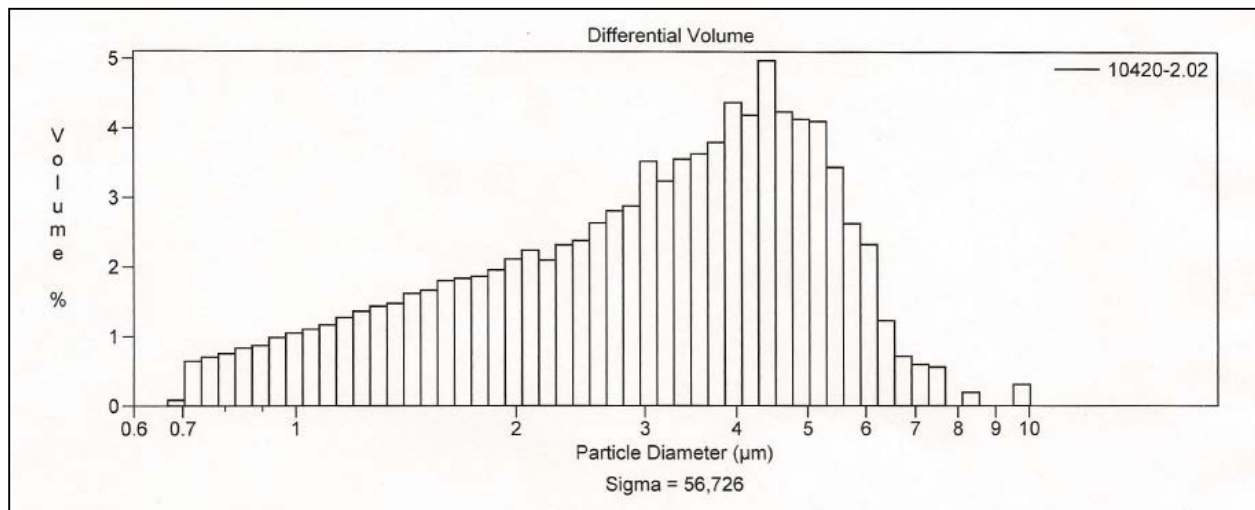


Figure 8

Task 3 / Element Four (Initial Screening)

During the period Trabits Group began research into additives for cement blend testing. Typical additives are silica flour for thermal stability and extenders and retarders. Also fly ash has been used as a light weight additive. Trabits Group received for testing a five gallon bucket of fly ash from Newmont Mining's Dunphy, Nevada plant. Trabits Group selected the Dunphy plant because of its location near geothermal resources.

Trabits Group made arrangements with Texas Lehigh Cement for the Class H and Class G cement to be used in the initial screening of cement test blends. Trabits Group also made arrangements with Dyckerhoff AG, Germany for their Class G cement to be used as a performance comparison to US Class G cement. All cement samples have been received.

Experimental protocols for the initial screening tests are being refined by UAF according to the API Recommended Practices 10B for oil well cements. Laboratory equipment and supply needs for initial tests at UAF were finalized and the items were ordered.

Zeolites and Class H and Class G cements have reached UAF. About 20 grams of cement sample was removed from each of Class H and G cements and sent to CCE Technologies in order to conduct particle size distribution (PSD) analysis on them. Figure 5 below shows the PSD for the US Class H cement. Figure 6 shows the PSD for the US Class G cement. Figure 7 shows the PSD for the Dyckerhoff Class G. It is interesting to note that the Dyckerhoff cement is much finer in size than the US cements. The median for the US Class H is 32.77 microns, the US Class G 34.15 microns and the Dyckerhoff Class G 16.68 microns.

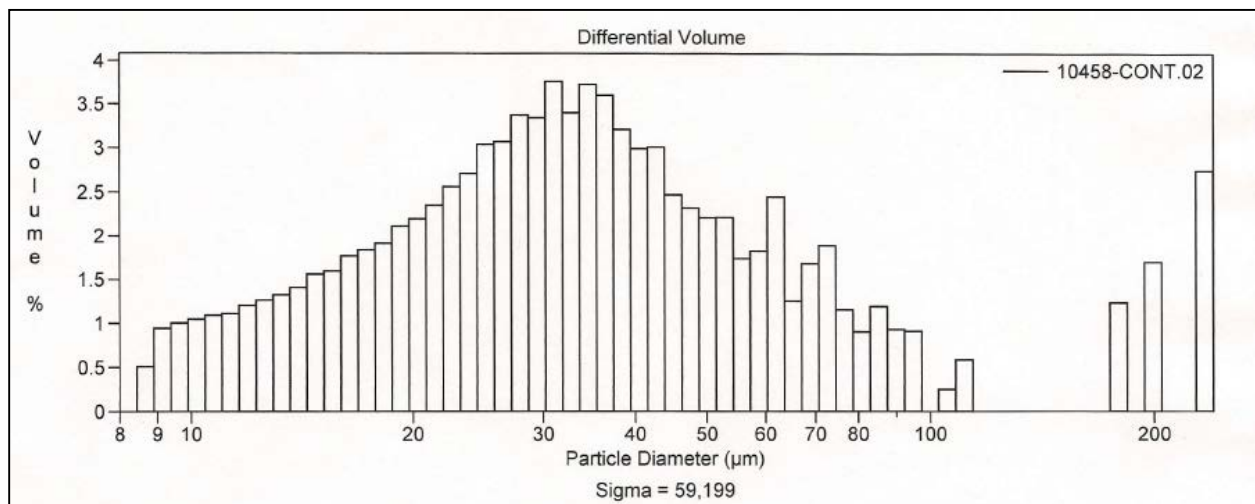


Figure 9

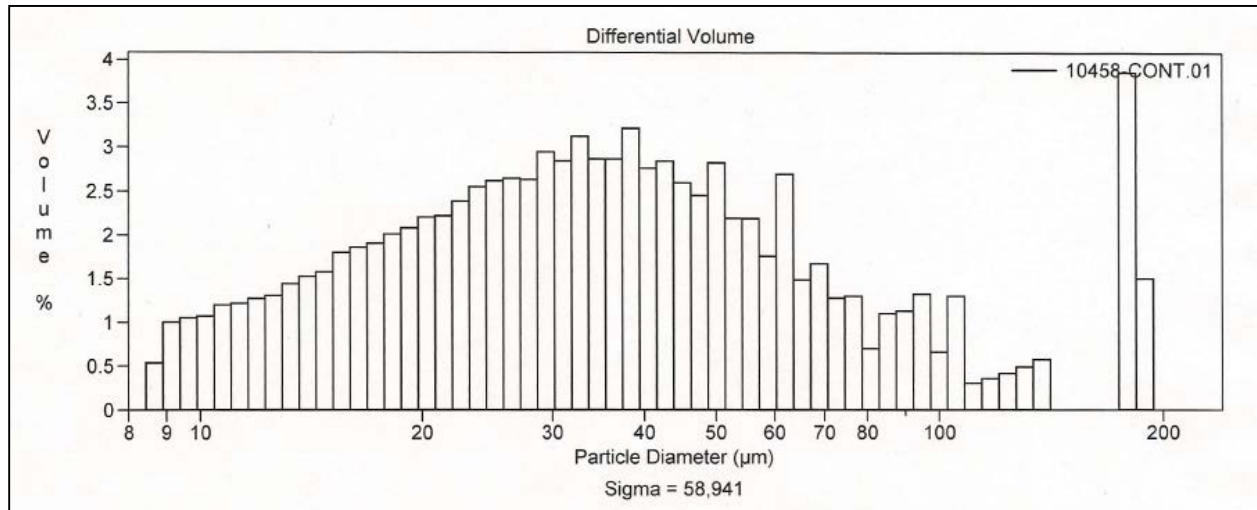


Figure 10

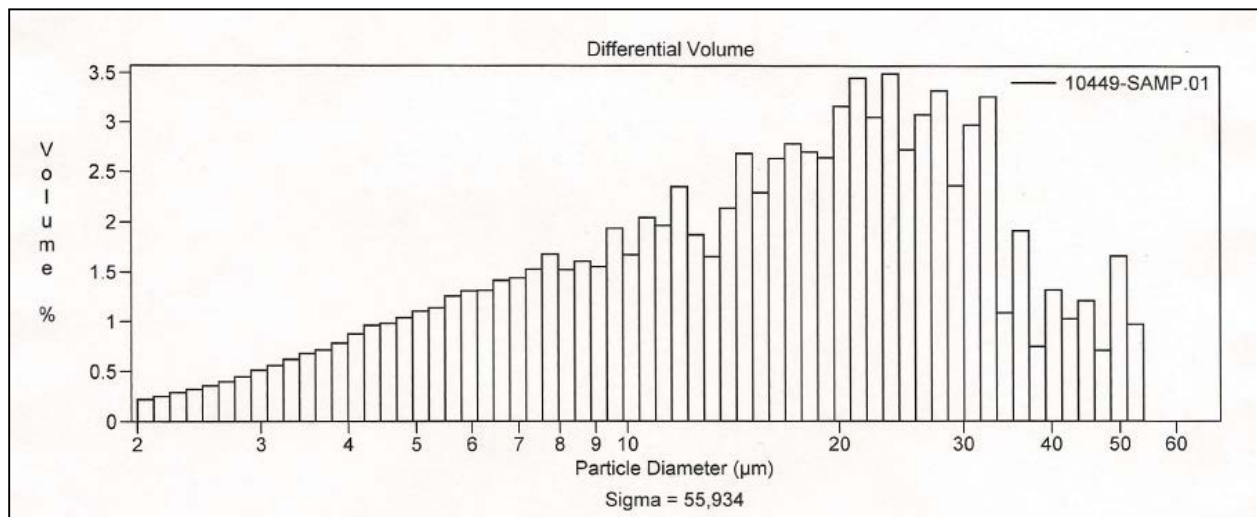


Figure 11

In preparation for the Initial Screening of cement blends in Task 3, Trabits Group and UAF visited the Halliburton Duncan Technology Center in Duncan, Oklahoma for instruction and demonstration of cement testing methods. Halliburton is providing certain support activities as In-Kind cost share for the project. The visit agenda established by Halliburton was as follows:

- 1) Introductions and general tour of Cementing Applied Sciences Group and Labs.
- 2) General information about Cementing Geothermal Wells.

- 3) Slurry Designs for Geothermal – pumpability, stability and mechanical integrity.
- 4) Lab equipment for testing Geothermal cement slurries, included live demonstrations.
- 5) Methods for testing and analyzing Geothermal cement slurries.

Project personnel at the Halliburton DTC were:

George Trabits
Geoff Trabits
Dr. Shirish Patil
Dr. Santanu Khataniar
Dr. Abhijit Dandekar



Project Team at Halliburton Duncan Technology Center
Pictured left to right – Dr. Abhijit Dandekar, Geoff Trabits, Dr. Shirish Patil, Dr. Santanu Khataniar, and George Trabits

FY2011 Q3

TASK 3

During the reporting period Trabits Group worked with the Halliburton Duncan Technology Center and the University of Alaska Fairbanks (UAF) to make arrangements for two UAF Graduate Students to attend training at Halliburton's field lab in Rock Springs, Wyoming. The training will take place July 11th through July 15th.

CCE Technologies finalized work on the final preparation of the Coyote Cliff Clinoptilolite in the 5, 10 and 44 micron sizes for initial screening. There were two Coyote Cliff Clinoptilolites that were prepared. These were designated as Mine 1 and Mine 2. One is from a mining lease on State Lands and the other from a mining lease on Federal Lands. These two areas are separated by approximately one mile. They are geologically similar with one being slightly higher in Clinoptilolite purity. The preparation protocol established for the Project was for duplicate batches with one going to UAF and the other to ThermaSource. CCE was already processing the Coyote Cliff material when efforts ended with ThermaSource. Accordingly there is a duplicate Coyote Cliff Clinoptilolite as well as duplicate Mud Hills Clinoptilolite, Nevada Ferrierite and Arizona Chabazite that is being held at CCE free of charge to the Project. It is thought that these duplicate batches could be used in later testing or in testing by third parties such as Halliburton at some future time. Shipping bulk samples is expensive and it is appreciated that CCE is storing these for the Project. The batch run of the Coyote Cliff material has been shipped to UAF.

During the reporting Trabits Group and UAF worked on the Summary and Presentation for the Geothermal Technologies Program Peer Review. The Project Team was somewhat limited in what could be presented due to the limit of 15 slides. Of this total nine were mandatory procedural slides which only left six for the presentation of actual project work. The Short Summary and Presentation were uploaded to the Peer Review site on April 29th.

UAF developed experimental protocols for drying of zeolite samples, blending with cement, and performing free water tests. Cement slurries will be prepared and free water tests will be performed per API specifications for testing of oil well cements. The experimental protocols are summarized in the following section. Because of loss of partnership with ThermaSource Cementing Inc., UAF is preparing to take over the laboratory testing previously assigned to TCI. In this regard, UAF is in the process of identifying the additional equipment and additional personnel time needed. The UAF budget will be revised accordingly.

EXPERIMENTAL PROTOCOLS

Drying of zeolites:

The amount of moisture in the zeolite during testing should not exceed 5%. Zeolite samples will be baked in an oven to achieve required dryness.

- 1) Preheat the oven to 300°F.

- 2) Spread the zeolite on an open tray in a layer not more than 5mm thick.
- 3) Place the tray into the preheated oven.
- 4) Let the zeolite stay in the oven for 30 minutes.
- 5) Turn off the oven and let the zeolite cool in the oven for 30 minutes to prevent moisture from entering the zeolites.
- 6) Remove the zeolites and mix it with dry cement according to proportion required for preparation of the cement slurry.

Preparation of Cement – Zeolite Slurry:

- 1) Prepare the dry cement-zeolite mixture according to the mixing proportion as weight percent of the cement.
- 2) Weigh the cement-zeolite dry mixture according to API Spec 10A Clause 7
- 3) Blend the dry mixture thoroughly.
- 4) Weigh distilled water according to API Spec 10A Clause 7 and add it to the mixer jar.
- 5) The cement and water should be weighed in dry containers.
- 6) The temperature of water and dry cement-zeolite mixture and water should be $73^{\circ}\text{F} \pm 2^{\circ}\text{F}$
- 7) Measure and record the temperature and weight of both, water and dry cement zeolite mixture.
- 8) Start the mixer at a low speed and let it stabilize.
- 9) Add the dry cement-zeolite mixture at a uniform rate into the rotating mixer in no more than 15 seconds.
- 10) Close the lid of the mixer and turn it at high speed for $35\text{s} \pm 1\text{s}$.

Free Water Test:

- 1) Free water test will be conducted according to API RP 10B, Clause 15.5
- 2) Clean and dry the graduated cylinder and the funnel to prevent contamination.
- 3) Pour the prepared slurry into the graduated cylinder up to the 250ml mark with the help of the funnel.
- 4) Cover it with plastic wrap to prevent any evaporation.
- 5) Keep it static for 2 hours.

- 6) Measure the amount of free water present on top of the slurry.

Also during the period the University of Alaska Fairbanks continued work on the test methods and procedures to be used in the initial screening of cement test blends.

American Petroleum Institute (API) Specification 10 compliant cement blender/mixer was tested by conducting free water test on regular Portland cement. The results were compared with those from mixing the same cement in a regular non-API spec mixer. The water cement ratios used in both the tests are kept the same for a valid comparison.

The mixing time in the non API spec blender was also kept at 50 seconds in accordance with the API Spec 10.

Cement slurry was prepared with water to cement ratio as mentioned in API Specifications. The blended mixture was poured in a 250 ml graduated cylinder and covered in order to avoid any water loss due to evaporation. After 2 hours, amount of free water on the top of the cylinder was measured. The results are tabulated below.

Free Water Test Results	Regular Blender		API Spec Blender	
	I (ml)	II (ml)	I (ml)	II (ml)
	1.2	1.4	2.8	2

Table 1: Free Water tests results for regular Portland cement using Regular Blender and API Spec Blender

Thus, mixing of cement in API specified blender is absolutely essential for this project.

TASK 4

Trabits Group obtained a new equipment quote from Chandler Engineering for the high pressure / high temperature curing chamber to be used in second stage testing. The chamber is a Model 7375 and capable of a maximum pressure of 3,000 psi and a maximum temperature of 700° F.

FY2011 Q4

TASK 2

Project Team Meeting

A Project Team Meeting was held at UAF on September 21st. In attendance were; George Trabits, Dr. Santanu Khataniar, Dr. Abhijit Dandekar, and Graduate Students Prachi Vohra and Dhaval Patel.

The main topic of discussion was the cement blend screening matrix. The Statement of Project Objectives sets the methodology and goals of the screening process:

“A large number of cement samples will be prepared for initial screening using permutations of zeolite species, particle size, percent zeolite by weight of cement and certain additives. Cement samples may contain more than one zeolite species and particle size in a test blend to take advantage of the properties of each. Sample preparation will be a heuristic process as the sample composition will need to be fine tuned based on the feedback from sample testing. API Class G and Class H cements will be used as the base for making the zeolite test samples.

The following properties are expected to be the primary criteria for initial screening:

- Zero Percent free water
- Rheological properties of less than 200 reading at 300 rpm
- 24 Hour compressive strength greater than 500 psi
- Thickening time and consistency, end thickening under 70 Bc
- Slurry density less than 13.5 lbs/gal”

Using the above SOPO as the guide UAF prepared the following Testing Matrix:

		Class G						Class H						Total Samples
		11.5ppg slurry (Light)			13.5ppg slurry (Medium)			11.5ppg slurry (Light)			13.5ppg slurry (Medium)			
	Size	% Zeolite, replacement of cement						% Zeolite, replacement of cement						
Ferrierite	5	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	Total Samples 180
	10	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	44	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Clinoptilolite Mud Hills	5	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	10	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	44	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Chabazite	5	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	10	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	44	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Clinoptilolite NM Mine 1	5	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	10	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	44	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Clinoptilolite NM Mine 2	5	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	10	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	44	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
					Initial Screening Criteria						Initial Screening Criteria			

Given the critical importance of this initial screening the Project Team thought it advisable to seek Peer Review comments from Halliburton and Dr. Karen Luke with Trican Well Services. Dr. Luke was formally with Halliburton and the main inventor of the zeolite-containing cement technology.

The Project Team also reviewed the zeolite and cement inventory and determined that more than enough material had been prepared for the project.

Halliburton Review Comments

Halliburton commented only on the number of tests and thought the large number of individual tests at varying particle sizes, type of zeolite and slurry density would provide a good basis for screening.

Dr. Luke Review Comments

Dr. Luke was more at issue with the test methods and in particular the use of Free Water and 24 Hour Compressive Strength as main elimination criteria. Dr. Luke's comments follow:

"My major concern over the current testing matrix at UAF is that the testing on free water does not really address the issues associated with geothermal wells and as such could eliminate some of the better performing zeolites in a geothermal environment. Free water tests are quick and easy but in this case not really applicable. Compressive strength retrogression is one of the primary major issues in geothermal wells and although it takes time to run the tests it is the one I would consider the best to give an indication on whether or not the zeolites are beneficial. My thought would be to take one zeolite and cure at temperature of interest over 1, 3, 7 and 28 days and determine the compressive strength and if possible permeability. You may also want to look at several different percentages of silica flour addition. Once you have that data you can focus in on one or two curing conditions and tests that give the best data or trend and then choose those test criteria to check out the other zeolites to see if their performance is better or worse.

Although zero free water is ideal, many low density slurries with added viscosifier can still have up to 0.4% free water and be acceptable. In terms of the current study if you do not have a viscosifier then I would consider the rejection point at 2.0% free water. Above 0.4% I would not recommend using the slurry for compressive strength measurements as settling will occur and densification of the slurry leading to erroneous results (overestimation of compressive strengths values)

Compressive strength at 24 hours will give no indication on the HTHP strength retrogression. This is due to a phenomena that occurs with a change in the cement chemistry whereby the amorphous non-structured C-S-H binder phase is converted into crystalline C-S-H phases that are distinct mineralogical species such as dicalcium silicate (associated with strength retrogression) or tobermorite, xonotlite, truscottite (on addition of silica flour and associated with good strength) or hydrogarnet, hydrogrossular etc associated with the aluminum phases in the cement or zeolite (tends to give lower strength) or anorthite with additional alumina(improved or poor strength depending on form). These phases only form above, around 302°F, and which phase(s) form depend on both the bulk chemistry of all inorganic products present and on localized concentrations. 24 hour compressive strength is not a good criteria for HTHP conditions. A sample could fail the 24 hours strength and give the higher strength, better permeability etc. at HTHP."

TASK 3

Halliburton Training at Rock Springs, Wyoming

Training was provided to UAF Graduate Students Vohra Prachi and Dhaval Patel by Halliburton from 11th July to 15th July at their Rock Springs Facility in Rock Springs, WY. The training was for Halliburton Cementing Field Engineers as well as their Lab Technicians. The training exposed the students to the

equipment that will be used for the tests at UAF. Although the training was focused around the proprietary additives and their properties that Halliburton uses, the students gained understanding on which additives to add and how much to add when cement slurry behaves in a certain way. The students were allowed into the Laboratory to oversee some of the experiments that the Lab Technicians were doing and also got to do some of the experiments. Several insights were gained on how to follow API specs wherever applicable. Handouts were provided which will help UAF in conducting the experiments at UAF in a safe and precise manner in accordance with industry standards. Contacts were made during the training which will help in the future if any problems are encountered with the experiments at UAF.

Cement Baseline Tests

Free Water tests were conducted on API Class G and Class H cements from Texas Lehigh Cements. Tests were carried out using the API Spec Blender from Chandler Engineering. Cement slurry was prepared according to API Spec 10 and poured into the graduated cylinders. The results are tabulated on the following page. The results show a good repeatability with four out of the five readings within the standard deviation as shown in the table and figure below.

Test	API Class G			API Class H		
	Free Water (ml)	Slurry Volume (ml)	Free Water (%)	Free Water (ml)	Slurry Volume (ml)	Free Water (%)
1	5	250	2	1.4	240	0.58
2	4.8	250	1.92	1.2	230	0.52
3	4.8	250	1.92	1.2	240	0.50
4	4.2	250	1.68	1.3	230	0.57
5	4.4	250	1.76	1.2	230	0.52

Table 1: Free Water Test Results for API Class G and Class H cements

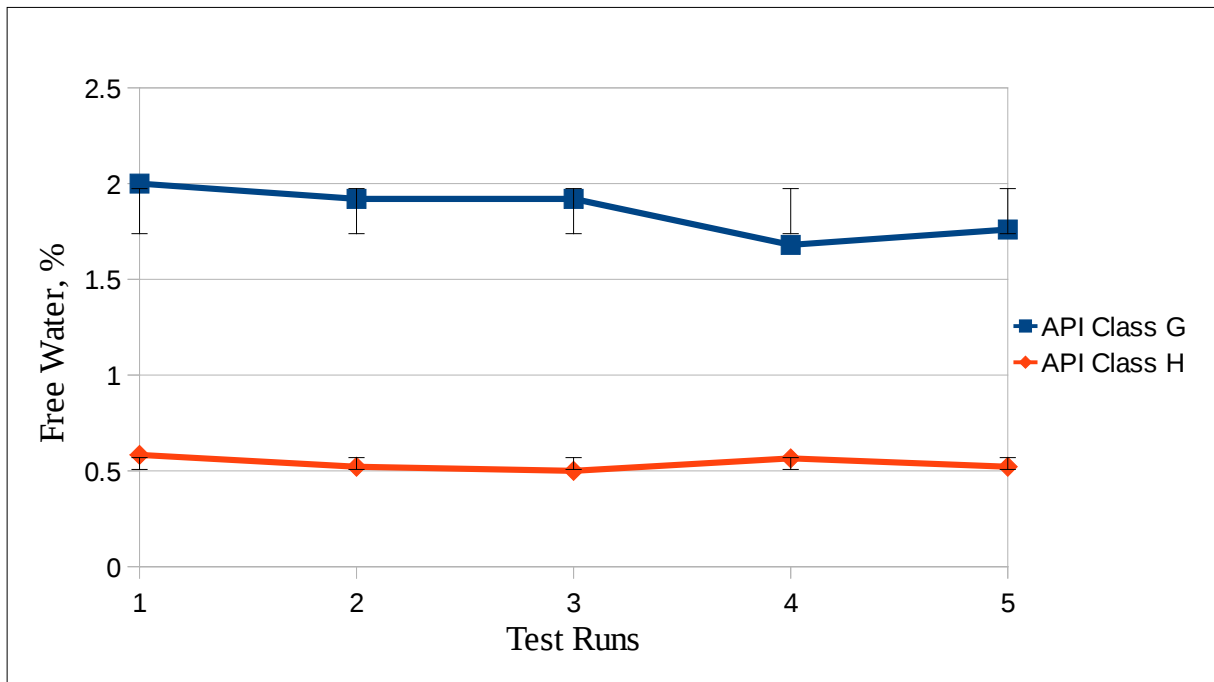


Fig 1: Free Water Test Results for API Class G and Class H cements

These results show that more zeolites might be needed to reduce the amount of free water in the API Class G cement than in Class H cement.

Initial Free Water Tests

Free Water tests were conducted on blends of API Class G and Class H cements with Ferrierite and Calcined Analcime. Largest particle size i.e. 44 μ m of both the zeolites was used for the test. Tests were carried out using the API Spec Blender from Chandler Engineering. The amount of zeolite added was 11.11% by weight of cement. The amount of water added to the blend of cement and zeolite was calculated by having a slurry density of 17.1ppg (Specific Gravity of 1.76) for all the blends. The results are tabulated below.

Test	Class G					
	Ferrierite			Calcined Analcime		
	Free Water, ml	Slurry Volume, ml	Free Water, %	Free Water, ml	Slurry Volume, ml	Free Water, %
1	4.40	250.00	1.76	1.40	250.00	0.56
2	4.40	250.00	1.76	1.50	250.00	0.60

Table 1: Results for API Class G cement using Ferrierite and Calcined Analcime

Test	Class H					
	Ferrierite			Calcined Analcime		
	Free Water, ml	Slurry Volume, ml	Free Water, %	Free Water, ml	Slurry Volume, ml	Free Water, %
1	2.90	250.00	1.16	1.00	250.00	0.40
2	3.00	250.00	1.20	1.00	250.00	0.40

Table 2: Results for API Class H cement using Ferrierite and Calcined Analcime

From the results we can see that addition of Calcined Analcime reduces the amount of free water for the slurry drastically than Ferrierite or even pure Class G and H cements. Performance of Ferrierite is almost on par with pure Class G and H cements. Although this slurry is slightly lighter than tests conducted on pure cements (18.3ppg). It would be interesting to note that in the XRD analysis, Calcined Analcime had just 1% Analcime and 61% Feldspar.

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Element 2 – Modification of Tasks 3 and 4

Trabits Group and UAF held a telephone audio conference on October 6th to consider making changes in the screening test matrix. Changes to the screening approach were suggested by Dr. Karen Luke in a Peer Review requested by Trabits Group and UAF. The audio conference participants were; George Trabits, Geoff Trabits, Dr. Shirish Patil, Dr. Santanu Khataniar, Dr. Abhijit Dandekar, and Graduate Students Prachi Vohra and Dhaval Patel. The participants agreed that the test matrix could be improved following Dr. Luke's suggestions. Central to Dr. Luke's concerns was the elimination of a "good" zeolite that failed screening but could be improved with common cement blend additives. As an example, a screening blend could fail based on free water but additives used to control free water and such a "failed" zeolite might actually perform well under high temperature/high pressure conditions. Also

during the conference the question was raised on if 11.5 ppg was a good screening target. The concern here is that in deep EGS wells even our upper end of 13.5 ppg would in fact be a lightweight cement. A more realistic screen, and again not to eliminate too many potentially good candidates, could be perhaps 12 ppg.

Element 4 – Initial Screening of Cement Formulations

The test matrix developed initially was revised and the numbers of samples to be tested in the initial screening were cut so as to optimally decrease the amount of time spent on the initial screening of samples. These changes took effect after several interactions with Dr. Karen Luke from Trican Well Services and phone meetings between the team at UAF and Trabits Group.

The primary concern from Dr. Luke was using both Class G and Class H for the initial screening. The argument was that chemically Class G and H are similar, Class H being used in the USA and easily available, while Class G is used elsewhere. Hence Class G is not included in the revised matrix prepared for initial screening. The test matrix for Class G cement will be heuristically deduced from the results of Class H cement. Other concern shown by Dr. Luke was conducting the initial screening of samples under atmospheric conditions. Properties of cement drastically change with the increase in temperature. Strength development is rapid, retrogression is equally rapid. Hence she suggested conducting the initial screening under HPHT conditions. Although, given the equipment, time and effort constraints, it was decided to conduct initial screening at atmospheric conditions. Although one more test for measuring the permeability using a probe permeameter was added for initial screening of the samples.

Addition of additives was discussed as well. It was decided to keep the blend as pure as possible so as to make it easier to blend and get consistent result on field. Although, additives might be added if the initial screening results for free water and compressive strength fall into an initial set limit.

The initial screening limits as decided are:

- Free Water: <2%
- 24 hour compressive strength: at least 500psi
- Permeability: <1mD
- Rheology: <200 reading at 300rpm

The samples will be prepared in two different densities of 13.5ppg and 12.5ppg. The test matrices are provided below.

Initial Screening Matrix								
Zeolites	Class H, 13.5ppg slurry			Class H, 12.5ppg slurry			Tests	
	% Zeolite, Replacement of Cement			% Zeolite, Replacement of Cement				
Ferrierite	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	1) Free Water Test: Acceptable free water of <2%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%		
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%		

Clinoptilolite-Mud Hills	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	2) Permeability using a probe permeameter: Acceptable permeability <1mD
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Chabazite	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	3) Rheology: <200 reading at 300rpm
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Clinoptilolite-NM1	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	4) 24hr compressive strength: Acceptable ≥500psi
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Clinoptilolite-NM2	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	

Table 1: Initial Screening Matrix using Class H cement and the screening criteria

Screened samples will be subjected to tests under HPHT conditions

Zeolites	Class G, 13.5ppg slurry			Class G, 12.5ppg slurry			
	% Zeolite, Replacement of Cement			% Zeolite, Replacement of Cement			
Ferrierite	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	This matrix will be heuristically modified according to results from tests using Class H cement
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Clinoptilolite-Mud Hills	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Chabazite	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Clinoptilolite-NM1	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
Clinoptilolite-NM2	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	
	15.0%	27.5%	40.0%	15.0%	27.5%	40.0%	

Table 2: Test matrix using Class G cement. This matrix will be reduced according to results from Class H cement.

A 45° stand was made for measuring free water in an inclined cylinder. This procedure was suggested by Halliburton because it is supposed to provide free water under the worst case scenario. The difference in

free water measurements using vertical cylinder (standard API procedure) versus inclined cylinder (Halliburton approach) was tested by using two graduated cylinders: one at vertical and the other at 45°. Two types of zeolites were used to compare, Mudhill Clinoptilolite and Ferrierite, both having particle size of 44µm.

Before preparing the slurry, the zeolites were dehydrated by spreading on an oven tray in a thin layer and heating in an oven at 266°F (130°C) for 30 minutes. This would ensure that there was no moisture content in the zeolites before blending the Class H cement and zeolites. In order to eliminate error associated with mixing separate slurries for vertical and 45° cylinders, only one blend was mixed and poured into the two cylinders.

The differences in results for vertical and 45° cylinders are significant. Ferrierite performed worse than Clinoptilolite due to its lower pore volume. The results are realistic as no well drilled is perfectly vertical. The results are tabulated below. Based on these results, it was concluded that free water test at 45 degree angle is indeed a more stringent screening test than the API standard procedure. Therefore, the 45 degree free water test would be used in all future free water tests.

Table 1: Comparison of free water test results for Mudhill Clinoptilolite and Ferrierite for vertical and 45° angle of graduated cylinder.

Cylinder Position	Clinoptilolite			Ferrierite		
	Free Water, ml	Total Fluid, ml	Free Water, %	Free Water, ml	Total Fluid, ml	Free Water, %
Vertical	3.2	250	1.28	6.2	250	2.48
45°	4.5	250	1.80	11.0	250	4.40

Atmospheric consistometer from Chandler Engineering was received, assembled, and calibrated to condition the cement slurries for all future tests in this reporting period. All the necessary plumbing work was performed to so as to make sure that the water does not leak into the equipment.

Free water tests were performed on the Mud Hill Clinoptilolite and the New Mexico Mine 2 Clinoptilolite for both 5µm and 44µm sizes at 15% replacement of Class H cement. The zeolites were spread on a tray in a thin layer heated in the oven for at least 30 minutes at 284°F (140°C) to make sure there was no moisture in the zeolites. The slurries after mixing were conditioned in the consistometer at 80°F for 20 minutes, per Halliburton test protocol, and then poured into the graduated cylinders for measuring the free water. The results are very encouraging for both Clinoptilolites. The results are tabulated below. We also conclude from these results that the free water tests with the cylinder at 45 degree angle do represent the “worst case” scenario i.e. they show higher free water than the vertically placed cylinders.

Cylinder Position	44µm			5µm		
	Free Water, ml	Total Slurry, ml	Free Water, %	Free Water, ml	Total Slurry, ml	Free Water, %
	Mudhill Clinoptilolite					
45°	7.0	250	2.8	1.0	250	0.4
Vertical	3.4	210	1.6	0.6	210	0.3
	New Mexico Mine 2 Clinoptilolite					
	Free Water, ml	Total Slurry, ml	Free Water, %	Free Water, ml	Total Slurry, ml	Free Water, %
	New Mexico Mine 2 Clinoptilolite					
45°	8.6	250	3.4	2.4	250	1.0
Vertical	3.6	210	1.7	1.0	200	0.5

Table: Results for free water test for 13.5 ppg slurry using 5µm and 44µm Mudhill and New Mexico Mine 2 Clinoptilolite and Class H cement at 15% replacement of cement.

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Element 4 – Initial Screening of Cement Formulations

Trabits Group made arrangements with CCE Technology in Minnesota to ship to Trican Well Service in Calgary 100 gram sample splits of the same zeolite types and particle sizes shipped to the Baker Hughes lab in Bakersfield for a determination of Specific Gravity. During the period Trican completed these determinations using a Micrometrics AccuPyc II 1340 gas pycnometer. The results are tabulated below.

Chemical's Supplier: Trabits Group, LLC

Sample Description: 4 sets of hydrated potassium-calcium-sodium-aluminosilicates samples (2 different particle size each set, for a total of 10 samples) were sent to the lab to determine their SG by using the pycnometer

Product Name	Mass (g)	SG	SDTV
Chabazite < 5µm	17.2730	2.0495	0.0030
Chabazite < 44µm	22.9280	2.0608	0.0015
Mud Hills Clinoptilolite < 5µm	20.9163	2.1339	0.0030
Mud Hills Clinoptilolite < 44µm	32.0070	2.1603	0.0024
Ferrierite <5µm	25.2819	2.1854	0.0020
Ferrierite <44µm	39.1704	2.2318	0.0027
Mine#1 Clinoptilolite < 5µm	23.4705	2.2656	0.0016
Mine#1 Clinoptilolite < 44µm	33.5408	2.2868	0.0019
Mine#2 Clinoptilolite < 5µm	24.4447	2.3023	0.0022
Mine#2 Clinoptilolite < 44µm	35.5808	2.3459	0.0015

Dr. Luke stated in her report that “one notable feature in the data is the consistently higher values for the coarser material in comparison to the finer material.”

A meeting was held with Baker Hughes in Anchorage to discuss the initial results of testing at the Baker Hughes laboratory in Bakersfield, California. Rod Edwards reported that Baker Hughes was successful in making 10.5 ppg (pound per gallon) cement using Clinoptilolite but the strength was not very high. Trabits Group suggested that a blend of Clinoptilolite and Ferrierite could improve strength. Early tests of Ferrierite blends at 14.0 ppg resulted in a strength of 2677 psi at 24 hours. By adding Ferrierite the compressive strength should improve but the 10.5 ppg may be difficult to maintain. A blend using two different types of zeolite has not been done before.

As reported above, the specific gravity provided by Karen Luke from Trican using a Pycnometer differed from the ones provided on the MSDS sheet for the zeolites. The specific gravity used before was much

lower than the actual values after measuring them in the pycnometer. As a result, the free water tests had to be conducted again due to increased amount of water required to make the 13.5ppg slurry.

Ferrierite 44 μm

Free water test was performed on Ferrierite of 44μm size for replacements of 15%, 27.5% and 40% of Class H cement.

A thin layer of Ferrierite was spread on a tray and heated in the oven for at least 30 minutes at 284°F (140°C) to make sure there was no moisture in the zeolites. The slurries after mixing were conditioned in the consistometer at 80°F for 20 minutes and then poured into the graduated cylinders and placed at an angle of 45° for measuring the free water.

The results as expected yielded more free water for the 15% replacement due to higher amount of water. The results are tabulated below.

Ferrierite(44μm)								
% Zeolite Replacement of Cement								
15%			27.50%			40%		
Free Water, ml	Total Slurry, ml	Free Water, %	Free Water, ml	Total Slurry, ml	Free Water, %	Free Water, ml	Total Slurry, ml	Free Water, %
28	250	11.2	7.2	250	2.88	3.2	250	1.28

Table 1: Results for free water test for 13.5 ppg slurry using 44μm Ferrierite and Class H cement at 15%, 27.5%, 40% replacement of cement.

Ferrierite 5 μm

Free water tests were performed on Ferrierite of 5μm size and replacements of 15%, 27.5% and 40% of Class H cement. Compressive strength tests were also performed on 5 and 44μm Ferrierite.

Ferrierite was spread on a tray in a thin layer heated in the oven for at least 30 minutes at 284°F (140°C) to make sure there was no moisture in the zeolites. The slurries after mixing were conditioned in the consistometer at 80°F for 20 minutes and then poured into the graduated cylinders and the cube molds. The cylinder was placed at an angle of 45° for measuring the free water. The molds were kept in an oven in controlled temperature of 100°F.

The results are tabulated below. Free water decreases with increasing amount of zeolite. The 27.5% replacement appears to be close to an optimum blend.

Ferrierite(5μm)								
% Zeolite Replacement of Cement								
15%			27.50%			40%		
Free Water, ml	Total Slurry, ml	Free Water, %	Free Water, ml	Total Slurry, ml	Free Water, %	Free Water, ml	Total Slurry, ml	Free Water, %
9	250	3.6	1	250	0.4	0	250	0

Table 1: Results for free water test for 13.5 ppg slurry using 5μm Ferrierite and Class H cement at 15%, 27.5%, 40% replacement of cement.

The compressive strength tests showed somewhat surprising results. A few 44μm samples were damaged while de-molding the cubes (Figure 1). The 5μm (27.5% and 40% replacement) samples performed better than the 44μm ones, and met the criteria for free water and compressive strength. The results are plotted in Figure 2.



Figure 12 Damaged Ferrierite samples while de-molding

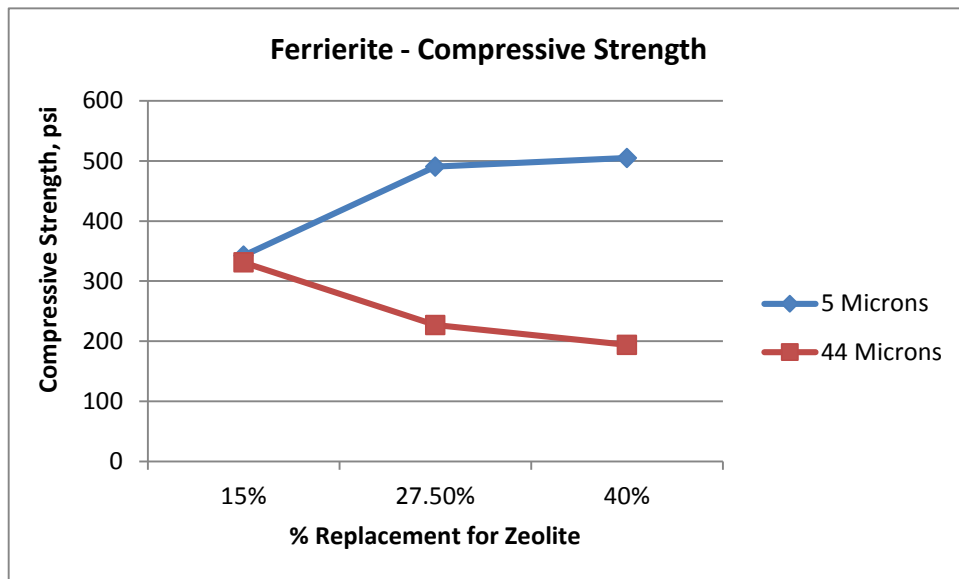


Figure 13 Compressive strength results for Ferrierite.

UAF and Trabits Group conferred on the zeolite replacement percentage. UAF reported that it appears that zeolite replacement of 27.5% is near some kind of optimum for free water and compressive strength. The drop at 15% replacement is quite large. Based on these observations, UAF was thinking of doing some tests at 20% replacement to see if the critical or threshold zeolite amount is near 20%. The question was referred to Dr. Karen Luke for comment.

Dr. Luke Comments

“The results do not surprise me based on the limited data provided. The free water was something I noted with the Ferrierite also, however, in the industry we have additives to deal with this. It is interesting to note though that there is such a notable decrease in free water at the higher Ferrierite concentrations. On the basis of the data I would think that 30% is more the optimum value as this is likely to give 0 mL free water and have the 500 psi strength. However, I would agree with testing the Ferrierite at 20%, since there is such a large change in values between 15 and 27.5% replacement and this would definitely give a valuable data point in determining more precisely the threshold amount.”

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Element 1 – Zeolite Sample Acquisition

Due to an improvement in the zeolite processing method additional Mud Hills Clinoptilolite and Ferrierite for use in First Stage screening and Second Stage development were prepared. A little more than 500 pounds of these two zeolites were transported to a FedEx Freight terminal for shipment to CCE Technologies in Minnesota to be prepared in 5, 10 and 44 micron particle sizes. Coordination was

conducted with CCE to split the final particle runs with one half going to UAF and the other half to Baker Hughes.

Element 3 – Zeolite Particle Size Preparation

CCE Technologies competed and shipped the micronized runs of Ferrierite and Mud Hills Clinoptilolite. Identical spits were shipped to UAF and to Baker Hughes. The UAF shipment totaled 370 pounds and the Baker Hughes shipment totaled 372 pounds.

Element 4 – Initial Screening of Cement Formulations

Free Water Tests – Mud Hill Clinoptilolite 44µm Size

Mud Hill Clinoptilolite was spread on a tray in a thin layer and heated in the oven for at least 30 minutes at 284°F (140°C) to make sure there was no moisture in the zeolites. The slurries after mixing were conditioned in the consistometer at 80°F for 20 minutes and then poured into the graduated cylinders and the cube molds. The cylinder was placed at an angle of 45° for measuring the free water. The molds were kept in an oven at controlled temperature of 100°F.

Mud Hill Clinoptilolite (44µm)								
% Zeolite Replacement of Cement								
15%			27.50%			40%		
Free Water, ml	Total Slurry, ml	Free Water, %	Free Water, ml	Total Slurry, ml	Free Water, %	Free Water, ml	Total Slurry, ml	Free Water, %
17.4	250	6.96	4.2	250	1.68	0.2	250	0.08

Table 1: Results for free water test for 13.5 ppg slurry using 44µm Mud Hill Clinoptilolite and Class H cement at 15%, 27.5%, 40% replacement of cement.

Compressive Strength - Mud Hill Clinoptilolite 44µm Size

The compressive strength test showed some surprising results. The increase in the amount of zeolite resulted in decrease in the strength of the cement. The particle size of both the cement and the zeolite is same at 44µm. Also, zeolite being a pozzolan reacts slower than the cement. Since there is no net increase in surface area and an overall slower rate of hydration by increasing the zeolite content, this might have resulted in lower compressive strength with increase in the amount of zeolite. Figure 1 shows the result for compressive strength of 44µm Mud Hill Clinoptilolite for different replacements.

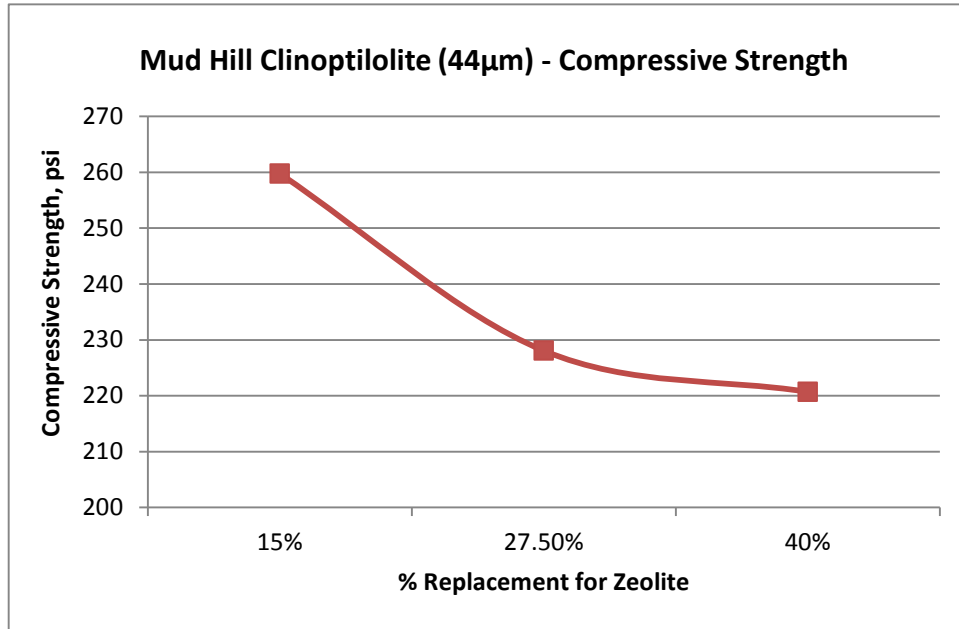


Figure 14: Compressive strength for 44µm Mud Hill Clinoptilolite using Class H cement

Free Water Tests – Mud Hill Clinoptilolite 5 µm Size

Free water tests were performed on Mud Hill Clinoptilolite of 5µm size for 15%, 27.5% and 40% replacement of Class H cement.

The results for Mud Hill Clinoptilolite (5µm) free water test are tabulated below.

Table 2: Results for free water test for 13.5 ppg slurry using 5µm Mud Hill Clinoptilolite and Class H cement at 15%, 27.5%, 40% replacement of cement.

Mud Hill Clinoptilolite (5µm)								
% Zeolite Replacement of Cement								
15%			27.50%			40%		
Free Water, ml	Total Slurry, ml	Free Water, %	Free Water, ml	Total Slurry, ml	Free Water, %	Free Water, ml	Total Slurry, ml	Free Water, %
3.6	250	1.44	0	250	0	N/A	250	N/A

The slurry does not mix for Mud Hill Clinoptilolite of 5 µm size at 40% replacement and so we do not have free water test results at 40%. As expected, the 5µm sample performed better than the 44µm for 15 % and 27.5 % replacement in the free water test.

Free Water Tests – New Mexico Mine #1 44 µm Size

The results for New Mexico Mine #1 (44µm) free water test are shown in table 3.

Table 3: Results for free water test for 13.5 ppg slurry using 44µm New Mexico Mine #1 Clinoptilolite and Class H cement at 15%, 27.5%, 40% replacement of cement.

New Mexico Mine #1 Clinoptilolite (44µm)								
% Zeolite Replacement of Cement								
15%			27.50%			40%		
Free Water, ml	Total Slurry, ml	Free Water, %	Free Water, ml	Total Slurry, ml	Free Water, %	Free Water, ml	Total Slurry, ml	Free Water, %
17	250	6.8	3.8	250	1.52	1.8	250	0.72

Compressive Strength – Mud Hills Clinoptilolite 5 µm Size

The increase in the amount of zeolite resulted in a slight increase of the 24 hour compressive strength of the cement. Figure 2 shows the result for compressive strength of 5µm Mud Hill Clinoptilolite for different replacements.

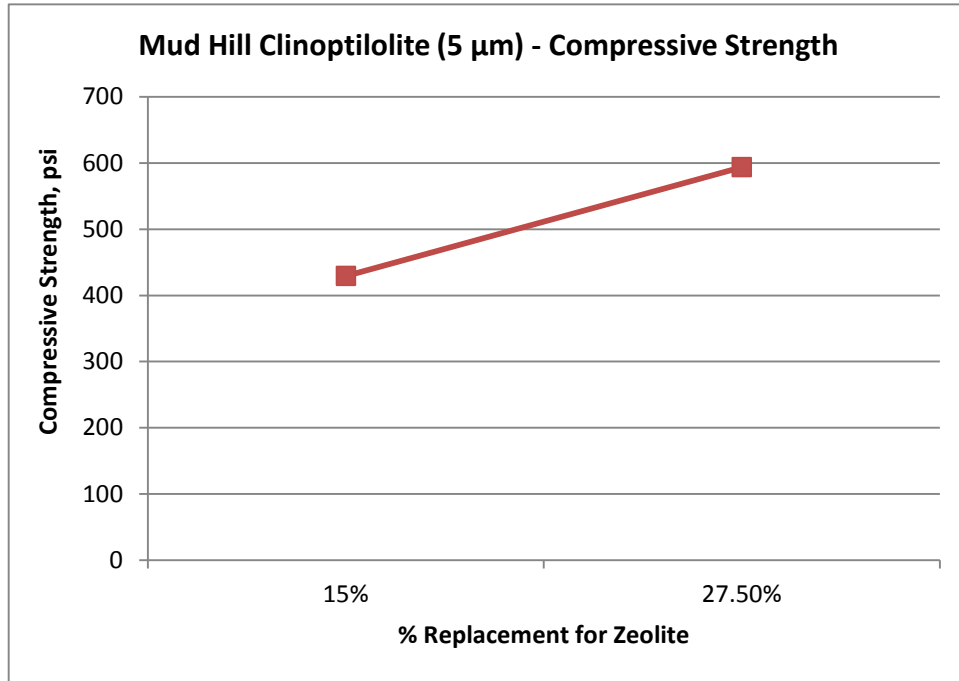


Figure 2: Compressive strength for 5μm Mud Hill Clinoptilolite using Class H cement

The 5μm (27.5%) sample performed better than the 44μm samples, and it appears to have satisfactory free water and compressive strength.

Summary Free Water Tests

Table 4: Free water (%) of all 5, 10, and 44 micron samples at various cement replacements

Zeolite Sample	at 15% replacement	at 27.5% replacement	at 40% replacement
Chabazite, 5 micron	1.0	0	NA*
Chabazite, 10 micron	1.76	0.20	NA*
Chabazite, 44 micron	4.4	0.40	0
Mudhill Clinopt. 5 micron	1.44	0	NA*
Mudhill Clinopt. 10 micron	2.2	0.24	NA*
Mudhill Clinopt. 44 micron	6.96	1.68	0.08
Ferrierite, 5 micron	3.6	0.40	0
Ferrierite, 10 micron	4.4	0.68	0.16
Ferrierite, 44 micron	11.2	2.88	1.28

NM Mine #1, 5 micron	1.28	0.40	NA*
NM Mine #1, 10 micron	1.76	0.52	NA*
NM Mine #1, 44 micron	6.8	1.52	0.72
NM Mine #2, 5 micron	1.72	0.32	NA*
NM Mine #2, 10 micron	2.56	0.2	0.16
NM Mine #2, 44 micron	7.2	1.6	0.48

NA* = does not blend due to clumpiness or excessive thickening

From the free water results, it appears that 10 micron may be the optimum size, if it is cheaper to make than the 5 micron sample.

Summary Compressive Strength

Table 5: Compressive strengths (psi) after 24 hours for all 5 and 44 micron samples at various cement replacements

Zeolite Sample	at 15% replacement	at 27.5% replacement	at 40% replacement
Chabazite, 5 micron	711.94	1844.99	NA*
Chabazite, 44 micron	318.10	512.05	1313.32
Mudhill Clinopt. 5 micron	429.31	593.68	NA*
Mudhill Clinopt. 44 micron	259.75	228.06	220.7
Ferrierite, 5 micron	342.44	490.5	504.88
Ferrierite, 44 micron	331.0	226.79	193.80
NM Mine #1, 5 micron	291.92	285.1	NA*
NM Mine #1, 44 micron	209.97	230.22	176.73
NM Mine #2, 5 micron	288.43	305.47	NA*
NM Mine #2, 44 micron	237.64	187.0	117.73

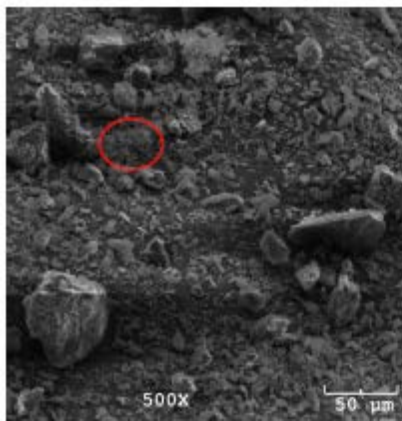
The compressive strengths of Chabazite are far better than all other zeolites, and compressive strength increases significantly with increasing % of Chabazite. This observation leads us to believe that Chabazite may have some kind of cement-like bonding property. We are wondering if Chabazite will behave like a “catalyst” if added to other zeolites, i.e., add very small amount of Chabazite to another promising zeolite (e.g. Ferrierite) to see if that significantly increases compressive strength of the promising zeolite.

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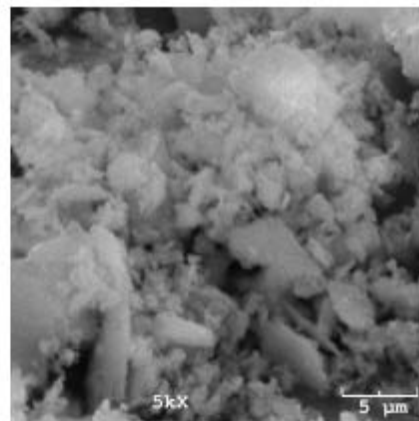
Additional literature searches were conducted as a continuation of research into the reasons for the unexpected high compressive strength results noted with the Bowie, Arizona Chabazite. As previously reported XRD studies had identified that the zeolite was 50% Chabazite and 50% Offretite which is another zeolite. As previously reported, Offretite is often associated with Erionite. Erionite is a naturally occurring zeolite that is fibrous and has similar properties of asbestos. Erionite has an internal molecular structure similar to Chabazite. Offretite is difficult to distinguish from Erionite. Accordingly, the question is if the Offretite noted is actually Erionite. If so, is the fibrous nature providing improved compressive strength.

In response to the question UAF conducted a SEM scan on the 44 micron Chabazite. From observations, the sample did not display any significant (or at all) fibrous particles. The left image below depicts a representative image of the sample at 500x magnification and the small area circled in red was viewed at 5000x magnification on the right. This may or may not represent a “fibrous” particle group. Looking at SEM images of Offretite and Erionite from the internet, both minerals display a fibrous nature. So it is very possible that even if the fibrous particles were visible, the distinction between the two from SEM may not be possible.

Basically, the SEM did not yield any significant or conclusive results.



Characteristic of the sample. The area circled in red is magnified in the image to the right.



5000 x magnification of area circled in red on the left image. Possible offretite or erionite???

Element 4 – Initial Screening of Cement Formulations

Compressive Strength Measurements 10 µm Samples

The compressive strength measurements for 10 micron samples were completed. Table 1 shows a comprehensive listing of the 24 hour compressive strengths for all three particle sizes. The 40% blend with 10 micron Mudhill Clinoptilolite gave very high compressive strength, and the result appeared anomalous. So, this compressive strength measurement was repeated, however, the result remained unchanged.

Because of high compressive strengths shown by Chabazite and Mudhill samples, SEM analysis of these two zeolite samples is being planned. SEM analysis will be done on at least one of the New Mexico Clinoptilolites as well, to see how these differ from Mudhill Clinoptilolite.

Table 1: 24 Hour Compressive Strength [psi]

Replacements:		15%	27.5%	40%
Chabazite	5 µm	712	1845	*
	10 µm	660	1519	*
	44 µm	318	512	1337
Mudhill	5 µm	429	594	*
	10 µm	329	416	1263
	44 µm	260	228	221
Ferrierite	5 µm	342	491	505
	10 µm	269	302	297
	44 µm	331	227	194
NM #1	5 µm	292	285	*
	10 µm	324	328	442
	44 µm	210	230	177
NM #2	5 µm	288	305	*
	10 µm	307	264	234
	44 µm	238	187	118

* Unable to mix samples

Free Water and Compressive Strength

Free water and compressive strength (24 hour at 45 degree C) of regular and thermally treated zeolite samples have been completed. In order to get an idea of effect of curing temperature on 24 hour compressive strength, some samples were cured at 70 degree C and atmospheric pressure (so that the water would not boil off). In addition, consistency and rheology measurements are in progress as well. Some permeability measurements on cured samples have been done using a mini-probe permeameter. The results obtained so far are summarized in Tables 2 and 3. (* please note that the values in red are just fillers and not actual values.)

The 24 hour compressive strength was tested for curing temperatures of 70°F for mudhill clinoptilolite, ferrierite, NM#1 clinoptilolite, and NM#1 clinoptilolite at 27.5% replacement levels. Significant strengths gains were observed. The ferrierite 24 hour compressive strength increased by 3.8 to 5.4 times as compared to the 45°F curing temperatures. The mudhill, NM#1, and NM#2 clinoptilolite compressive strength increased on average 3 to 4 times. The results indicate that at elevated curing temperatures; previously unsuitable zeolite replacements may become viable.

Mudhill and ferrierite were mixed in equal volumes for the 27.5% replacement level. The resulting 24 hour compressive strengths at 45°F are intermediate between the two individual zeolites. At the 40% replacement level there is a bias towards the ferrierite properties.

As far as consistency and rheology are concerned, all samples tested so far have behaved well and show no signs of concern. Additional tests are in progress.

Table 2.

Free Water [% free water per 250 mL]				
Cement H		34.8%		
		15%	27.5%	40%
Chabazite	5 µm	1.00%	0%	*
	10 µm	1.76%	0.20%	*
	44 µm	4.40%	0.40%	0%
Mudhill	5 µm	1.44%	0%	*
	10 µm	2.20%	0.24%	*
	44 µm	6.96%	1.68%	0.08%
1/2 Mudhill 1/2 Ferrierite	5 µm			
	10 µm			
	44 µm			
Ferrierite	5 µm	3.60%	0.40%	0%
	10 µm	4.40%	0.68%	0.16%
	44 µm	11.20%	2.88%	1.28%
NM #1	5 µm	1.28%	0.40%	*
	10 µm	1.76%	0.52%	*
	44 µm	6.80%	1.52%	0.72%
NM #2	5 µm	1.72%	0.32%	*
	10 µm	2.56%	0.20%	0.16%
	44 µm	7.20%	1.60%	0.48%
Mudhill Treated	5 µm	2.04%	0.20%	*
	10 µm	1.68%	0.28%	*
	44 µm	6.88%	0.76%	0.48%
Ferrierite Treated	Out Spec	5.36%	0.56%	0%
	5 µm	5.04%	0.32%	0%
	10 µm	8.64%	1.36%	0.12%
	44 µm	14.40%	5.72%	2.72%
Mordenite	5 µm			
	10 µm			
	44 µm			

Compressive Strength [psi]							
Cement H		847.0			70°C 27.5%	5% Chab 27.5%	5% clay 27.5%
		15%	27.5%	40%			
Chabazite	5 µm	712	1845	*			
	10 µm	660	1519	*			
	44 µm	318	512	1337			
Mudhill	5 µm	429	594	*	1628		
	10 µm	329	416	1263	1211		
	44 µm	260	228	221	909		
1/2 Mudhill 1/2 Ferrierite	5 µm	414	440	820			
	10 µm	348	385	495			
	44 µm	0	267	220			
Ferrierite	5 µm	342	491	505	1898		
	10 µm	269	302	297	1615		
	44 µm	331	227	194	950		
NM #1	5 µm	292	285	*	1185		
	10 µm	324	328	442	1164		
	44 µm	210	230	177	762		
NM #2	5 µm	288	305	*	1204		
	10 µm	307	264	234	1160		
	44 µm	238	187	118	763		
Mudhill Treated	5 µm	329	635	1393			
	10 µm	351	560	1266			
	44 µm	285	227	198			
Ferrierite Treated	Out Spec	401	409	536			
	5 µm	367	446	615			
	10 µm	372	357	383			
	44 µm	408	286	215			
Mordenite	5 µm	0	0	0			
	10 µm	0	0	0			
	44 µm	0	0	0			

needs 3rd verification run

edge/face disintegration issues, run 2nd verification

Denisty avg. of comp. samp. [g/cc]					Permeability (using Tiny Perm) [mD]									
Cement H					(before crushing after Crushing Dried not crushed)									
					15%			27.5%			40%			
Chabazite	5 µm													
	10 µm													
	44 µm			1.640									0.0	
Mudhill	5 µm													
	10 µm													
	44 µm													
1/2 Mudhill	5 µm	1.641	1.575	1.595										
1/2 Ferrierite	10 µm	1.609	1.591	1.585										
	44 µm	0.000	1.579	1.591										
Ferrierite	5 µm													
	10 µm													
	44 µm													
NM #1	5 µm													
	10 µm			1.499										
	44 µm													
NM #2	5 µm													
	10 µm													
	44 µm													
Mudhill Treated	5 µm	1.570	1.548	1.599				0.0					0.0	
	10 µm	1.578	1.573	1.584				6.8					0.0	
	44 µm	1.598	1.532	1.477				0.0					0.0	
Ferrierite Treated	Out Spec	1.654	1.626	1.623				2.7	2.1	11.6	1.9	3.7	11.6	
	5 µm	1.650	1.640	1.631									0.0	
	10 µm	1.670	1.641	1.644				0.0					0.0	
Mordenite	44 µm	1.716	1.653	1.634				0.0					0.0	
	5 µm	0.000	0.000	0.000				0.0	0.0		0.0	0.0	0.0	
	10 µm	0.000	0.000	0.000				0.0	0.0		0.0	0.0	0.0	
	44 µm	0.000	0.000	0.000				0.0	0.0		0.0	0.0	0.0	

Table 3.

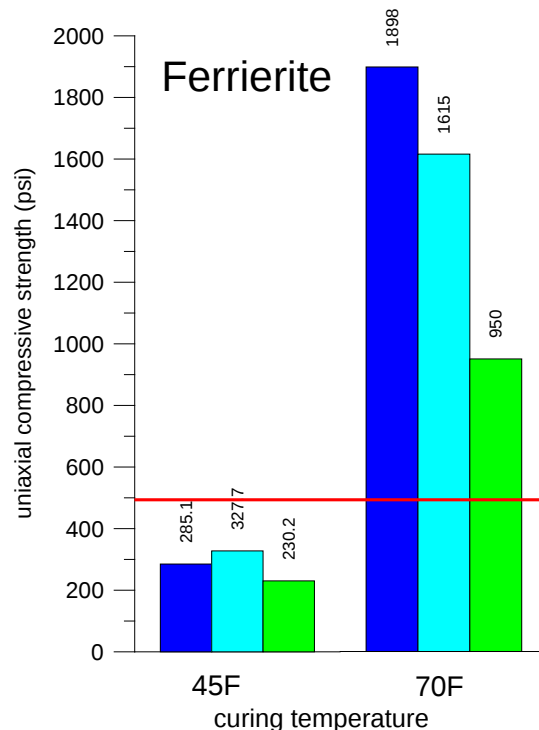
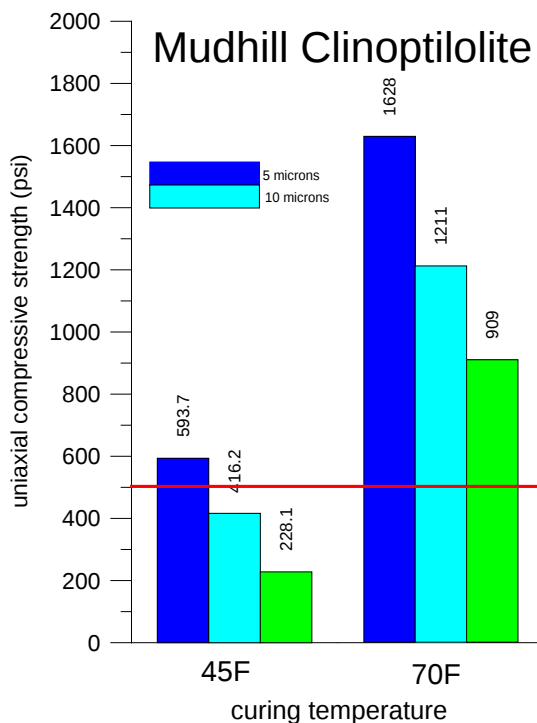
Consistency (5 h Atmo 80°F) [Bc]					Viscosity (avg reading at 300 rpm)				
					15%	27.5%	40%		
Chabazite	5 µm	12	45	*		237.5			
	10 µm	8	34	*					
	44 µm	4	13	31		106			
Mudhill	5 µm	10	25	*					
	10 µm	8	20	47					
	44 µm	5	7	14		48.5			
Ferrierite	5 µm	6	11	30		28.5	67		
	10 µm	5	10	28					
	44 µm	3	6	7		16	33.5		
NM #1	5 µm	8	19	*			120		
	10 µm	8	14	31					
	44 µm	5	6	11			49.5		
NM #2	5 µm	7	20	*			90		
	10 µm	8	10	27					
	44 µm	3	7	10			64.5		

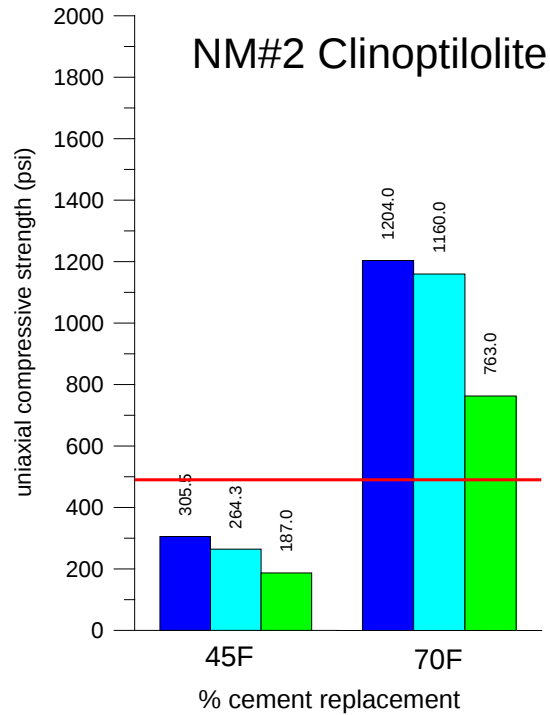
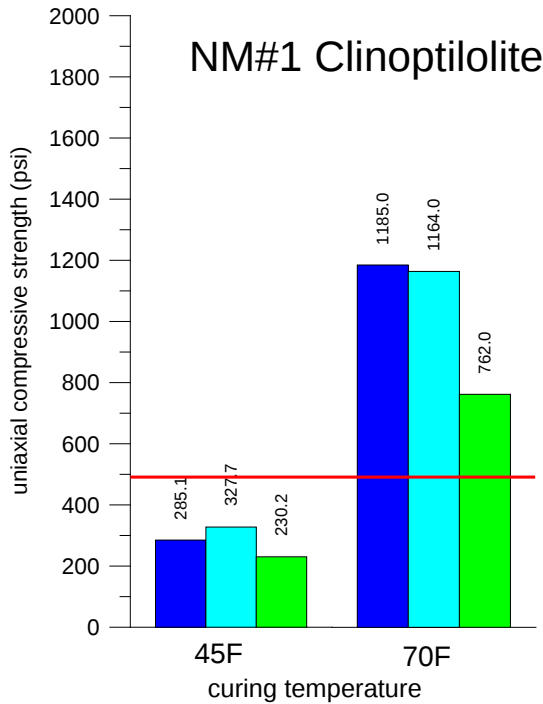
Compressive Strength: Cured at 70°F

To explore the influence of temperature on the 24 hour compressive strength of the zeolite/cement mixes, several mixes were cured at 70°F. Initially ferrierite was targeted as a base test. Ferrierite was tested at the 27.5% replacement levels for particle sizes of 5µm, 10 µm, and 44 µm. Significant strength gains were observed over the 24 hour compressive strength at curing temperature of 40°F. The 24 compressive strength was 3.8x (5µm), 5.4x (10 µm) and 4.9x (44 µm) larger at 70°F than at 45°F.

In response to the results from the ferrierite experiment, the experimental testing was expanded to include mudhill clinoptilolite, NM#1 clinoptilolite, and NM#2 clinoptilolite at the 27.5% replacement level for all three particle sizes. For mudhill, the compressive strength increased from 3 to 4 times. Similar increases were observed for NM#1 and NM#2. Significant increases in the 24 hour compressive strength from 10µm to 5µm were not observed for ferrierite, NM#1, and NM#2. The data suggests that minimal returns are gained from using 5µm as compared 10µm. The 5µm and 10µm mudhill samples experienced edge and face degeneration, so the results will need to be verified.

Based on 24 hour compressive strength data obtained at a curing temperature of 45 °F, NM#1 and NM#2 do not meet the 500 psi strength criteria. Similarly, only for the 5µm and 10µm particle size at high replacement levels do mudhill and ferrierite meet the 500 psi strength criteria. Based on the 70°F results, the preliminary data suggest that at elevated curing temperatures, the zeolite/cement mixes will meet the minimum strength criteria. As a result, the extent of viable zeolite mineral types is greatly increased.





The 24 hour compressive strength is provided by mudhill, ferrierite, NM#1, and NM#2 as a function of curing temperature.

Mixed Zeolites

In response to the higher performance of chabazite and mudhill clinoptilolite as compared to ferrierite, NM#1, and NM#2, it was deemed that the higher performing zeolites should be combined with the lower performing zeolites. As initial baseline, mudhill was mixed with ferrierite and tested for the 24 hour compressive strength at a curing temperature of 45°F.

Mudhill/Ferrierite

At the different replacement ratios, mudhill and ferrierite were replaced by equal mass. For example, for the 15% zeolite replacements, the zeolite contribution consisted of 7.5% mudhill and 7.5% ferrierite. The 24 hour compressive strength falls between the values of the individual zeolites, with a bias towards ferrierite at the 40% replacement levels. The largest gains in compressive strength are observed for the 40% replacement levels (20% Mudhill and 20% ferrierite). The ferrierite addition at the 40% replacement level does improve the mixability. At the 40% mudhill replacement, the mix is quite thick and mixes poorly.

Combining Zeolites

The effects of combining the zeolites with montmorillonite or chabazite were studied during the reporting period.

The addition of 5µm montmorillonite provides an increase in the 24 hour compressive strength at 45°C curing temperatures. The greatest strength increase is observed for the higher montmorillonite replacements of 7% to 10% with 24 hour compressive strength increases up to 98%. Not all montmorillonite replacements lead to significant increases in the 24 hour compressive strength. Based on strength values, the montmorillonite replacements appear to have merit. One difficulty is high montmorillonite replacement increase the consistency of the resulting mixes.

Efforts focused on compressive strength testing of zeolite mixes containing a portion of montmorillonite clay and chabazite. An updated summary of the compressive strengths is provided in Table 4. The clay referred to in the Table is montmorillonite.

Exploration of the influence of montmorillonite and chabazite were concentrated at the 27.5% total replacement levels. For the 27.5% replacement levels, 5% montmorillonite or chabazite replaced a portion of the zeolite thus reducing the mixture to 22.5% zeolite and 5% montmorillonite or chabazite. At the 40% total replacement of the zeolite/clay mix, typically the total percent of clay replacement is based on the assumption that the mudhill clinoptilolite contains approximately 18% montmorillonite. The mixture is thus reduced to approximately 32.8% zeolite and 7.2% clay. If different replacement ratios were used, these are noted.

Mudhill/Chabazite

No montmorillonite replacements were made for mudhill clinoptilolite as it is assumed that the deposit already contains montmorillonite. At the 27.5% replacement levels, 5% of zeolite was replaced with chabazite. In this case, the particle size of the chabazite replacement matched the particle size the zeolite replacement. At the 5µm particle size, the 24 hour compressive strength at 45°C increased by approximately 44% or 260 psi. At the 10µm level, the compressive strength increased by 30% to value passing the 500 psi criteria. For the 44µm level, little is gained by the addition of chabazite.

Ferrierite/Montmorillonite

A portion of the ferrierite at the 5µm and 10µm particle size was replaced by 5µm montmorillonite. At the 27.5% replacement level, the 5µm ferrierite showed only a minor increase in compressive strength, but met the 500 psi criteria. The 10µm ferrierite showed a 39% increase in the compressive strength with the addition of 5µm montmorillonite, however, the 500 psi criterion was not achieved. At the 40% total replacement level, the addition of 5µm montmorillonite (7.2% replacement level) showed noticeable gains in the compressive strength with a 65% increase at the 5µm level and 98% increase at the 10µm level. Both values achieve the 500 psi criteria. The addition of the montmorillonite to the ferrierite yield slightly higher 24 hour compressive strength than the substitution of half the ferrierite by mudhill clinoptilolite. The values are similar however. At this time, the 44µm ferrierite/montmorillonite combination has not been tested.

Table 4. Compressive strength summary

Compressive Strength [psi]								
Cement H	847.0				70°C	5% Chab	5% clay	7.2% clay
		15%	27.5%	40%	27.5%	27.5%	27.5%	40.0%
Chabazite	5 µm	712	1845	*				
	10 µm	660	1519	*				
	44 µm	318	512	1337				
Mudhill	5 µm	429	594	*	1628	854		
	10 µm	329	416	1263	1211	542		
	44 µm	260	228	221	909	258		
1/2 Mudhill 1/2 Ferrierite	5 µm	414	440	820				
	10 µm	348	385	495				
	44 µm	0	267	220				
Ferrierite	5 µm	342	491	505	1898		505	835
	10 µm	269	302	297	1615		420	588
	44 µm	331	227	194	950			
NM #1	5 µm	292	285	*	1185		538	897
	10 µm	324	328	442	1164	458	466	
	44 µm	210	230	177	762		286	519
NM #2	5 µm	288	305	*	1204			
	10 µm	307	264	234	1160			
	44 µm	238	187	118	763			
Mudhill Treated	5 µm	329	635	1393				
	10 µm	344	547	1266				
	44 µm	285	227	198				
Ferrierite Treated	Out Spec	401	409	536				
	5 µm	367	446	615				
	10 µm	372	357	383				
	44 µm	408	286	215				
Mordenite	5 µm	0	0	0				
	10 µm	0	0	0				
	44 µm	0	0	0				
Used 10 micron chabazite								
Used 44 micron chabazite								
Mix ended up as 34.5% zeolite, 7.6% clay, density 1.562 g/cm ³								
30% NM1 44 & 10% Clay 5 microns								

NM#1 Clinoptilolite/Montmorillonite

Replacement of a portion of the NM#1 clinoptilolite was conducted with 5µm montmorillonite. At the 27.5% total replacement level, the compressive strength increased by 89%, 42%, and 24% at the 5µm, 10µm, and 44µm particle sizes. The most noticeable gains appear to be at the 40% total replacement. Most noticeably, the 44µm particle size passed the 500 psi criteria. For the 5µm level, the total

replacement was 34.5% zeolite and 7.6% clay. At the 44 μ m level, the total replacement was 30% zeolite and 10% clay. A 15% montmorillonite replacement at the 44 μ m level will be conducted thus spanning the range of 5% to 15%. A 5% 5 μ m chabazite replacement was conducted on the NM#1 10 μ m at the 27.5% total replacement level. The compressive strength between the 5 μ m montmorillonite and chabazite are very similar. This has relevance due to the cost of chabazite and the erionite mineral concerns associated with it.

Concern with Montmorillonite Addition

As evidenced by the data, the addition of montmorillonite clay can aid in the 24 hour compressive strength at curing temperatures of 45°C. The impact increases with increasing montmorillonite additions (up to 10% replacements which have been tested in this portion of the study). The potential difficulty is the increased thickness/viscosity of the resulting mix with increasing montmorillonite fractions. For example, 5 μ m NM1 34.5% replacement mixed with 5 μ m montmorillonite 10% replacement yielded a very thick mix which required scooping into the molds rather than pouring. The initial consistency was 40 Bd units and 33 Bd units after 20 minutes of conditioning. The mixture of 44 μ m NM1 30% replacement and 5 μ m montmorillonite 10% replacement was identified as “sticky” with an initial consistency of 15 Bd units and 12 Bd units after 20 minutes of conditioning. For the 27.5% zeolite/montmorillonite mixtures, all samples were pourable.

Stress-Strain Patterns

Figure 1 shows representative stress-strain curves for the ferrierite and NM1 montmorillonite mixtures. The higher compressive strength samples represent 5 μ m ferrierite and NM1 at the 40% replacement levels. The post peak strength reduction rate is higher than lower replacement values or the 44 μ m particle sizes. This is consistent with a material that has better developed cementitious properties (also evidence by higher compressive strength), which are most likely due to a greater degree of pozzolanic activity. The samples showing a broad peak and a slow post peak strength reduction tend to be friable in nature.

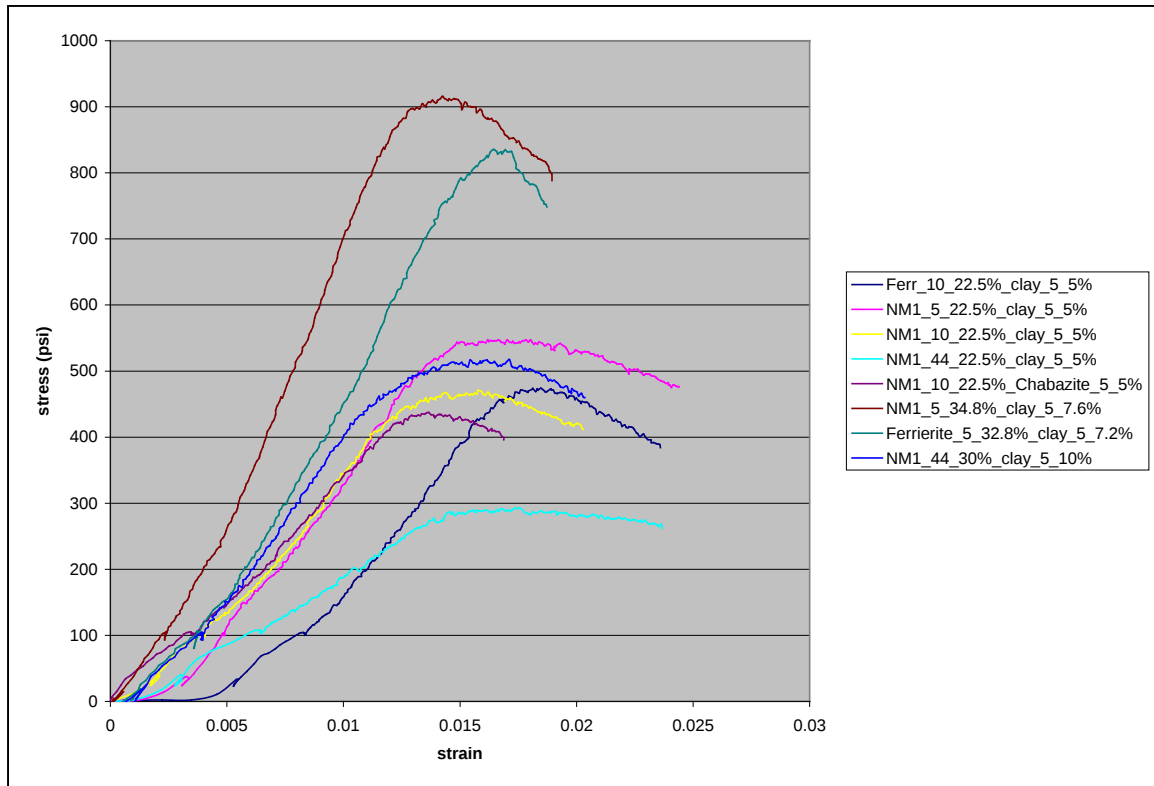


Figure 1. Stress-strain patterns for ferrierite and NM1 montmorillonite mixtures.

HPHT Ultrasonic Tests:

One trial test was run on the Chandler HPHT Ultrasonic Cement Analyzer (UCA) for a 10 μ m mudhill clinoptilolite at a 27.5% replacement level. Curing temperature was set to 70°C, with a curing pressure of approximately 3000 psi. Atmospheric curing at 70°C yielded a 24 hour compressive strength of 1211 psi. An example of the test results (screen shot) is shown in Figure 2. The figure represents approximately 48 hours of test time. The deviation in compressive strength as compared to the atmospheric test may be the result of the pressure and calibration curve deviations.

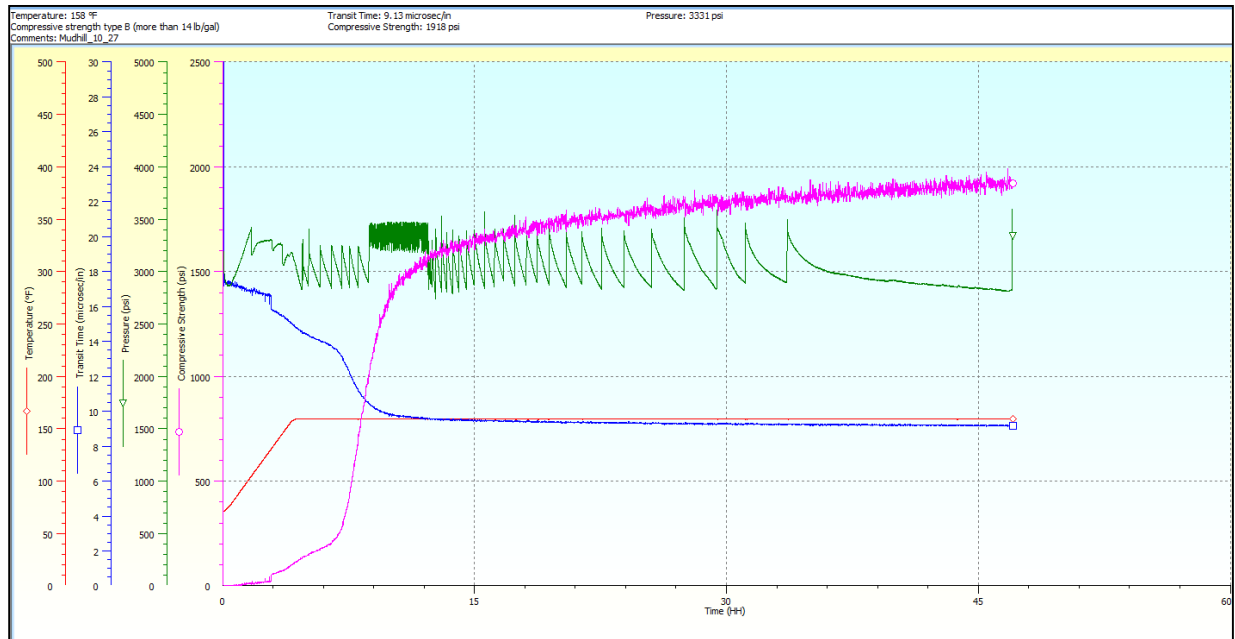


Figure 2. UCA analysis of 10µm mudhill at 27.5% replacement level at 70°C. The pink/purple curve is the compressive strength and correlates to the first y-axis (far right).

Peer Review

In preparation for Second Stage Cement Development research findings are submitted for Peer Review. The Peer Reviewer for the Project is Dr. Karen Luke. Dr. Luke's Peer Review comments during the reporting period were as follows:

July Report

"The free water tests are what I would expect and do not surprise me. My testing showed similar results with chabazite have the best free water control and the ferrierite the worst. The 10 micron data does not look too bad and the industry does have free water control additives that would readily decrease the values to zero.

I am a little concerned about the high free water samples and the compressive strengths – did those samples show any indication of settling and what about the height of the cubes were they all the same and if not were these factors taken into account when measuring the compressive strength? The results differ from what I had observed where the ferrierite give more strength than the chabazite or clinoptilolite though in the test matrix I was looking at we had significantly more additives and these could have influenced the behavior of the zeolites. The results obtained with the chabazite are certainly interesting and worth looking into in more detail. I agree completely with the U of A in looking at combinations of chabazite with other promising zeolites, my thoughts would be to replace 5% of the ferrierite with 5% chabazite the 27.55 replacement value and see the effect on both the free water and

compressive strength. That was an area I had hoped to pursue as I felt that the zeolites having different properties could be used in combinations to enhance each other's beneficial properties.

The results do indicate that the finer micron sizes are more reactive and I did obtain data at higher temperature that indicated that the finer material was more reactive in terms of the pozzolanic reaction and provided higher early strength. Clearly the finer the particle size the more surface area for dissolution and hence reaction and precipitation of cement phases with the calcium hydroxide formed from the cement reaction to produce more binder either as C-S-H or C-A-S-H. As for the chabazite I also think that the "other" components, given this is not the B-bed pure chabazite, also played a significant role in the hydration reaction accelerating the cement phase hydration. Another area that I think needs to be investigated. It will be interesting to see the results of the 10 micron samples and see if they are close to the 5 micron data."

Additional July

"The data in the attached presentation are more or less the same as given in the UAF June report with the addition of the 10 micron data and as such the comments I made previously still hold. The high compressive strengths of the chabazite samples even at 44 micron is very interesting and definitely worthy of further study. My impression is that there is definitely some form of chemical reaction going on. Interestingly in the studies I performed at the higher temperatures, 356°F, my results indicated the ferrierite to have more strength. From a research perspective it would be good to do a study to see what is happening in terms of the chemistry. I am assuming UAF did not keep any of the cement samples after testing? It would be good to do an XRD, DTA and SEM study on them to see what the differences were between the Class H, the chabazite and the ferrierite blends to see what impact there was on chemistry and microstructure.

The results clearly show differences between the zeolites in performance which is what you would tend to expect. Given the fact that the zeolites are not pure samples I am also curious as to the effects of the other components present.

It would be interesting at some point to see the effect of mixing different zeolites to see if the properties of the blend can be enhanced with regards to the performance criteria. Though that would be a big undertaking."

August Report

"As Dr Khataniar pointed out that with the 70°C data it is more difficult to make an elimination choice which was my concern from the start. The chemistry does change with temperature and even more so above 110°C and with addition of silica flour, necessary for eliminating

strength retrogression. The changes in chemistry and the resulting microstructure do have a significant impact on physical properties such as compressive strength, porosity and permeability – factors critical for geothermal cements. However, the current testing does give a good indication on the zeolite/cement interactions and does provide data that in my opinion, gives a good indication for elimination.

My thoughts would be to use the Mudhill clinoptilolite (5 or 10 μ m) and the ferrierite (5 or 10 μ m) for Stage 2 and eliminate both the NM#1 and NM#2 clinoptilolite on the basis that:

- Both NM#1 and NM#2 clinoptilolite show very similar performance at 45 and 70°C and,
- Performance is not as good as the Mudhill clinoptilolite or ferrierite at least at the 5-10 μ m particle size at 45°C (note compressive strength graphics for the 45°C ferrierite are actually those of the NM#1 clinoptilolite). On basis of table the 27.5% ferrierite, 5 μ m, give 491 psi).
- The compressive strength at 70°C indicates that the zeolites are less reactive with the cement and/or have hydration products with different morphology (Do you have 70°C compressive strength data for the Class H?)

It would be interesting to know if replacement of either the NM#1 or NM#2 clinoptilolite with 10 to 20% montmorillonite clay to see if the performance then matched the mudhill clinoptilolite properties, in particular the compressive strength at 70°C. If this were the case then it would further justify using only the Mudhill clinoptilolite for Stage 2 and if the results for that looked good to then spot check some of the data with the NM#1 or NM#2 clinoptilolite with 10 to 20% montmorillonite replacement. My thoughts here are that if the NM#1 and NM#2 clinoptilolite with 10 to 20% replacement with montmorillonite behaves the same as the Mudhill clinoptilolite then theoretically having similar chemistry they should give similar hydration products and morphology for HTHP testing and ultimately similar properties.

The ferrierite does give me some concern over the free water content as this can adversely affect the compressive strength data and permeability data etc. Typically in the industry when designing a slurry for particular well conditions that shows free water we would add an additive to bind that water to prevent any possibility of free water occurring downhole. As this would compromise the slurry designs in the present study my thoughts to minimize the free water would be to replace about 5% of the ferrierite with 5 μ m chabazite. This is more critical for the HTHP testing as you will need to add a retarder to allow the cement to react more closely to that of a field slurry otherwise you can compromise on the data obtained. Retarders in general will disperse the slurry and reduce the viscosity and may exacerbate the free water content. The reduction in viscosity may also be of benefit for some of the more viscous zeolite slurries. Point to note is that above approximately 30Bc the slurry can no longer be pumped downhole.

The Mudhill/ferrierite combination looked interesting and I think this is also something worth pursuing, in that it benefits both zeolites – it however does not seem to give improved overall performance so indicates no real synergistic effect. In terms of the HTHP Stage 2 study I would

probably only consider looking at the combination if it looked like would give an improvement over the individual zeolites.

A final note is that the minimum strength criteria quoted is not universal and depends on the energy board of the state and/or country where the well is to be cemented. The 500 psi in 24 hours is probably reasonable though for commercialization of geothermal cements other factors such as permeability and resistance to aggressive ground waters would also have to be considered. “

FY2013 Q1

Element 1 – Zeolite Sample Acquisition

Mordenite Bulk Sample

The zeolite Ferrierite was collected from a deposit located near Lovelock, Nevada. At this deposit there is an upper horizon of the zeolite Mordenite. Ferrierite has shown interesting properties in the geothermal cement trial screening blends. The Project Team decided to conduct basic screening tests to determine if Mordenite had any potential given the association with Ferrierite. Accordingly, Trabits Group met with the partners of Nevada Specialty Minerals (NVSM). NVSM holds the mining lease to the Ferrierite/Mordenite deposit located near Lovelock, Nevada. The topics discussed were the permit status of the mine and possible processing methods. Geoff Trabits and George Trabits traveled to the mine site and collected an approximate 500 pound Mordenite sample. The sample was collected from a dozer cut in the center area of the zeolite deposit. Trabits Group used a report prepared by Keith Papke in 1974 for the Nevada Geological Survey to locate the highest concentration of Mordenite.



Mordenite Dozer Cut

Element 4 – Initial Screening of Cement Formulations

Ultrasonic cement tests at 70°C and 3000 psi indicate the initial reactivity for all geo-materials occurs at 3 to 4 hours, post mixing. The reactivity rates are highest for chabazite, mudhill clinoptilolite, and montmorillonite clay. The 24 hour compressive strengths are comparable for all materials, except NM clinoptilolite which exhibit lower compressive strength. The addition of 60 µm diatomaceous earth adds a potential source of amorphous silica and offers a slight improvement in the 24 hour compressive strengths when combined with zeolites at the 40% replacement level. As a single addition at the 27.5% replacement, diatomaceous earth yields compressive strengths that are comparable to 5µm zeolites. Results from combining Mudhill clinoptilolite, montmorillonite clay, and diatomaceous at replacement levels between 40% and 60% suggest that low densities cements in the range of 11.5 to 12.0 ppg are achievable based on compressive strength data. The data is based on no additives. Montmorillonite provides short term strength gains similar to chabazite with a production cost of \$70 to \$90 per ton as compared to \$2000 per ton for chabazite.

Results and Discussion

A summary of the 24 hour compressive strength, density, and permeability data is provided in the appendix. Data is not available for all samples. As testing progressed, the testing was tuned towards the zeolites and replacements levels exhibiting the most favorable results.

UCA tests

Ultrasonic Cement tests were conducted using a Chandler UCA 4265 HT to provide real time data on the development of compressive strengths for several zeolite mixes. Tests were run at 70°C for direct comparison to 24 hour compressive strength data from the conventional compressive strength tests. Tests were performed at the 27.5% replacement level using 5 µm and 10µm zeolites. A pressure of approximately 3000 psi was applied during the test. The 24 hour compressive strength from UCA tests are provided in Table 2. Real time data is provided in Figure 1. Chabazite is not considered to be a viable zeolite due to its production cost exceeding \$2000 per ton. However, in initial screening chabazite yielded high quality results, especially the 24 hour compressive strength at 45°C. From Figure 1, it can be observed that at time over 24 hours, the results suggest that the compressive strength is lower than ferrierite, mudhill, or montmorillonite. In terms of 24 hour compressive strength, the zeolites yield similar results. NM#1 clinoptilolite compressive strength is noticeably less. All samples exceed 500 psi at 24 hours. As compared to conventional compressive strength (hydraulic), the UCA estimates are comparable or slightly higher. This is to be expected.

The UCA data indicates that the initial reaction begins at approximately 3 to 4 hours following mixing. A period of 2 to 3 hours of low reactivity occurs followed by a period of high reactivity in which the major portion of strength is developed. Chabazite, mudhill clinpotilolite, and montmorillonite show the quickest reaction and development of strength. Ferrierite develops strength at a slower rate, however 24 hour strengths are comparable. Longer term tests suggest that montmorillonite shows additional strength gains over the other zeolites.

Table 1. UCA 24 hour compressive strength.

Sample	24 hour compressive strength (psi)
Chabazite_10µm_27.5%	1633
Ferrierite_10µm_27.5%	1704
Mudhill_10µm_27.5%	1752
NM1_10µm_27.5%	1337
Ferrierite_5µm_27.5%	1691
Mudhill_5µm_27.5%	1664
Montmorillonite_5µm_27.5%	1691

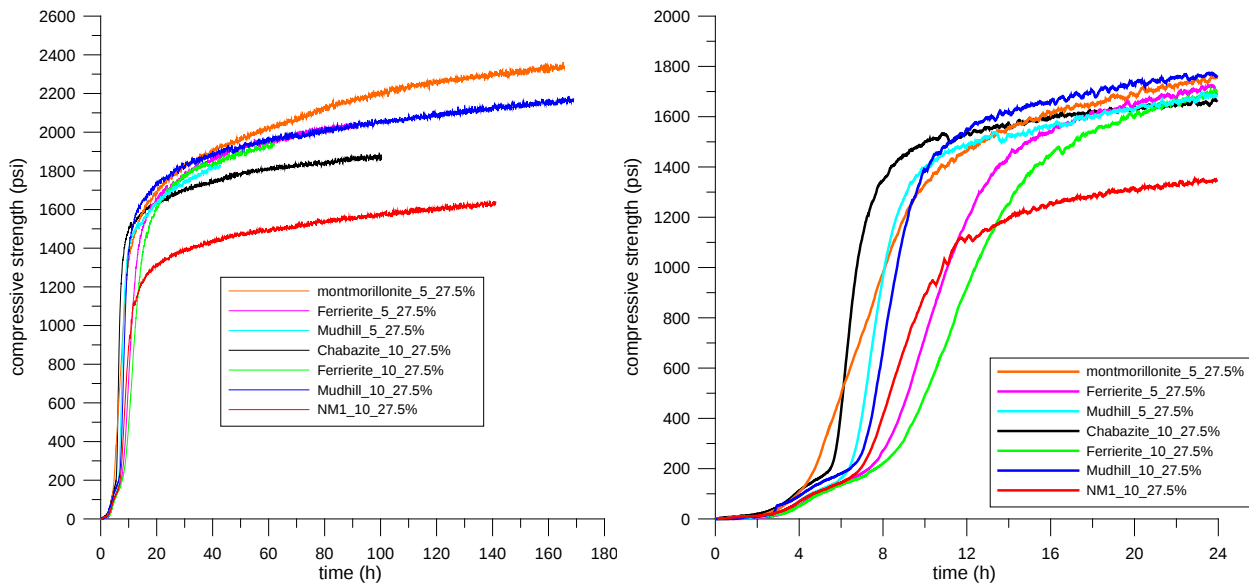


Figure 1. Real time compressive strength test at 27.5% replacement levels. Test conditions: 70°C, pressure ~3000 psi.

Diatomaceous Earth

Diatomaceous earth (DE) is sedimentary deposit in lacustrine or marine sediments and represents the accumulation of dead diatoms. The deposit is primarily amorphous silica with small amounts of aluminum. It is thought the DE may offer an advantageous source of silica for high temperature mitigation of strength retrogression. This will be tested. The DE tested has a particle size that is 80% less than 60 μm . All compressive strength results are atmospheric pressure at curing temperatures of 45°C. As an individual replacement at the 27.5% level, the 24 compressive strength of DE exceeded all except chabazite and montmorillonite. This is interesting in that the 60 μm DE outperformed most 5 μm zeolites.

Partial replacements of DE were added to 5 μm mudhill, NM#1, NM#2, and ferrierite at the 27.5% and 40% replacement levels. With a 5% DE substitution at the 27.5% level, a small increase in strength was observed for NM clinoptilolite and a small decrease for mudhill clinoptilolite and ferrierite. At the 40% level with a 7.2% DE substitution, small gains were observed for tested zeolites. The largest gain was for the NM#2 replacements.

The mudhill/DE 40% mix yields high compressive strengths. The mix is extremely viscous with an initial consistency of 85-90 Bc and 20 minute consistency of 58 Bc. The mix needs to be less than 30 Bc for downhole pumping. For comparison, the zeolite/DE 40% mixes yielded initial and 20 minute consistencies of 14 Bc and 12 Bc for ferrierite, 33 Bc and 25 Bc for NM#1, and 24 Bc and 20 Bc for NM#2 respectively. In response to the consistency for the mudhill/DE 40% mix, the consistency and density was lowered by the addition of water. The results are shown in Table 2. Nearly linear relationships are observed for decreasing density and decreasing compressive strength. Little change in the permeability

was seen despite reduction in density. The consistency measurements indicate that small additions of water significantly influence fluidity of the mix. Generally, consistencies below 10-15 Bc are quite fluid. Free water does not appear to be an issue at densities from 12.5-13.5 ppg as evidenced from compressive strength molds.

Table 2. Influence of changing density for mudhill/DE mix at the 40% replacement level. (1 ppg = 0.12 g/cm³)

Sample	C _{init} (Bc)	C _{20 min} (Bc)	ρ (g/cm ³)	q _u (psi)	K (mD)
Mudhill_5μm_32.8%_DE_7.2%_13.5ppg	85-90	58	1.64	1496	3.02
Mudhill_5μm_32.8%_DE_7.2%_13.0ppg	24	19	1.55	1008	3.85
Mudhill_5μm_32.8%_DE_7.2%_12.5ppg	9	7	1.45	532	2.55

C_{init} = initial consistency; C_{20 min} = 20 min consistency, ρ = density, q_u = 24 hour compressive strength,

K = permeability (relative measure using TinyPerm probe permeameter)

Lightweight Cement

The combination of zeolites may provide a means to produce low density cements. Mudhill clinoptilolite and montmorillonite are quite viscous at certain replacement levels. As discussed in the diatomaceous earth section, the mudhill mix at 40% levels far surpass the 30 Bc level required for down hole pumpability. Montmorillonite at the 27.5% replacement had an initial and 20 minute consistency of 55 Bc and 38 Bc respectively for 5μm particle size. For 44 μm montmorillonite, the consistencies fell to 20 Bc and 12 Bc for initial and 20 minute consistencies. In testing, there is a rough relationship between the mix consistency and compressive strength. More viscous mixes seem to yield higher compressive strengths. The viability of a lightweight cement was briefly explored by mixing mudhill clinoptilolite and montmorillonite for 5 μm particle sizes. The results are shown in Table 3. At these densities, free water was not an issue as evidenced from molds. The 12.0 ppg mix (50% total replacement) yielded satisfactory results. The 60% total replacements did not pass the compressive strength criteria. Results suggest that cements in the density range from 11.5-12.0 ppg have potential. Highly fluid mixes at the low density and high replacement levels do not yield encouraging results.

Table 3. Influence of changing density for mudhill/montmorillonite mix at total replacement levels of 50% to 60%. (1 ppg = 0.12 g/cm³)

Sample	C _{init} (Bc)	C _{20 min} (Bc)	ρ (g/cm ³)	q _u (psi)	K (mD)
Mudhill_5μm_25%_MM_5μm_25%_12.0ppg*	35	26	1.46	874	2.51
Mudhill_5μm_30%_MM_5μm_30%_11.5ppg	27	20	1.40	394	3.57
Mudhill_5μm_30%_MM_5μm_30%_11.0ppg	8	7	1.33	267	2.56

C_{init} = initial consistency; C_{init} = 20 min consistency, ρ = density, q_u = 24 hour compressive strength,

K = permeability (relative measure using TinyPerm)

* Did not mix at 12.5 ppg, too viscous.

Appendices show a comprehensive summary of results to date. The blank cells in the Tables represent data not yet measured (Mordenite, for example), but are planned to be tested in near future.

Appendix: 24 hour compressive strength, density, and permeability measurements.

24 hr Compressive Strength [psi]					45°C									
Cement H	847.0	45°C			70°C	5%_Chabazite	5%_MM_5µm	5%_MM_44µm	7.2%_MM_5µm	7.2%_MM_44µm	10%_MM_5µm	15%_MM_5µm	5%_DE	7.2%_DE
		15%	27.5%	40%	27.5%	27.5%	27.5%	27.5%	40.0%	40.0%	40.0%	45.0%	27.5%	40.0%
Chabazite	5 µm	712	1845	*										
	10 µm	660	1519	*										
	44 µm	318	512	1337										
Mudhill	5 µm	429	594	*	1628	854*							538	1496
	10 µm	338	533	1263	1316	542*								
	44 µm	260	228	221	909	258*								
1/2 Mudhill 1/2 Ferrierite	5 µm	414	440	820										
	10 µm	348	385	495										
	44 µm	307	267	220										
Ferrierite	5 µm	342	491	505	1898	545	505		835				326	576
	10 µm	269	302	297	1615		420		588					
	44 µm	331	227	194	950									
NM #1	5 µm	292	285	614	1185	561	538	476	**897				408	739
	10 µm	324	328	442	1164	458	466		453					
	44 µm	210	230	177	762		286		351		519	739		
NM #2	5 µm	288	305	490	1204		446	433		906			373	715
	10 µm	307	264	234	1160			318		526				
	44 µm	238	187	118	763			292		279				
Mudhill Treated	5 µm	329	635	1393										
	10 µm	344	547	1266										
	44 µm	285	227	198										
Ferrierite Treated	Out Spec	401	409	536										
	5 µm	367	446	615										
	10 µm	372	357	383										
	44 µm	408	286	215										
Mordenite	5 µm													
	10 µm													
	44 µm													
Montmorillonite (MM)	5 µm		1332											
	44 µm		896											
Diatamaceous Earth (DE)														
	60 µm		624											

* For 5% chabazite replacement, the particle size of the chabazite matches the particle size of zeolite

** Actual mix: 34.5% zeolite, 7.6% clay, density 1.562 g/cm³

Mudhill with DE at 40%, high compressive strength but very thick with 20 min consistency = 58-59 Bc.

Denisty avg. of comp. samp. [g/cc]					45°C									
Cement H	0.0	45°C			70°C	5%_Chabazite	5%_MM_5µm	5%_MM_44µm	7.2%_MM_5µm	7.2%_MM_44µm	10%_MM_5µm	15%_MM_5µm	5%_DE	7.2%_DE
		15%	27.5%	40%	27.5%	27.5%	27.5%	27.5%	40.0%	40.0%	40.0%	45.0%	27.5%	40.0%
Chabazite	5 µm													
	10 µm													
	44 µm			1.64										
Mudhill	5 µm				1.54	1.56							1.54	1.64
	10 µm	1.57	1.53		1.53	1.55								
	44 µm				1.49	1.55								
1/2 Mudhill 1/2 Ferrierite	5 µm	1.64	1.57	1.59										
	10 µm	1.61	1.59	1.59										
	44 µm	1.65	1.58	1.59										
Ferrierite	5 µm				1.60	1.56	1.61		1.61				1.57	1.57
	10 µm				1.58		1.61		1.60					
	44 µm				1.56									
NM #1	5 µm			1.47	1.49	1.49	1.59	1.59	1.56				1.51	1.52
	10 µm			1.50	1.50	1.55	1.61		1.59					
	44 µm				1.51		1.60		1.58		1.60	1.60		
NM #2	5 µm			1.48	1.48		1.61	1.62		1.62			1.51	1.54
	10 µm				1.50			1.62		1.62				
	44 µm				1.49			1.62		1.61				
Mudhill Treated	5 µm	1.57	1.55	1.60										
	10 µm	1.57	1.55	1.58										
	44 µm	1.60	1.53	1.48										
Ferrierite Treated	Out Spec	1.65	1.63	1.62										
	5 µm	1.65	1.64	1.63										
	10 µm	1.67	1.64	1.64										
	44 µm	1.72	1.65	1.63										
Mordenite	5 µm													
	10 µm													
	44 µm													
Montmorillonite (MM)	5 µm		1.64											
	44 µm		1.64											
Diatamaceous Earth (DE)	60 µm		1.64											

Permeability (using Tiny Perm) [mD]														
before crushing					45°C									
Cement H	0.0	45°C			70°C	5%_Chabazite	5%_MM_5µm	5%_MM_44µm	7.2%_MM_5µm	7.2%_MM_44µm	10%_MM_5µm	15%_MM_5µm	5%_DE	7.2%_DE
		15%	27.5%	40%	27.5%	27.5%	27.5%	27.5%	40.0%	40.0%	40.0%	45.0%	27.5%	40.0%
Chabazite	5 µm													
	10 µm													
	44 µm			0.00										
Mudhill	5 µm				11.26	n/a							3.30	3.02
	10 µm				3.43	2.64								
	44 µm				12.58	4.15								
1/2 Mudhill 1/2 Ferrierite	5 µm	2.75	2.16	2.66										
	10 µm	4.50	3.20	17.27										
	44 µm	4.62	4.48	6.16										
Ferrierite	5 µm				2.63	2.68	3.17		2.22				13.12	2.58
	10 µm				3.93		2.59		2.76					
	44 µm				12.50									
NM #1	5 µm			6.57	15.33	2.65	2.55	4.35	2.76				2.68	2.89
	10 µm				2.40	2.78	2.70		3.11					
	44 µm				7.55	5.66	3.40				3.11	6.26		
NM #2	5 µm			2.12	5.79		5.65	3.88		2.26			3.97	2.31
	10 µm				7.90			4.30		4.35				
	44 µm				10.20			5.19		3.76				
Mudhill Treated	5 µm													
	10 µm	3.70	4.57											
	44 µm													
Ferrierite Treated	Out Spec	3.20	2.45	2.72										
	5 µm				2.63									
	10 µm				3.93									
Mordenite	44 µm				12.50									
	5 µm													
	10 µm													
Montmorillonite (MM)	44 µm													
	5 µm		3.03											
Diatamaceous Earth (DE)	44 µm		7.90											
	60 µm		8.08											

FY2013 Q2

Element 1 - Second Stage Cement Development

Consistency and Retarders

The base zeolite mixes require the addition of a retarder for use under high temperature conditions. Using 10 µm ferrierite, various retarders were tested at 300°F and 8.5 ksi. The results are summarized in

Table 1 and Figure 1. Initially, a retarder from Baker Hughes called R8 was tested from 0.8% BWOC to 1.6% BWOC. Only the 1.3% BWOC data is provided. The R8 retarder does not achieve the target working time of 4 to 5 hours. It has a strong dispersant effect resulting in low consistencies. The use of the retarder generally results in segregation of the slurry resulting in inconsistent properties through the vertical profile. The results indicate that the R8 retarder is not suitable without the addition of chemical additives to address the segregation issue. A basic principle of the study is to limit the amount of chemical additives to broaden the applicability of the cement.

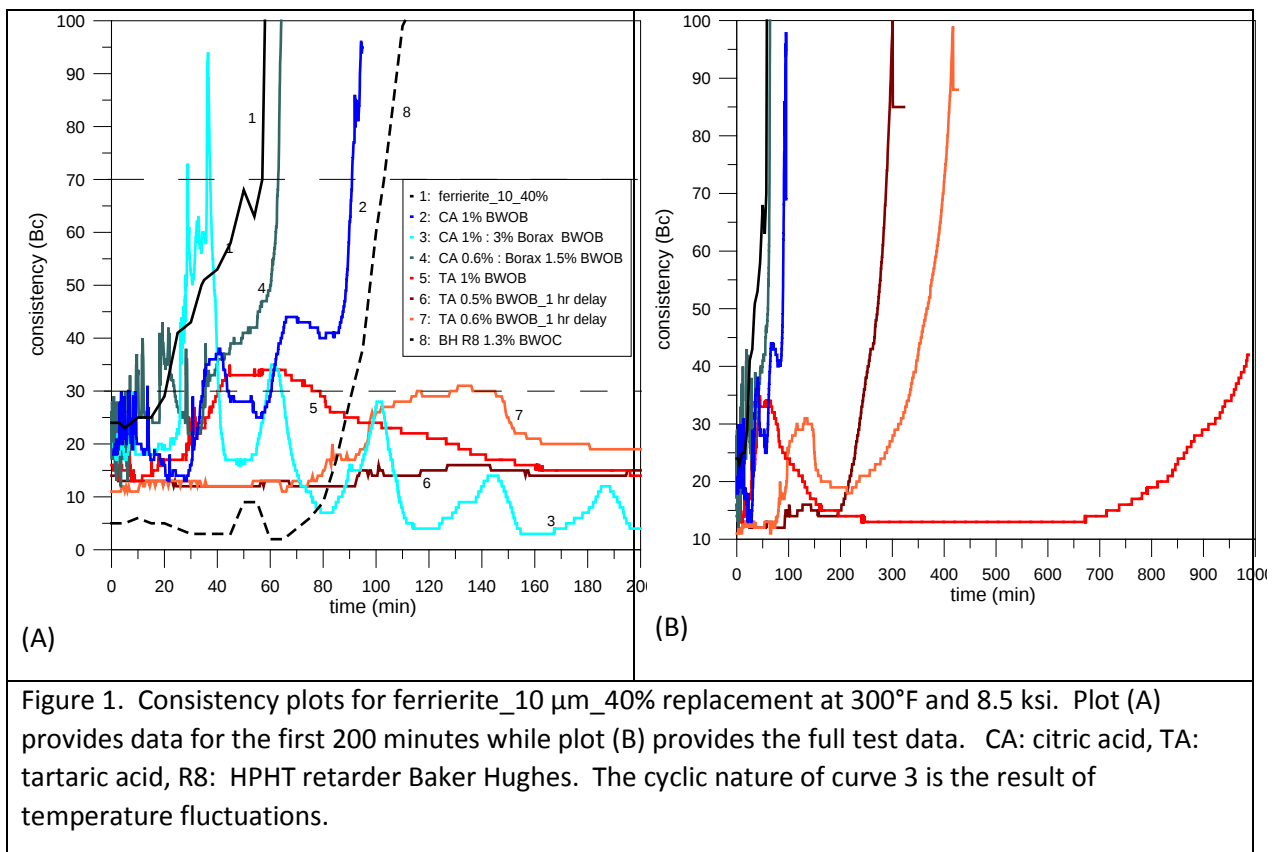
In response to the R8 results, it was recommended to try a generic form of a HPHT retarder containing a hydroxycarboxylic acid with or without borax. Two hydroxycarboxylic acids were tested including citric acid and tartaric acid. Tartaric acid generally provided better results than the citric acid with a lower percentage addition required. A common occurrence with the hydroxycarboxylic acid is the emergence of a peak in the consistency profile at a period generally close to 60 minutes. This peak can be quite intense, surpassing 70 Bc. In most cases there is a post peak reduction in the consistency to the base consistency of the mix, which can be maintained for a considerable length of time. The first 60 minutes also tend to show erratic consistencies. This was especially noticeable for the citric acid. In response, samples of tartaric acid of 0.5% and 0.6% BWOB (by weight of dry blend) were preconditioned for 60 minutes at 80°F and 0.5 ksi before initiation of the temperature and pressure ramping schedule. With the 0.5% addition, no anomalous peak occurred. A peak did develop for the 0.6% addition, but did not exceed 30 Bc. It is recommended that the slurries with hydroxycarboxylic acid be preconditioned at a low temperature for a user defined period, but 2 hours would be a reasonable recommendation.

Tartaric acid appears to be the best retarder at this point for 300°F. At 40% zeolite replacement, additions of tartaric acid of 0.6% BWOC appears close to ideal. As the amount of zeolite replacements decrease, so should the amount of tartaric acid. A 0.5% BWOC addition of tartaric acid to a 27.5% replacement yielded thickening times on the scale of 11 hours.

The hydroxycarboxylic acids do not appear to have the same impact on the base consistencies and thus free water as the R8 retarder. They appear to retain the base consistencies of the non retarded mixes. As a consequence, segregation issues of the slurry mixes was not a major issue and thus do not require the addition of mitigative chemical additives. This is concluded to be an important property of the hydroxycarboxylic acids as potential retarder.

Table 1. Summary of HPHT consistency data for 10 μ m ferrierite with the addition of various retarders.

Sample	retarder	Time (min)	
		30 Bc	70 Bc
Ferrierite_10 μ m_40%	base, no retarder	21	57
	Baker Hughes R8 1.3% BWOC	91	104
	citric acid 1% BWOB	61	91
	citric acid 1%: 3% Borax BWOB	peak 36 min, post peak drop	>22 hrs
	citric acid 0.6% : 1.5% Borax BWOB	36	63
	tartaric acid 0.5% BWOB	177	228
	tartaric acid 0.6% BWOB	256	338
	tartaric acid 1.0% BWOB	peak (40-60 min), drop then 910 min	>16.5 hrs.
Ferrierite_10 μ m_27.5%	base, no retarder	57	63
	tartaric acid 0.5% BWOB	619	662

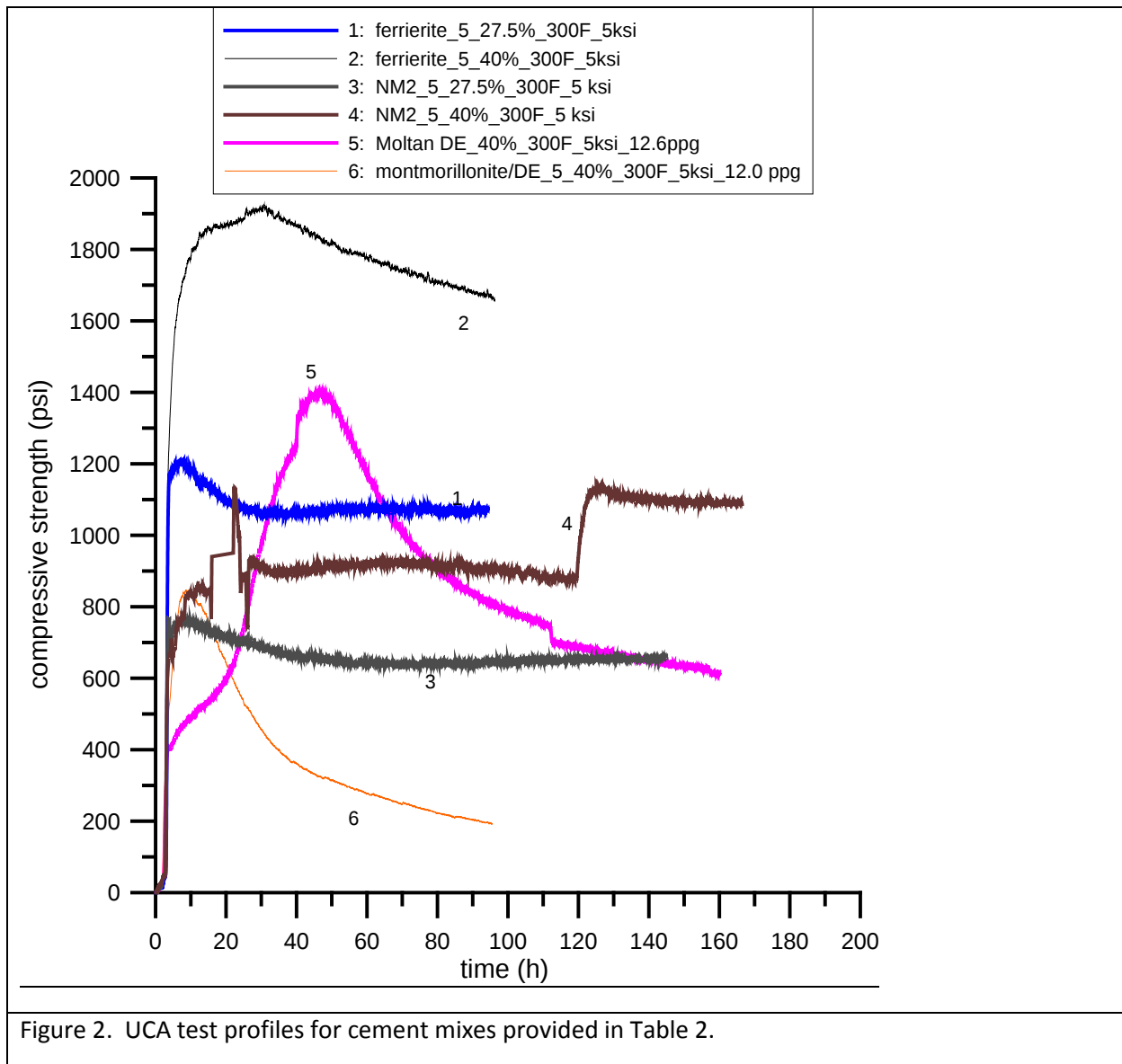


UCA and Compressive Strength

A series of tests were run on several of the base samples tested at 300°F in the HPHT UCA. Table 2 provides a comparison of compressive strength and elastic properties based on UCA outputs and actual crushing data. It can be seen that in all cases the actual compressive strengths exceed those estimated by the UCA's less than 14.0 ppg algorithm. The crushing compressive strength is based on a 7 day cure time. The basic compressive strengths trends hold true for ferrierite and NM2 clinoptilolite with ferrierite showing increased compressive strengths over NM2 clinoptilolite. The Moltan DE data shows considerable variation. UCA data predicts (Figure 2) a strongly decreasing strength profile with time. From Table 2, it can be seen that the crushing compressive strength is close to 4 times the predicted UCA value at the termination of the test. The montmorillonite/DE UCA trend shows a blend with very little compressive strength by the termination of the test. In this situation, the crushing compressive strength confirms the UCA observation, with the resulting sample exhibiting a poorly bonded soft matrix. The replacement of 5% ferrierite by montmorillonite/DE for the 27.5% ferrierite sample shows improved compressive strength. The ferrierite samples show increased strength at the expense of decreasing ductility.

Table 2. Summary compressive strength comparison from UCA and physical crushing.

	ferrierite_5_27.5%	ferrierite_5_40%	NM2_5_27.5%	NM2_5_40%	Moltan DE_40%_12.6 ppg	montmorillonite/DE_5_40%_12.0 ppg	ferrierite_5_22.5%_chabazite_5_5%	ferrierite_5_22.5%_montmorillonite/DE_5_5%
UCA (compressive strength based on ultrasonic methods, less than 14.0 ppg algorithm)								
q _w , peak (psi)	1220	1920	760	1400	1400	838	--	--
q _u at termination of test (psi)	1070	1670	660	870	619	191	--	--
Compressive strength (molds): direct measurement at 7 days cure								
q _w , peak (psi)	1997	3181	1605	1447	2489	405	2082	2813
E (ksi)	949	1500	850	1000	593	147	786	826
v	0.35	n/a	0.65?	0.38	0.26	0.70?	0.45	0.21



Silica Additions

A series of tests were conducted looking at the influence of various forms of silica additions to a base ferrierite cement blend. The tests were run at 400°F for 7 days. Longer tests periods are desirable, but for sake of efficiency, the shorter test period was adopted. Silica additions were made by weight of cement. The base blend is characterized by 40% replacements. For the addition of silica flour (SF) only, 5 μ m ferrierite was used resulting in a base mix of ferrierite_5 μ m_40%. The results from the addition of silica flour are shown in Table 1. When Moltan diatomaceous earth (MDE) was added, a portion of the 5 μ m ferrierite was replaced by 44 μ m ferrierite resulting in a base mix of ferrierite_5 μ m_30%_44 μ m_10%. The MDE has a high water demand, thus the insertion of 44 μ m

ferrierite. Combinations of SF and MDE additions are summarized on Table 2. A series of real time compressive strength trends from UCA analysis are provided in Figure 1.

From Table 1, the addition of silica flour results in increasing compressive strengths up to 40% BWOC. From 40%BWOC to 60%BWOC, compressive strengths are similar. Literature suggests a silica flour addition of 40%BWOC to aid in strength retrogression. The addition of a tartaric acid retarder appears to reduce the compressive strength.

Moltan diatomaceous earth (MDE) was explored as a potential source of silica. The same basic amount of silica BWOC was added, however, a portion of the SF was replaced by MDE. Based on a 7 day cure, it is clear that the addition of MDE increases the compressive strength and modulus of elasticity. The addition of SF reduces the compressive strength when added to MDE, this is likely due to the increased water content and lower viscosity resulting from the higher specific gravity of SF and the constant density restraint of the test design. UCA data for the SF/MDE additions in Figure 2 (profiles 3 and 4) provide slightly contrasting data. Profile 4 indicates early pozzolanic strength from the MDE, however the strength drops to a value consistent with the base blend/SF40%BWOC mix. The more pronounced drop could be associated with the influence of tartaric acid or the increased water content as compared to profile 3. Profile 3 shows a steadily decreasing strength profile. It is clear than the addition of silica improves the 7 day compressive strength of the base ferrierite blend. The addition of SF 40%BWOC appears to stabilize the compressive strength profiles by 7 days. The addition of MDE adds additional strength at 7 days. The long term affects of MDE additions are not known at this time. Portions of each mix have been preserved for future XRD analysis of hydration phases.

For recent UCA tests, data was recorded during the cooling off period to monitor changes during this stage. In each case, the UCA compressive strength increases upon cooling, based on the mfg. less than 14.0 ppg algorithm. In addition, for profiles 2, 3, and 4, destructive tests were conducted on the samples upon removal from the UCA. In each case the destructive compressive strength is 1000 psi higher than the "cooled" UCA output. Even if a 20% reduction is applied to the results due to 1:1 diameter/height ratio of the cores, the destructive compressive strength is significantly higher than UCA outputs.

Table 1: Varies proportions of silica flour (SF) were added to the base blend and cured at 400°F for 7 days. Base blend, ferrierite_5μm_40%.

Trial Group	density (ppg)	% BWOC				q _u (psi)	E (ksi)
		SF	MDE	water	TA		
1	13.5	60	0	1.46	0	1845	581
2	13.5	40	0	1.33	0.5%	1638	641
3	13.5	40	0	1.33	0	1834	206
4	13.5	20	0	1.21	0	1523	701
5	13.5	0	0	1.08	0	1340	601

Table 2: Various combinations of silica flour (SF) and Moltan diatomaceous earth (MDE) were added to the base blend and cured at 400°F for 7 days. Base blend, ferrierite_5μm_30%_44μm_10%.

Trial Group	density (ppg)	%BWOC				q _u (psi)	E (ksi)
		SF	MDE	water	TA		
1	13.0	20	40	1.40	0.8%	1841	623
2	13.5	20	40	1.64	0.8%	2545	802
3	13.5	0	40	1.27	0.8%	3297	1112
4	13.5	20	20	1.30	0.8%	2499	889
5	13.5	0	20	1.17	0.8%	1976	784

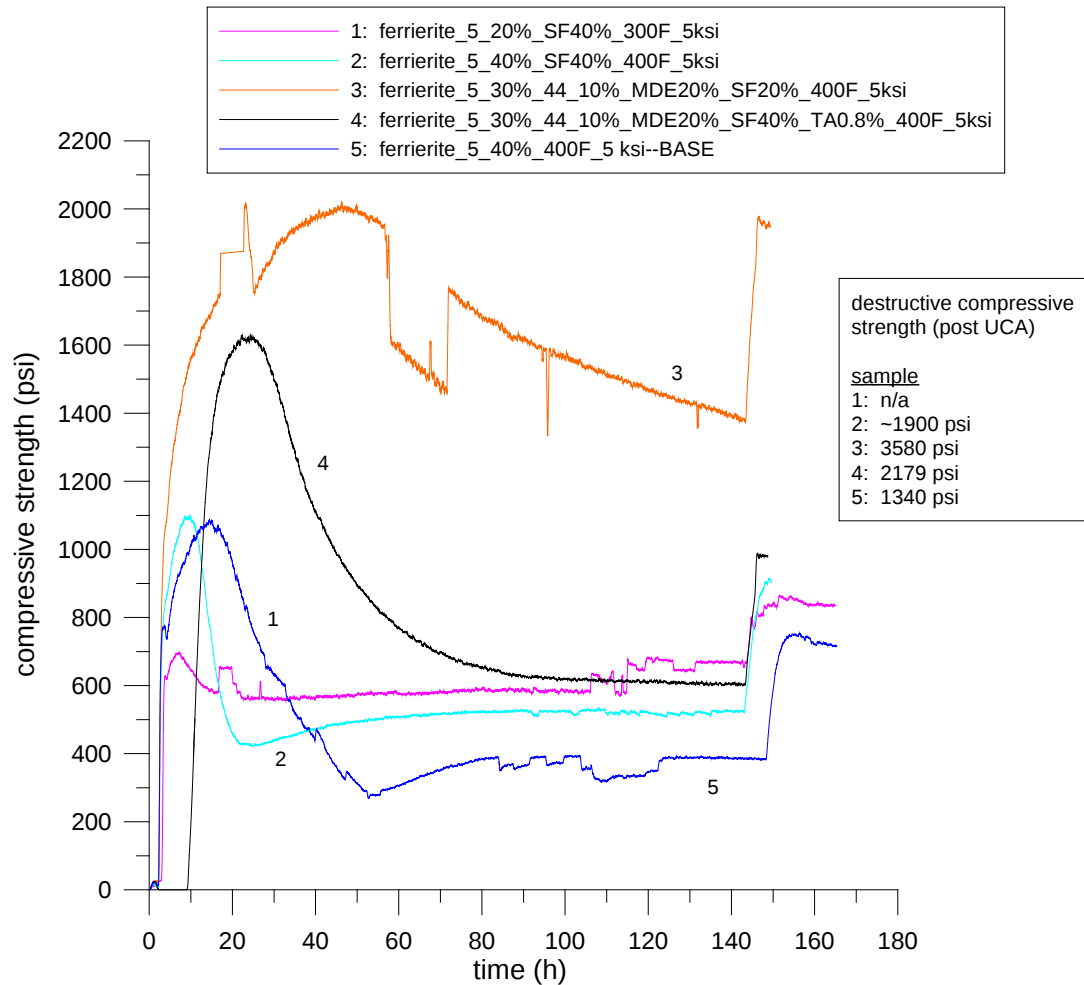


Figure 1. UCA test profiles for various forms of silica additions BWOC to a base ferrierite mix using 40% zeolite replacements. Note: profile 1 is for 300°F, other profiles are for 400°F.

Temperature Impacts on Base Ferrierite Blend

The UCA compressive strength profiles for the base blend consisting of ferrierite_5 μ m_40% are shown in Figure 2 for temperature of 300°F, 400°F, 572°F (i.e. 150°C to 300°C). The UCA results suggest dramatically reduced strengths with increasing temperatures. The 572°F profiles suggest zero compressive strength, which is not realistic based on visual inspection of the sample. Destructive testing on cube molds provide average compressive strengths of 3181 psi at 300°F and 1340 psi at 400°F. This data supports the weakening trend with temperature, suggesting the high temperature hydration phases are not characterized by good strength characteristics.

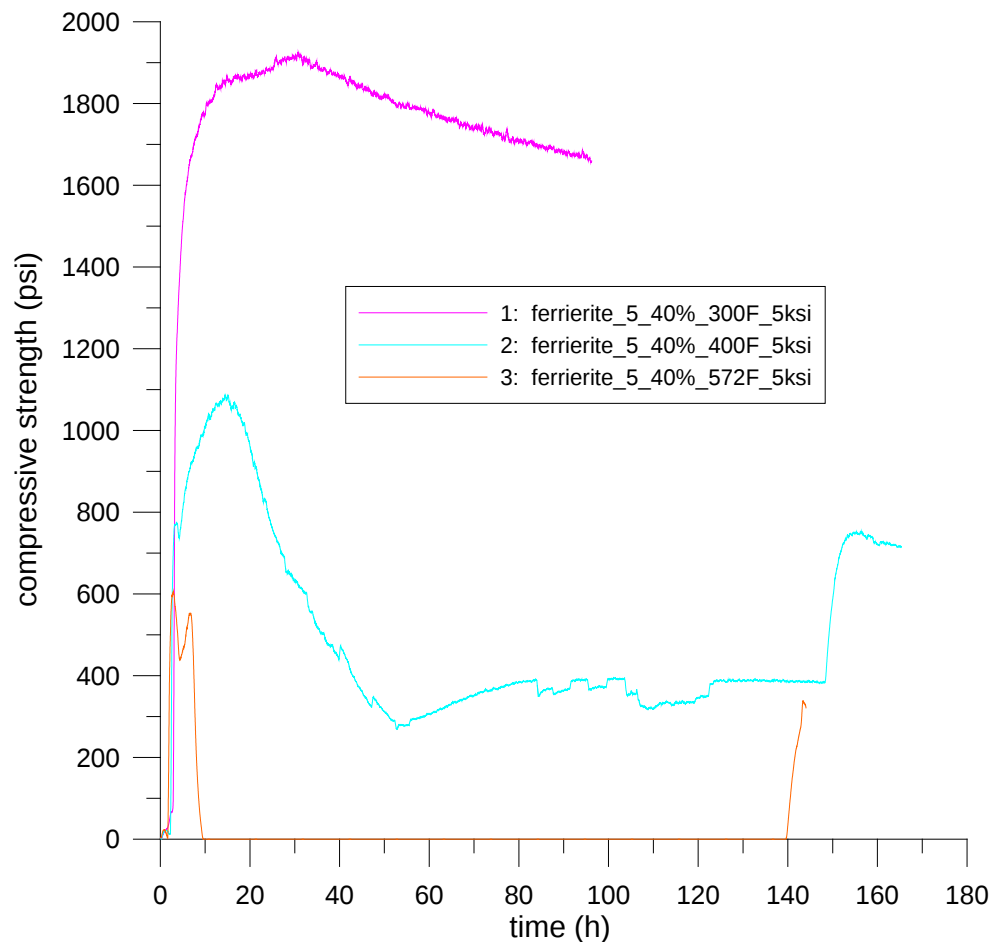


Figure 2. The impact of curing temperature on the compressive strength of the base ferrierite blend consisting of ferrierite_5 μ m_40%.

Silica for Strength Retrogression

The addition of silica flour to cement to reduce strength retrogression at higher well temperatures is a standard industry practice. Unfortunately the added silica is rapidly affected by carbonation in geothermal well environments resulting in failure of the cement. During the reporting period UAF conducted additional literature searches and basically “rediscovered” a 1979 paper that was presented at an SPE International Symposium on Oilfield and Geothermal Chemistry. The paper titled Effect of Silica Particle Size on Degradation of Silica Stabilized Portland Cement was funded under a Department of Energy contract coordinated by Brookhaven National Laboratories. The basic finding of the paper was:

“Portland cements stabilized with 35-40 percent silica will deteriorate when contacted by dense brines at temperatures above and including 232°C (450°F) if the silica is coarser than 325 mesh, but will not if the silica is finer than 325 mesh.”

Given that the effect of carbonation is a primary concern UAF and Trabits Group begin looking at the particle size of silica flour in common use. A sieve analysis was conducted on silica flour supplied to the Project by Baker Hughes. The Baker Hughes silica flour had a primary particle size around 100 mesh. The question was asked if Baker Hughes had finer silica flour and they reported that if they needed anything finer they always used silica fume. Silica fume is amorphous silica while silica flour is crystalline silica. The same question was presented to Trican Well Service and they did not know of “ultra fine silica flour”. After some search time two “ultra fine silica flour” sources were found. One was ground silica from U.S. Silica that is used in industrial applications. The other source was found in Canada manufactured by Sil Industrial Minerals as Product SIL 325 which is silica flour finer than 325 mesh. Samples were ordered from both sources for UAF.

Consistency and Fluid Loss

The cement retardation systems tested so far have not provided adequate working time at temperatures of 400°F and above. Fluid loss tests indicate that fluid loss is an issue in the basic cement mixes. The Project has been in communication with Dr. Karen Luke from Trican Well Services about compatible retarders and fluid loss additives. Dr. Luke has identified several additives that potentially may be effective. They will be tested once they are acquired.

Ferrierite and NM2 Clinoptilolite Base Mixes at 550°F

The first round of tests at 550°F using the base mixes of 5 μm ferrierite and NM2 clinoptilolite at the 27.5% and 40% replacement levels were conducted. The results are summarized in Table 1, along with test data for 300°F and 400°F for comparison. From the results, it is apparent that at 550°F, the samples show very low strength characteristics. Visual inspection showed that many of the samples contained noticeable cracks. The samples were poorly bonded and somewhat friable. We saw minor strength gains with 40% replacement over the 27.5% replacement for ferrierite. The strengths for NM2 are similar for both replacement levels. One sample of NM2_5 μm _40% was retained for permeability measurements. The sample had a permeability of 0.53 mD. It is likely the permeability of the other base mixes is comparable, based on visual observations. The data indicate that the base mixes do not pass the basic strength and permeability requirements at 550°F. We are currently in the process of conducting tests on the addition of the silica to the base mixes at 550°F. Even though the tests are not complete and data have not been fully analyzed, the initial impression is that silica may greatly improve the strength characteristics of the base mixes.

Table 1. Summary of data for base ferrierite and NM2 clinoptilolite mixes at the 27.5% and 40% replacement level.

	Ferrierite_5μm_27.5%		Ferrierite_5μm_40%			NM2_5μm_27.5%		NM2_5μm_40%	
	300°F	550°F	300°F	400°F	550°F	300°F	550°F	300°F	550°F
q_u (psi)	1997	173	3181	1340	304	1470	403	1447	353
E (ksi)	949	91	1500	766	157	850	268	1000	197
ρ (g/cm³)	1.64	1.64	1.64	1.65	1.64	1.62	1.64	1.61	1.63
K (mD)	--	--	--	--	--	--	--	--	0.54

notes: q_u is compressive strength at 7 days. E is the Young's Modulus, ρ is the sample density, and K is the permeability.

* All samples at 550°F contained 0.8%BWOB tartaric acid

Peer Review

For Second Stage Cement Development research findings are submitted for Peer Review. The Peer Reviewer for the Project is Dr. Karen Luke. Dr. Luke's Peer Review comments during the reporting period were as follows:

Dr. Luke Comments

"I see that you are encountering some of the standard cementing problems in dealing with retarders and their secondary reactions. The lignosulfonate based retarders which I am assuming the R8 falls under are not as effective at the high temperatures and in addition do have a notable dispersing effect. The generic hydroxycarboxylic acids do tend to give better retardation with less secondary effects as your results have indicated and are more powerful at the higher temperatures. Results are basically what you would expect.

In terms of compressive strength there are 3 points I would highlight:

1. Loss in strength – this is due to changes occurring in the cement chemistry where the normal binder which is an amorphous calcium silicate hydrate (C-S-H) gel begins to transform into crystalline mineral crystalline hydrate phases. The calcium to silicon ratio of the cement phases becomes a crucial factor in determining the phases that form and if the bulk is above 1.0 then a phase known as alpha – dicalcium silicate hydrate (α -C₂SH) forms which is associated with high porosity and poor strength and can result in severe strength loss (retrogression) over time. To overcome this silica flour is added to the blend to decrease the ratio to 1.0 or less. Typically 35 to 40% bwoc, silica flour is added. The fineness of the silica is also important in that if it is too fine it reacts too fast with the cement and gives a metastable mixture of phases that can be silica rich and others silica poor (α -C₂SH) and ultimately poor strength. If the silica flour is too coarse it does not react fast enough to prevent the α -C₂SH forming. The amount of silica

from the zeolite is not sufficient to prevent α -C₂SH forming and the diatomaceous earth tends to be too reactive compared to silica flour. In addition the alumina in the zeolite reacts at the higher temperatures to form hydrogrossular and this too affects the strength – tends to be lower. I would recommend that you add silica flour to your blends to have at least a bulk CaO/SiO₂ ratio of 1.0

2. Compressive strength at the higher temperatures is dependent on the calcium (aluminate) silicate hydrate phases formed and as these tend initially to be metastable you may also see some decrease followed by increase in compressive strength with time. As long as α -C₂SH is not forming there should be no longer term strength retrogression.

3. In the Chandler HTHP UCA we noted that if the transit time and compressive strength continued to be monitored as the cell was cooling down after the test that compressive strength increased with decreasing temperature. This is something to do with the algorithm used. When we measured the compressive strength of the UCA sample versus that of a cube we found the compressive strength of the cube and that of the “cooled” UCA values matched.

In response to your other questions:

1. Effectiveness of zeolite-containing cement in CO₂ and H₂S environments and offshore applications such as with Class G mixed with salt water – zeolite blends could help reduce attack on the slurry in aggressive environments due predominantly to a reduction in permeability resulting from the pozzolanic reaction and formation of calcium alumino silicate hydrates. It would depend though on the water to cement ration of the original blend and how much water is tied up in cement hydration and pozzolanic reactions. Typically pozzolans are good in seawater and there is a lot of literature on that aspect. There is less on the effect of CO₂ and H₂S environments and essentially depends on how impermeable the matrix is. In cement slurries you have to consider the required density of the cement and that depends on down hole conditions and decreasing density typically involves increasing water contents or using lower SG material or a combination of both. The answer to this really depends on the actual well scenario.

2. Determination of bond to formation and casing – there is no standard test method for this. One method that I have seen used in several companies is to place the slurry in a cell (such as the UCA cell) without using grease on the interior of the cell and then allowing the cement to set for a given time period in the cell at temperature and pressure. The force required to remove the set cement using a press is used in a comparative means between slurries.”

Effects of Retarders

“The effect of the retarder in reducing the compressive strength is not uncommon. This is why companies have developed proprietary retarders for specific cement blends, a) to give the required thickening times, b) short transition from liquid slurry to set cement and c) compressive strength development. Some retarders are noted to give reasonable thickening times but never build strength, essentially they form a viscous gel that has more than 100Bc units of consistency and remains gel indefinitely with zero strength. The compressive strength that is obtained in your system is good even though it is reduced in comparison to the blends without retarder. The reason for the reduction in

strength is that the retarder alters the initial hydration chemistry and at higher temperatures this can affect the resultant phase composition, morphology characteristics, permeability and porosity.

Due to changes in phase composition, the phase assemblage is not in equilibrium and strengths may go up or down as phases composition changes with time. The 7 day data, however, does give some good comparative analyses and it is interesting to note the decrease in strength with decreasing SF. This morning I was at a presentation where they were discussing a 1974 SPE paper on geothermal blends (one of the most comprehensive sets of testing on the subject to date) and the effect of SF concentration and the results fit right in with the ones from UAF. At 20 %BWOC they found that the concentration was too low, and related to a higher amount α -C₂SH which increased over time with a continued loss in strength. Above 50 %BWOC SF they found the strength was less as they required more water to give a mixable slurry and the permeability of the set cement was greater and ultimate strength lower. At 0 %BWOC they had initial lower strength but still reasonable but this declined with time although not necessarily dropping off to zero. Current results appear to validate the data. The paper also has the XRD analyses showing the phase compositional changes too. The authors also studied the effect of DE and quote *"The first group includes the bentonite, diatomaceous earth and expanded perlite. The silica may react and be considered a portion of the silica to stabilize the Portland cement. They produce a lightweight, low permeability cement. These agents should not be added to Portland cement in the range of 5 to 15 per cent in hot wells without adding about 20 per cent extra silica to stabilise against degradation."* The use of MDE in the present case seems to be showing somewhat different properties than they report and it will be interesting to see how it responds in the long term. They also noted that extenders having high pozzolanic reactivity which would include the zeolites give good strength up to 450°F when used with SF. The 7 day data in the tests done so far suggest that the MDE may be even better at providing good strengths in ferrierite systems at least up to 400°F. The authors reported though that at 600°F the pozzolanic systems caused a re-crystallization of the cement hydration products giving lower strengths after several months. Definitely something to think about and to look for with some long term testing. Follows suite on some of the testing I have done too. Mineralogy gives a very good indication of what is going on and what to expect, though I would also suggest looking at the microstructure of the samples too and permeability/porosity if possible. It is good that UAF kept some samples.

Impact of temperature giving reduced strength tends to follow the trend as expected, though the values do seem to be more drastic than seen with cement and SF. It would be good to see what the phase assemblage is in these samples. It may be that with time the changes in the phases formed may give increase in strength with time. As long as the strength does not fall to below that needed to sustain the well then system is still good. As for the UCA data, there is definitely some problem at high temperature with the algorithms, particularly notable on heating and cooling. We did a study on a Portland cement + 40% SF blend where we cured at 95°F for either 3 or 14 days and followed by heated up to 446°F over 4 hours, maintaining the temperature at 446°F for 2 days and then cooled to ambient and monitored the compressive strength continuously in the UCA. The point of note was that immediately the temperature started to ramp up the compressive strength dropped and as soon as the system reached temperature the compressive strength stabilized at the new low value and then over

the 2 days at 446°F we saw some changes which I believe were due to phase changes in the cement, then as you noted as soon as we started to cool down the temperature went up again. In our case though when we did a crush on the cooled sample it has the same compressive strength as on UCA when we terminated the test. It definitely made us question as to what was the compressive strength at temperature and could data be compared between different samples if the algorithm had evident flaws. Looks like you may have the same issues in this case too. Although the UCA gives continual readout and we can see changes over time, the crush test I believe at present is more reliable.”

FY2013 Q3

Element 2 – Final Stage Cement Development

Strength response at 550°F

Table 1 provides the strength data for base mixes containing 5µm ferrierite and 5µm NM2 clinoptilolite cured for 7 days. As seen from Table 1, the base mixes, with no additional silica, show poor strength, despite water to cement ratios (W/C) that are lower as compared to the samples containing silica. It was previously mentioned that the samples have high permeabilities and have poor integrity. Figures 1 and 2 show SEM images for the samples ferrierite 5µm 40% and NM2 clinoptilolite 5µm 40%. The images confirm the open structure of the mixes and thus the high permeabilities and low strengths that have been observed.

Table 1. Base mixes with no additional silica. Cured at 550°F for 7 days.

Sample	TA (%BWOB)	W/C	q _u	
			(psi)	E (ksi)
ferrierite_5µm_27.5%	0.8	0.96	173	91
ferrierite_5µm_40%	0.8	1.08	304	157
NM2 clinoptilolite_5µm_27.5%	0.8	0.98	403	268
NM2 clinotilolite_5µm_40%	0.8	1.12	353	197

The addition of silica is known to stabilize high temperature cements. It primarily helps limit the amount of alpha dicalcium silicate hydrate formed if the proportion of Ca:Si is approximately 1:1 or lower. Four forms of silica were explored including Moltan diatomaceous earth (MDE), coarse silica flour with an average particle size of 150 µm (SF), silica flour from US Silica, MIN-U-SIL 40, with 98% less than 40 µm (MINUSIL), and a silica flour supplied to us by Trican Well Services, produced by SIL Industrial Minerals Inc, with 70% finer than 38 µm (SIL 325). Different combinations of silica were added to a base mix of ferrierite_5µm_30%_44µm_10%, with additions varying from 20-60%. A couple of samples were run

using a base of NM2 clinoptilolite_5 μ m_27.5%. Table 2 provides strength data for cure temperatures of 550°F, and Table 3 provides the data at 400°F for comparison.

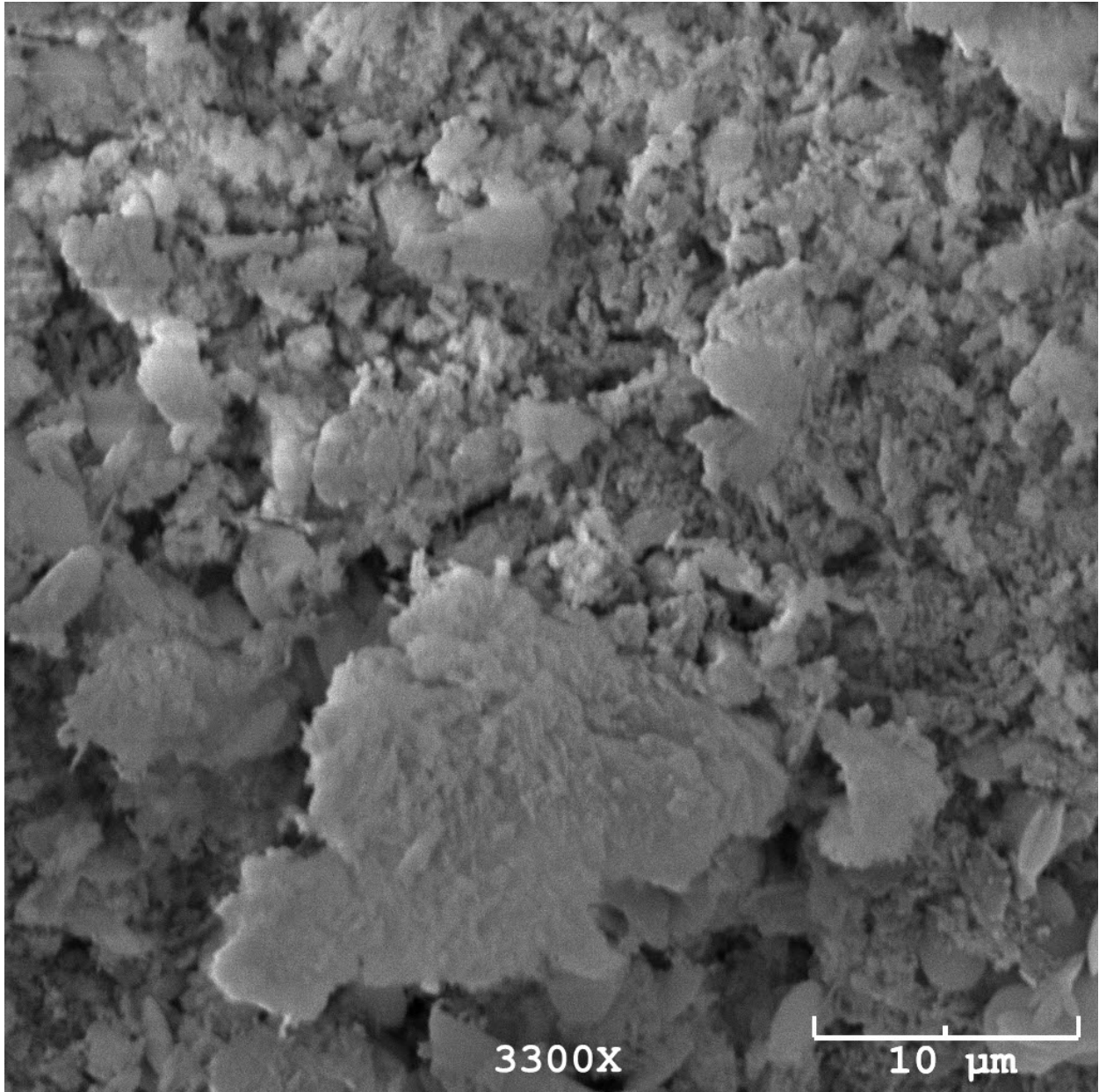


Figure 1. SEM image for ferrierite_5 μ m_40% cured at 550°F for 7 days.

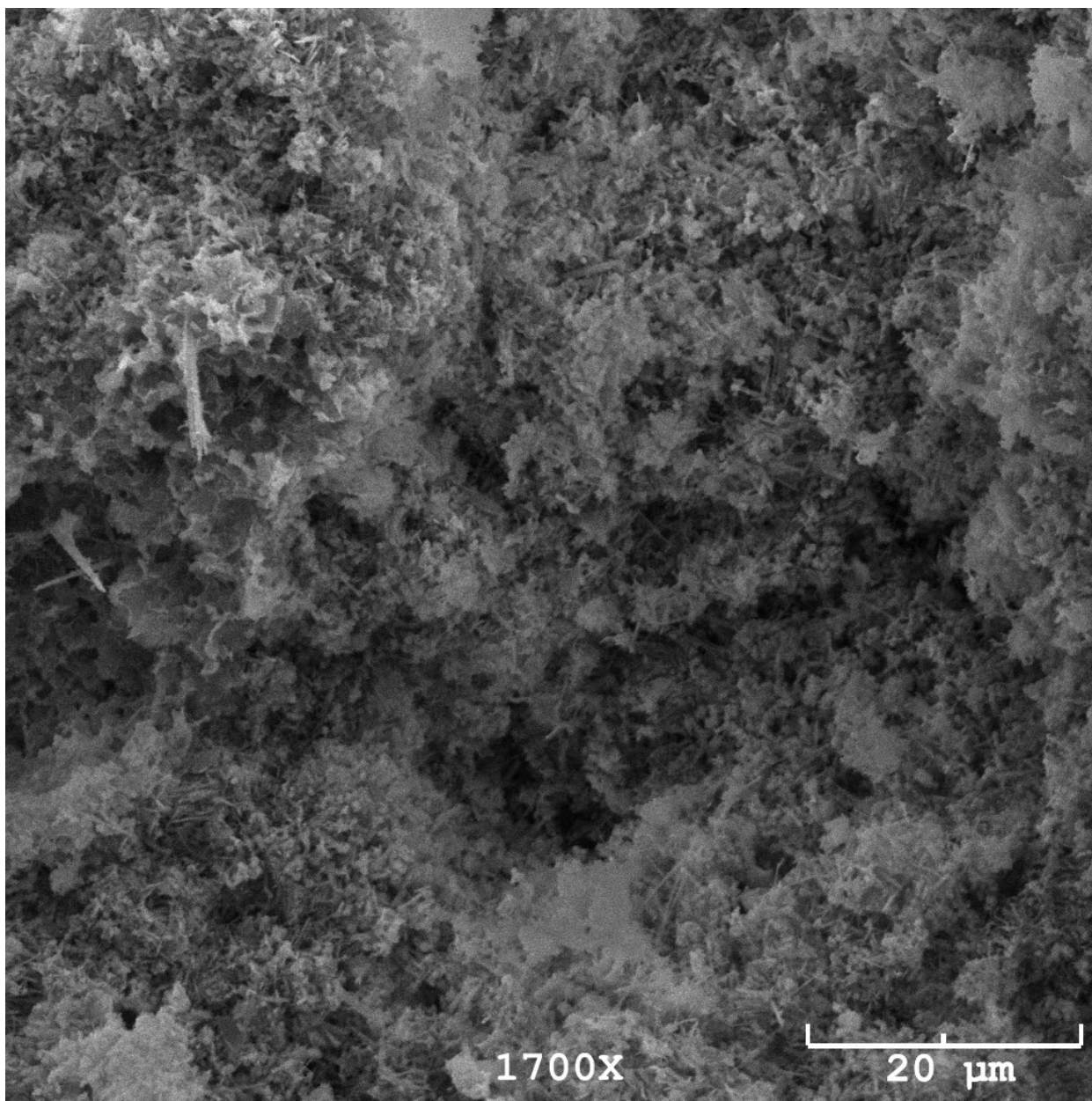


Figure 2. SEM image for NM2 clinoptililote_5μm_40% cured at 550°F for 7 days.

Table 2. Various silica added to base mixes. Temperature 550°F. Cure time 6 days

		% BWOC						
Sample	MDE	SF	MINUSIL 40	SIL 325	TA (%BWOB)	W/C	q _u (psi)	E (ksi)
base mix: ferrierite_5μm_30%_44μm_10%.								
S1	0	20	0	0	0.8	1.21	1622	624
S2	0	40	0	0	0.8	1.33	2208	749
S3	0	60	0	0	0.8	1.46	1973	661
S4	20	0	0	0	0.8	1.18	685	326
S5	40	0	0	0	0.8	1.27	1501	541
S6	20	20	0	0	0.8	1.30	2035	783
S7	20	40	0	0	0.8	1.43	2115	544
S8	30	30	0	0	0.8	1.41	2279	525
S9	20	0	20	0	0.8	1.30	2627	504
S10	20	0	40	0	0.8	1.42	2798	529
S11	20	20	20	0	0.8	1.42	2734	558
S12	0	0	20	0	0.8	1.21	2209	742
S13	0	0	40	0	0.8	1.33	3416	611
S14	20	0	0	20	0.8	1.30	2439	550
base mix: NM2_5μm_27.5%.								
S15	0	40	0	0	0.8	1.24	1808	685
S16	40	0	0	0	0.8	1.17	484	216

Table 3. Various silica sources added to base mixes. Temperature 400°F. Cure time 7 days

	% BWOC							
Sample	MDE	SF	MINUSIL 40	SIL 325	TA (%BWOB)	W/C	q _u (psi)	E (ksi)
base mix: ferrierite_5μm_30%_44μm_10%.								
1	40	20	0	0	0.8	1.40	2545	802
2	40	0	0	0	0.8	1.27	3297	1112
3	20	20	0	0	0.8	1.30	2499	889
4	20	0	0	0	0.8	1.17	1976	784
Base mix: ferrierite_5μm_40%								
5	0	60	0	0	0	1.46	1845	581
6	0	40	0	0	0.5%	1.33	1638	641
7	0	40	0	0	0	1.33	1834	206
8	0	20	0	0	0	1.21	1523	701
9	0	0	0	0	0	1.08	1340	601

The addition of Moltan diatomaceous earth as the only source of silica generally results in poor strength development. The ground silica flours, represented by MINUSIL and SIL 325, provide increased strength gains over the coarser silica flour (SF). This is expected due to the increased surface area of the reacting silica. For the MINUSIL, only small additional gains are seen by increasing the silica from 20% to 40% when added at a 20% addition of MDE. However, a significant increase is seen for MINUSIL when no MDE is added. The general trend is for higher strength development for equivalent silica replacements when the crystalline silica flour is the only source of added silica. However, the MDE does provide short term strength gains even if a slight reduction in strength results. It is predicted that the finer ground silica will provide reduced permeabilities over the coarser silica flour based on literature sources. The elastic modulus is similar between all test samples. Roughly, the crystalline silica sources result in slightly higher elastic moduli. That data suggests that the ground silica flour offers greater benefits than the coarse silica flour. However, the coarse silica flour (SF) has minimal water demand and can be used to reduce overall viscosity of the slurry and still offer strength gains at high temperatures. The data is limited to 7 days. Longer cure periods may offer different results.

It is clear that without additional silica, of which a component should be a crystalline silica source, the zeolite/cement H mix does not provide adequate strength, and shows low permeability. The addition of

even 20% silica offers significant gains. The addition of crystalline silica also shows improved properties at 550°F as compared to 400°F. However, at 400°F, the gains seen from MDE are substantially higher and appear to degrade at higher temperatures.

Retardation at 400°F

In this study, we have adopted thickening times between 6 and 8 hours as the target value. Using a combination of tartaric acid, sodium glucoheptonate, and sodium tetraborate (borax), these values are achievable. Sodium tetraborate in concentrations of 2-3% BWOB appear necessary in order to achieve the target thickening times. However, at this point, it appears the slurry is over retarded with respect to setting. Thickening times are achieved, but setting times are greatly extended to an unacceptable degree. Up to this point we have been using a base mix (ferrierite_10μm_40%) for all retardation studies to explore the variations based on the different retarders.

Consistency Tests at 400°F

A series of consistency tests were run at 400°F and 14 ksi using a ramping schedule of 60 minutes for both temperature and pressure. All tests, except two, were run on a standard base sample of ferrierite_10μm_40%. Three retarders were tested including sodium glucoheptonate (dry powder), tartaric acid, and sodium tetraborate (i.e. borax). All three retarders represent fairly cost effective and easily obtainable retarders. Various combinations of the above mentioned retarders were tested with the results presented in Table 1.

Sodium glucoheptonate and tartaric acid were combined at a 1:1 ratio using 0.73%BWOB and 1.0%BWOB for each retarder. As shown in Figure 1 and Table 1, increasing the quantity of retarder has minimal influence on the thickening time (70 Bc) and consistency profiles. The results suggest that increasing the quantity of retarder will have no significant gains in thickening time. In an earlier report, it was shown that small changes in tartaric acid have a strong retarding influence at 300°F. At 400°F, the results suggest that an additional retarding agent is necessary.

Sodium tetraborate (i.e. borax) is commonly added as a booster in combination with other retarders, which do not provide sufficient retardation ability alone. A series of tests were run to look at the retarding influence of sodium tetraborate. One group of tests were run keeping sodium glucoheptonate constant at 0.7% BWOB and varying the amount of sodium tetraborate from 1.8% BWOB to 3.0% BWOB. Consistency profiles are summarized in Figure 2. Once the target temperature is reached, a fairly stable viscosity is achieved until onset of thickening. With increasing quantities of sodium tetraborate, the stable consistencies (i.e. at 400°F) become progressively lower. This indicates that increasing sodium tetraborate concentrations results in increasingly dispersive behavior. Physical observations upon removal of slurry do not reveal slurry separation. The influence of sodium tetraborate on the thickening time is shown in Figure 3. The trend is for exponentially increasing thickening times with increasing concentrations. As will be discussed later, higher concentrations of sodium tetraborate may have a positive influence on extending thickening times, but for concentration over 2% BWOB, setting times are greatly extended.

Using a constant concentration of 0.7% BWOB sodium glucoheptonate and 2.0% BWOB sodium tetraborate, the amount of tartaric acid was varied from 0% BWOB to 0.7% BWOB. Results are shown in Figure 4 and Table 1. As seen in Figure 4, a damping trend is observed with increasing tartaric acid concentrations up to 0.3% BWOB. With concentrations of 0.7% BWOB, a substantial increase in thickening time is observed. It is anticipated that this changing behavior begins between 0.5% BWOB and 0.6% BWOB. Consistency profiles for varying concentrations of tartaric acid are shown in Figure 5. For the 0.7% BWOB addition, the presence of a quaternary gelation peak is present at approximately 56 min. This peak is not readily prevalent at the lower concentrations. In Table 1, several quaternary gelation peaks (QP) were identified. At tartaric acid concentration less than 0.5% no QP's were observed. At 0.5%, weak peaks were observed. The timing of the peaks is fairly consistent between 50 to 60 minutes, which corresponds to temperatures between approximately 360°F and 400°F. There appears to be an important reaction between tartaric acid and sodium tetraborate in which the resulting product acts as a strong retardant at 400°F. The quaternary gelation peak is not desirable and we will test several approaches to see if we can mitigate its occurrence. One possibility is the addition of polyvalent cations. Regardless, it appears this tartaric acid-sodium tetraborate reaction is important for retardation. In Table 1, a 1.0% BWOB tartaric acid : 2% BWOB sodium tetraborate mixture results in thickening times greater than 780 minutes with no apparent thickening trend. This suggests that thickening time is sensitive to increasing tartaric acid concentrations.

A ferrierite_5µm_30%_44µm_10%_MDE20%_MINUSIL20% blend was tested with 1% BWOB tartaric acid and the promising blend of 0.7%:0.7%:2.0% mixture of sodium glucoheptoante : tartaric acid : sodium tetraborate by weight of blend. As seen in Table 1, the tartaric acid alone provides little retardation. The retarder blend performs similarly between the two ferrierite based blends. Slightly longer thickening times were observed when Moltan diatomaceous earth and silica flour were added.

Table 1. Summary of consistency data conducted at 400°F. Retarder concentrations are listed as %BWOB.

Mix	Na Glucoheptonate	tartaric acid	Na tetraborate	consistency			quaternary gelation peak
				30 Bc	70 Bc	100 Bc	
ferrierite_10_40%	0.7	0.7	0.0	60	73	74	NP
	1.0	1.0	0.0	62	77	78	NP
	0.7	0.0	1.8	170	193	204	NP
	0.7	0.0	2.0	193	207	214	NP
	0.7	0.0	2.5	246	264	278	NP
	0.7	0.0	3.0	339	362	378	NP
	1.0	0.0	2.0	218	233	237	NP
	0.7	0.1	2.0	233	239	239	NP
	0.7	0.2	2.0	242	251	257	NP
	0.7	0.3	2.0	237	255	266	NP
	0.7	0.7	2.0	340	377	404	41 Bc @ 55 min
	0.5	0.5	1.0	121	121	121	NP
	1.0	0.5	1.5	162	179	191	29 Bc @ 57 min
	0.0	1.0	2.0	n/a	>780 min	n/a	75 Bc @ 41 min *
ferrierite_5_30%_44_10%_MDE20%_MINUSIL20%	0.0	1.0	0.0	55	58	59	NP
ferrierite_5_30%_44_10%_MDE20%_MINUSIL20%_F							
L-17 0.75%_FL-24 0.75%	0.7	0.7	2.0	315	409	522	63 Bc @ 56 min

* 1 hour preconditioning at 80F.

NP = not present

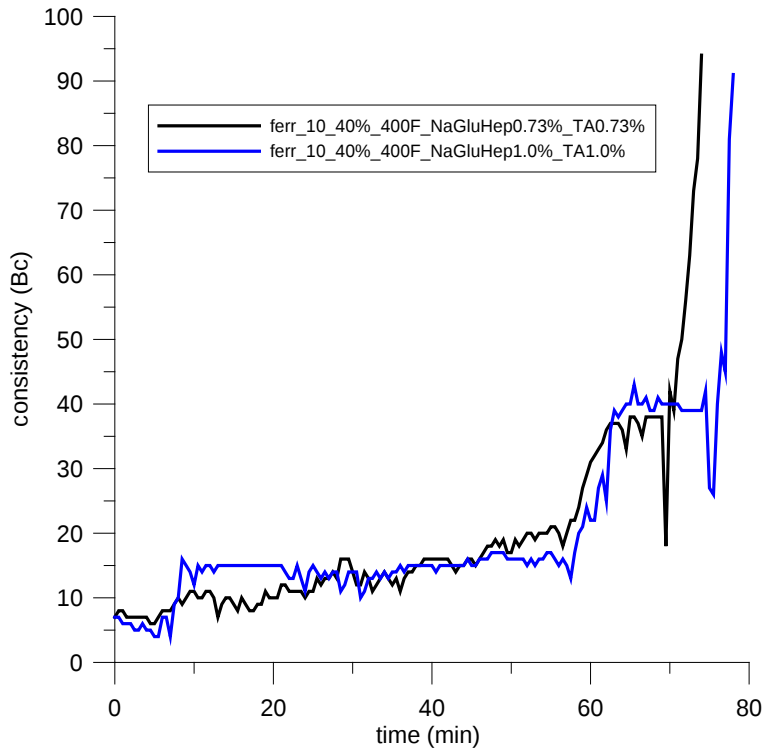


Figure 1. Consistency profiles for combinations of sodium glucoheptonate and tartaric acid. Percentages by weight of blend.

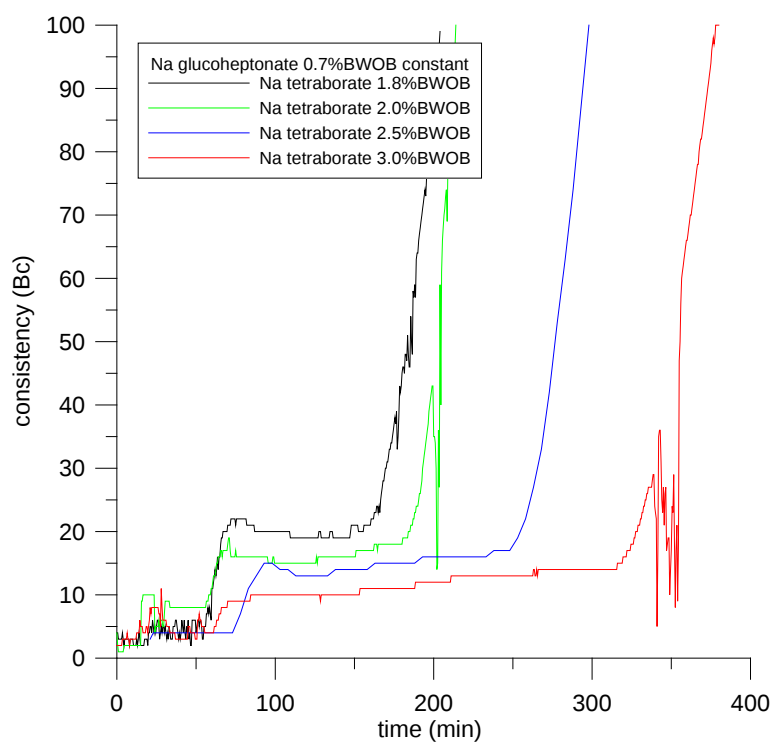


Figure 2. Consistency profiles showing the influence of sodium tetraborate on the slurry thickening profiles. Sodium glucoheptonate was held constant at 0.7%BWOB.

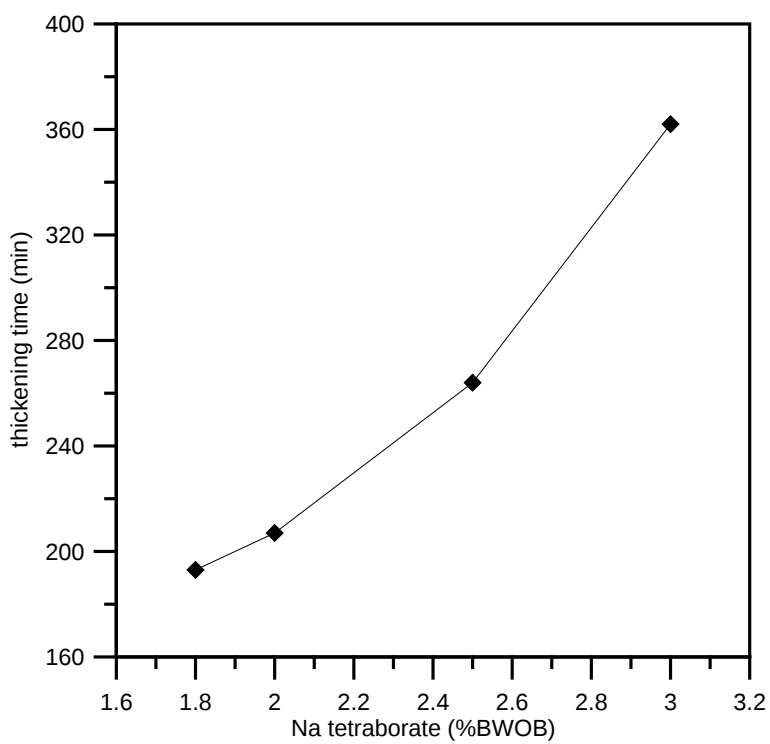


Figure 3. The thickening time influence of varying concentrations of sodium tetraborate with sodium glucoheptonate held constant at 0.7%BWOB.

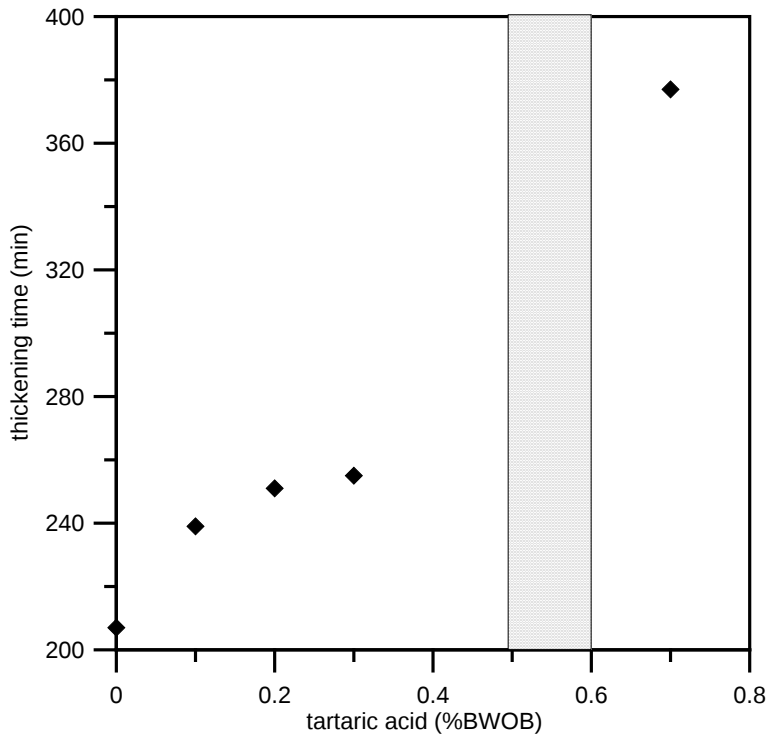


Figure 4. Influence of tartaric acid on the thickening time at 400°F. The tartaric acid concentration was varied as sodium glucoheptonate and sodium tetraborate were held constant at 0.7%BWOB and 2.0%BWOB respectively.

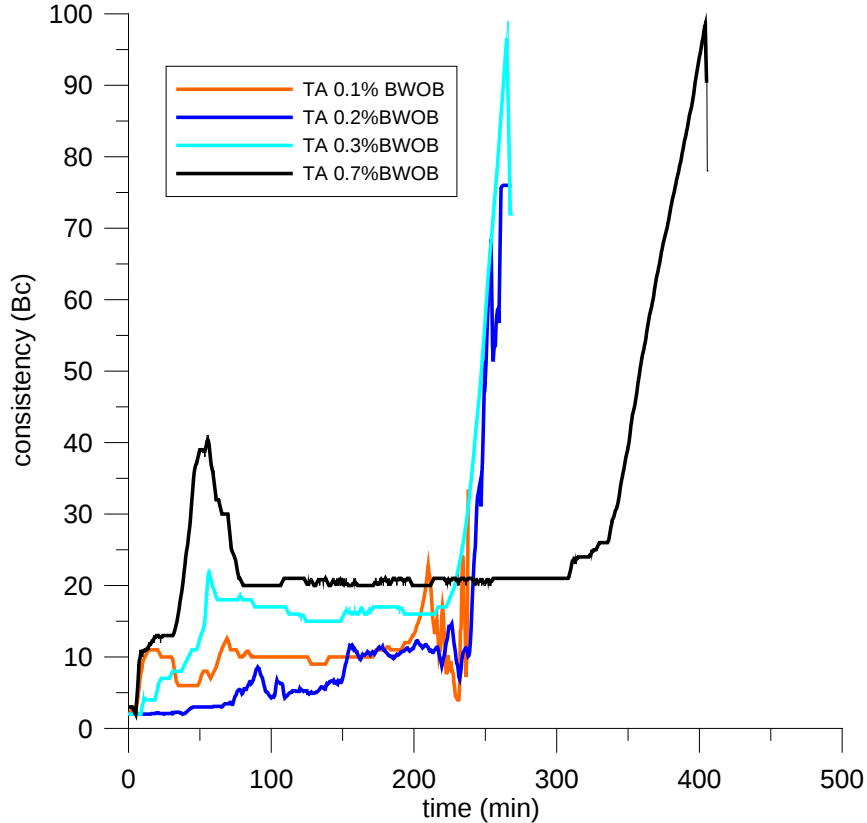


Figure 5. Consistency profiles for varying tartaric acid concentration with a constant concentration of 0.7% sodium glucoheptonate and 2.0% sodium tetraborate.

Setting Time

In the previous discussion, various combinations of retarders and their influence were discussed. The test results for setting time are presented for ferrierite_10 μ m_40%. The temperature was ramped to 400°F in 60 minutes to match the ramping profile for consistency tests. The setting profiles are provided in Figure 6. Transit times are presented as they provide a better estimate of the initiation of set. The blend containing 0.7% sodium glucoheptonate : 3% sodium tetraborate shows a very long setting time with onset of setting occurring at approximately 70 hours. The two blends with 0.7% sodium glucoheptonate : 0.3%-0.7% tartaric acid : 2.0% sodium tetraborate show the onset of setting occurs at approximately 18 hours. Post-test compressive strength measured with a hydraulic press was approximately 1300 psi. From the transit profiles, the blends with tartaric acid and 2.0% sodium tetraborate likely provide 500 psi working strength by 24 hours. The blend with 3.0% sodium tetraborate takes approximately 3 days for sufficient strength to develop. This is a primary justification for using sodium tetraborate concentrations that do not exceed 2% BWOB as discussed in the previous consistency discussion.

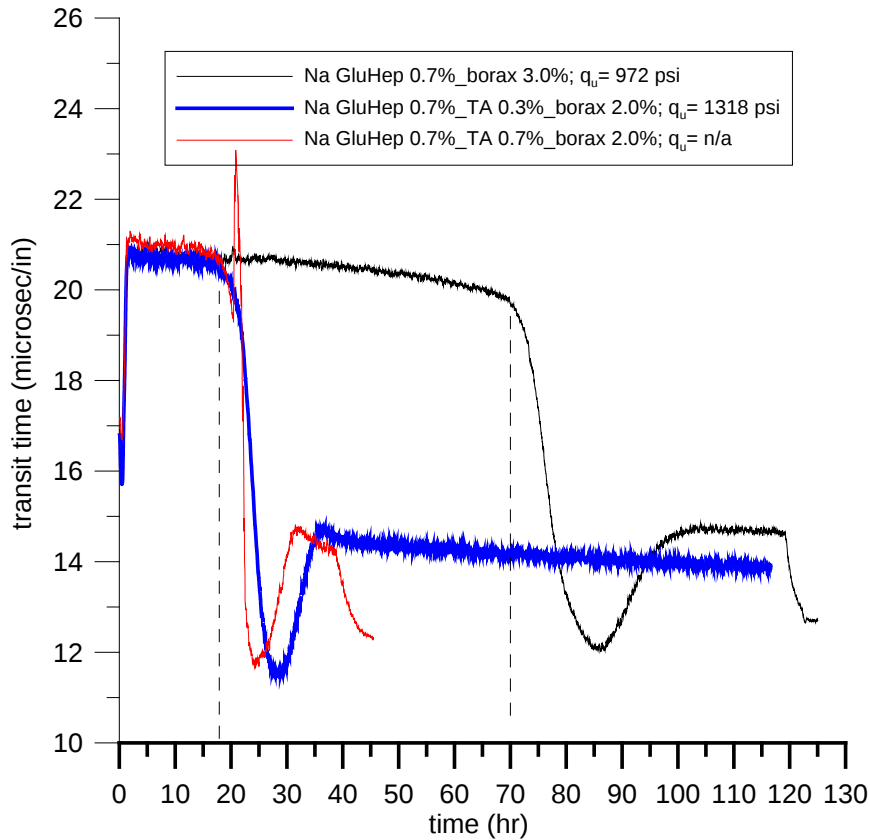


Figure 6: Setting profiles for ferrierite_10μm_40%_400°F. Transit times are provided.

Fluid Loss, Consistency, Retardation

The base ferrierite blend provides good strength characteristics at temperatures ranging from 300°F to 550°F based on 1 week tests. However, fluid loss control at temperatures of approximately 400°F and above remains a challenge. Therefore, efforts were focused at this point to characterize a potentially workable mix (Fmix1) at 300°F, while we continue to address the issue of fluid loss at higher temperatures.

At 300°F, the API fluid loss limit of less than 100 ml/30 min is achievable, without any unacceptable increases in slurry viscosity. Using a basic retardation system consisting of sodium glucoheptonate and tartaric acid, the degree of retardation can be controlled as it follows a linear trend with increasing concentrations. The onset of setting of the cement lags the thickening time by 1 to 3 hours. The HPHT free water characteristics are determined from mold properties.

The Fmix1 provides considerable strength based on short term curing times with unconfined compressive strengths approaching 6500 psi at 2 days cure for 13.5 ppg. The strength does drop with additional curing to a value between 4000 to 5000 psi. The 13.0 ppg sample showed strength greater

than 4000 psi at 2 days cure. The mix does exhibit some brittle tendencies, which are characteristic of pozzolanic cements. Competent samples exhibited tensile strengths approaching 1000 psi. Typical ranges likely vary from 500 to 1000 psi. Samples at 13.5 ppg and 13.0 ppg both show permeabilities less than 0.01 mD. The thermal conductivity of the 13.5 ppg and 13.0 ppg cements were measured.

Data are available for the Fmix1 after 1 week of curing in an Ormat/CO₂ brine at 300°F and 850 psi. Extensive alteration of the cement occurred as compared to the control. This alteration zone has a pH less than 10, while the non altered zone has a pH above 10. The Ormat/CO₂ brine has a pH of 5.8. The data suggest a loss of strength due to curing the brine solution.

The following sections provide detailed data for a promising mix at 300°F. The mix composition is ferrierite_5µm_30%_44µm_10%_MDE20%BWOC_MINUSIL 20%_BWOC. This will be referred to as "base Fmix1." MDE is Molten Diatomaceous Earth, and MINUSIL is a brand name for micro silica flour with a particle size of approximately 40µm.

Fluid Loss

Using the base Fmix1, various proportions of the Fritz fluid loss additives FL-17 and FL-24 were tested at 300°F. It was recommended by Dr. Karen Luke from Trican Well Services that these fluid loss additives have been effective in zeolite cements in the past. The results are summarized in Table 1. The additive FL-24 is fairly effective; however, it has the tendency to increase viscosities significantly when used in higher concentrations. Quantities of FL-17 are added in an attempt to aid fluid loss control without increasing the quantity of FL-24. Quantities as high as 3% of FL-24 have been added to the base Fmix1 at 400°F. The results are not reported here, however, the viscosities were sufficiently high (60-90 Bc) to make the additive impractical at quantities above 2%. The API fluid loss for the 1.0% FL-17 and FL-24 is a bit high based on the trends as outlined in Table 1. As a target value, the goal was to achieve an API fluid loss of less than 100 ml/30min.

Table 1. Summary of fluid loss characteristics for base Fmix1.

Density (ppg)	Cement	Na glucoheptonate (Russtech)	Tartaric acid	FL-17	FL-24	API fluid loss (ml/30min)
13.5	H	0.8%	0.8%	0.75%	0.75%	96
13.5	H	0.8%	0.8%	1.0%	1.0%	118 ?
13.5	H	0.8%	0.8%	1.5%	1.5%	73
13.5	H	0.8%	0.8%	0.5%	1.5%	74
13.0	H	0.8%	0.8%	0.5%	1.5%	209

* The quantity of retarders and fluid loss additives are based on the weight of the base blend (i.e. cement and zeolites).

Consistency and Setting characteristics at 300°F

Retardation of the cement slurry at 300°F does not require the addition of sodium tetraborate as was described in the May report for 400°F. A combination of equal parts sodium glucoheptonate and tartaric acid yields fairly predictable retardation. Consistency data for various quantities of retarders is provided in Table 2 and Figure 1. Note that the 0.8%:0.8% consistency profile contains 1.5% FL-24 fluid loss additive which is responsible for the increased base viscosity of the mix as compared to the other two profiles. Adjustment of the amount of retarder provides good control on the length of the working time as there appears to be a linear relationship between thickening time (70 Bc) and retarder concentration (Figure 2). The sodium glucoheptonate is in a liquid form from RussTech Admixtures with 51% actives. Quaternary gelation peaks are observed in Figure 1. The gelation peaks consistently occur between 25-35 minutes with magnitudes between 14 and 29 Bc. It is believed the tartaric acid is primarily responsible for the gelation peaks. It should be noted that for retardation at 400°F, the same basic quantities of sodium glucoheptonate and tartaric acid are used, except 2% BWOB sodium tetraborate is added as an additional retarder.

Several of the mixes from Table 2 were placed in the UCA for the determination of the onset of setting. The real time transit time profiles are shown in Figure 3. The thickening time for curve a) was 8.1 hrs (485 min) with the apparent onset of strength development occurring between 9 to 10 hrs. The thickening time for curve b) was 11.9 hrs (715 min) with the apparent onset of strength development occurring between 14 to 15 hrs. Note that the fluctuations in curve b) are instrument issues with the UCA and not real affects. Upon termination of the tests, the samples were subjected to a crushing test which provided strengths between 3500 and 4000 psi. Based on this data, ample strength is developed by 24 hours with fairly rapid strength development following thickening.

Table 2. Influence of retarders on consistency and thickening times for base Fmix1.

Additives: retarders and fluid loss				Time (min)		
Na GluHep	TA	FL-17	FL-24	30 Bc	70 Bc	100 Bc
0.8%	0.8%	0.75%	0.75%	166	168	168
0.8%	0.8%	0.75%	0.75%	679	715	715
0.8%	0.8%	0.50%	1.50%	448	485	485

Notes:

- 1) Na GluHep is a RussTech sodium glucoheptonate in liquid form with 51% actives.
- 2) TA: tartaric acid
- 3) FL-17 and FL-24 are fluid loss additives by Fritz Oilfield Products
- 4) Additive quantity based on weight of blend of zeolite and cement

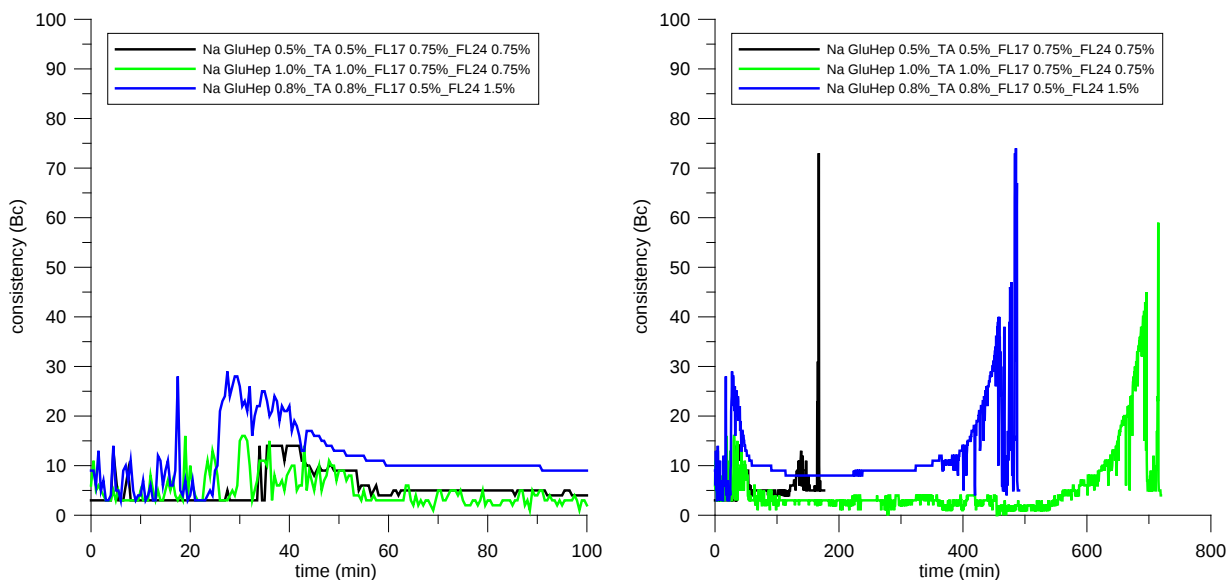


Figure 1. Consistency profiles for ferrierite_5µm_30%_44µm_10%_MDE20%BWOC_MINUSIL 20%_BWOC with variations in quantity of retarders.

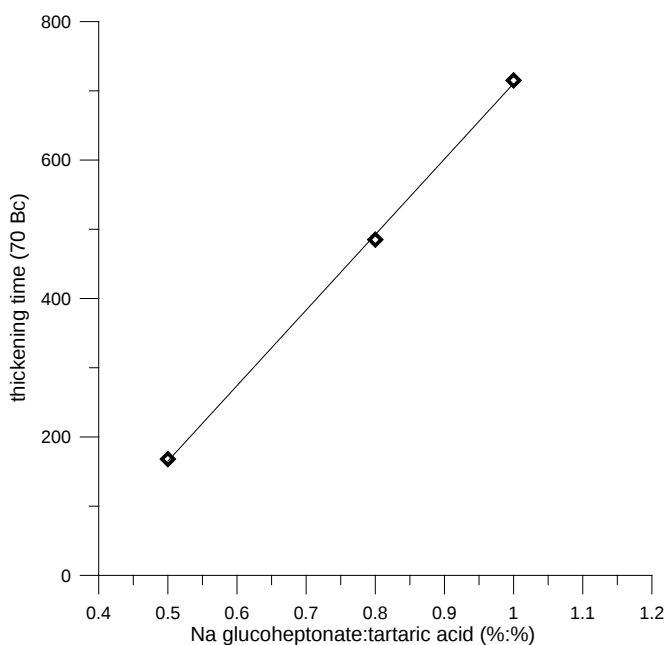


Figure 2. Thickening time vs. quantity of retarder. Note the quantity in the x-axis represents and 1:1 ratio of Na glucoheptonate and tartaric acid by weight of base blend.

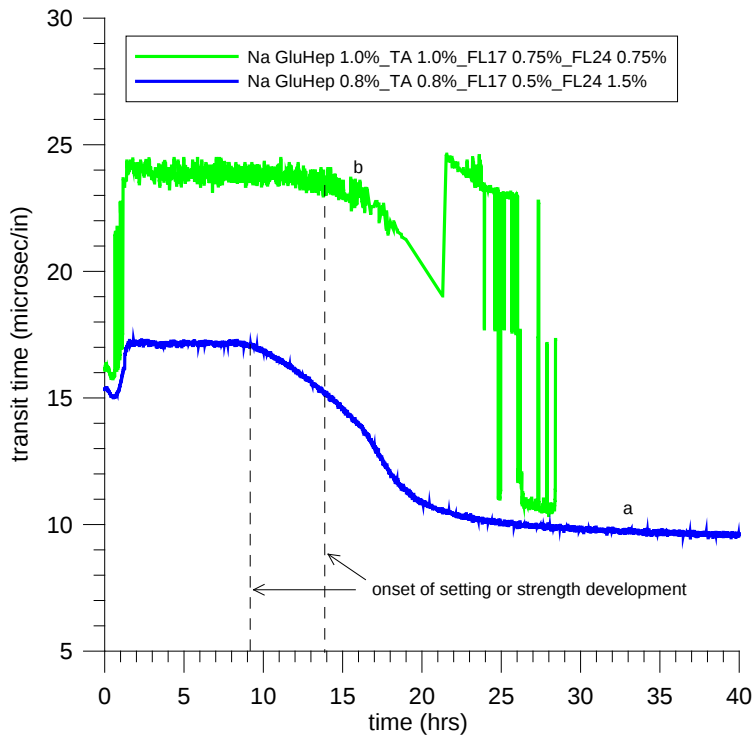


Figure 3. UCA results depicting the transit time vs. time.

Free Water

The best way to characterize free water at HPHT is directly from the cured molds. The molds are topped off during placement of the slurry. Post-cure measurement of the height of the sample provides an estimate of the potential free water. Using this approach, the free water is estimated at less than 2%. The average value ranges from 1% to 2%. The API specs specify free water should be less than 5.9%. Figure 4 provides an image of the typical cured cement in the molds.



Figure 4. Image of typical Fmix1 molds showing potential free water.

Mechanical Properties and Material Properties (300°F)

A series of tests were conducted on what will be referred henceforth as "Fmix1". Fmix1 can be defined as ferrierite_5 μ m_30%_44 μ m_10%_MDE20%BWOC_MINUSIL 20%_BWOC with retarder concentrations of 0.8%BWOB of sodium glucoheptonate (RussTech) and tartaric acid and fluid loss additives of 0.5%BWOB FL-17 and 1.5%BWOB FL-24. This differs from the "base Fmix1", which is the dry blend, without additives. The samples were placed in a curing chamber and heated to 300°F for 36 hours and then allowed to cool down to 180°F over 12 hours. This is considered a two day cure. Upon removal from the molds, the cubes were sub sampled as cores if necessary, and placed in a room temperature water bath. The samples were tested on the same day as removal from the curing chamber. Results are shown in Table 3.

Table 3. Mechanical and material properties for mix Fmix1 at 300°F.

Density (ppg)	Density (g/cm ³)	q _u (psi)	E (ksi)	ν	Tensile strength (psi)	Thermal conductivity (W/m°C)	Permeability (mD)
13.5	1.61	6484	1243	0.33- 0.38	990	1.11	0.005
13.5 (3 day cure)*	1.61	5533	1112	n/a	572	n/a	n/a
13.0	1.55	4255	993	0.28- 0.36	n/a	0.92	0.003

* based on a three day cure. Many of the samples showed cracks likely resulting from subsampling. The cracks may have been partially responsible for the lower strength values.

Compressive Strength:

The values listed for the 2 day cure at 13.5 ppg come from cores sampled from 2" cubes. The cores may supply compressive strength values up to 10% higher than the 2" cubes molds. This is based on a small run of trial samples composed of a chabazite mix. The height to diameter ratio for the cores ranges from 1.1-1.2. Ideal height to diameter ratio is 2:1. This may have some impact on the elastic properties as well.

Elastic Properties:

The cylinders are fitted with axial and lateral displacement transducers. An example of stress-strain behavior is shown in Figure 5. The elastic modulus reported is determined from the first linear portion of the curve at strains typically up to 0.003. Poisson's ratio is determined from linear curve fitting of the lateral to axial strain. The Poisson's ratio relationships typically show strong linear trends up to strains close to the failure point of the samples. Determination of the elastic modulus can be subjected depending on the point upon which it is determined. If based on deviation of the Poisson's ratio trends (strains 0.005 to 0.007 in Figure 5), the elastic moduli will be lower. The values reported are likely upper estimates.

Tensile Strength:

The tensile strength was determined using the indirect tensile strength tests based on ASTM D3967. This test is also known as the Brazil test or splitting test. A disc shaped sample is placed between end platens upon which the sample is split diametrically. The 3 day cure 13.5 ppg values listed in Table 3 contained cracks which influenced the results.

Thermal Conductivity:

The thermal conductivity of the sample is measured in a guarded hot plate apparatus. A cube sample is wrapped in a thin layer of polyethylene to prevent dehydration of the sample. The sample is then placed between a cold and hot plate. The hot plate is regulated at a temperature of approximately 48°C. The cold plate is maintained at approximately 17°C. A precision heat flux sensor is placed between the upper hot plate and the sample. A thin layer of thermal paste is placed between the temperature plates, heat flux sensor, and sample. The test is run until a steady state is reached (typically 3-5 hours).

Permeability:

A 1 inch (2.54cm) core is sampled from the cured cubes and placed in a water bath under vacuum for several hours to ensure saturation. The core is then placed in a standard cylindrical core holder device. A 500 psi confining pressure is applied. The outlet pressure is atmospheric. The inlet pressure is controlled by a precision syringe ISCO pump. Differential pressures are applied at 50, 100, 150, 200, and 250 psi. Water flux measurements are conducted when it appears steady state flow has been achieved. Tests are conducted at room temperature.

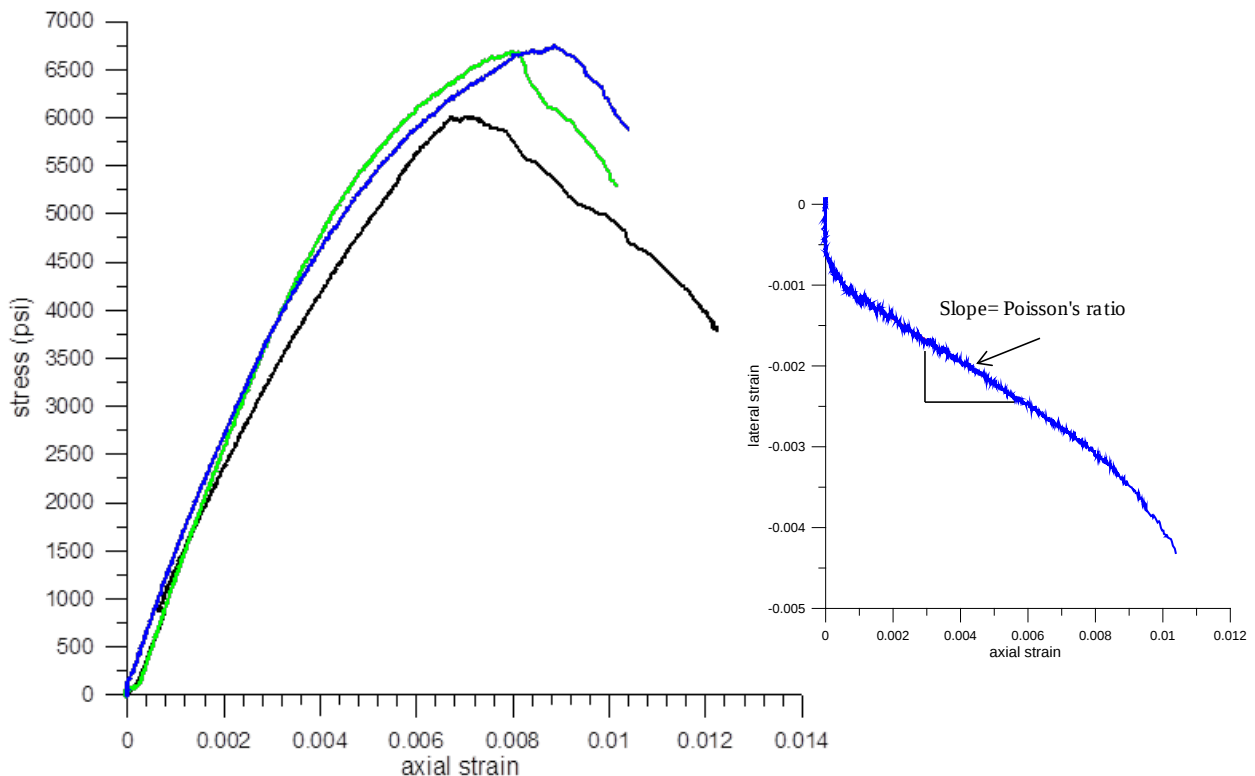


Figure 5. Stress-strain plots for 13.5 ppg, 300°F samples. Poisson's ratio plot shown on the right side.

Peer Review

For Final Stage Cement Development research findings are submitted for Peer Review. The Peer Reviewer for the Project is Dr. Karen Luke. Dr. Luke's Peer Review comments during the reporting period were as follows:

Dr. Luke Comments:

"The loss in strength and increased permeability at 550°F is what I expected based on chemistry as there is insufficient silica from the zeolite to prevent formation of the α -C₂SH which is known to give high permeability and reduced strength at temperatures above 300°F. The primary solution is to add additional silica which converts/prevents formation of α -C₂SH by forming calcium silicate hydrates such as tobermorite, xonotlite, truscottite etc that have Ca/Si ratio of ≈ 2.0 and more consistent with the Ca/Si ratio in cement of between 2-3."

"As stated in the report I am trying to get some fluid loss and retarders that I hope will work with the zeolites. The problem is that at the higher temperatures there is no one simple off the shelf product available and the service companies have proprietary products that depend on the slurry formulations/density and temperature ranges. Most of the additives are a combination specifically designed for purpose. This is something we may need to do for the zeolite blends since they have not been investigated for this high temperature range or at such high concentration in the past. The benefits of the silica flour at 550°F suggest that there is probably a change in the phases produced at this temperature which also may affect retarder properties. "

Additional Peer Review was provided during the period by Mr. Mike Stephens, Worldwide Cement Account Manager, Chevron Phillips Chemical Company. Mr. Stephens was impressed with the developed cement. The only comment he had was to use Class G rather than Class H. He stated that we could keep the same formulations but a switch to Class G would result in a one pound per gallon weight reduction.

FY2013 Q4

Carbonation Testing

The Fmix1 at 300°F shows significant alteration when cured in an high brine/CO₂ fluid. The 1 week permeability is still low, despite the alteration. The permeability was tested at 3 week upon which the entire sample will have undergone alteration as seen in Figure 2.

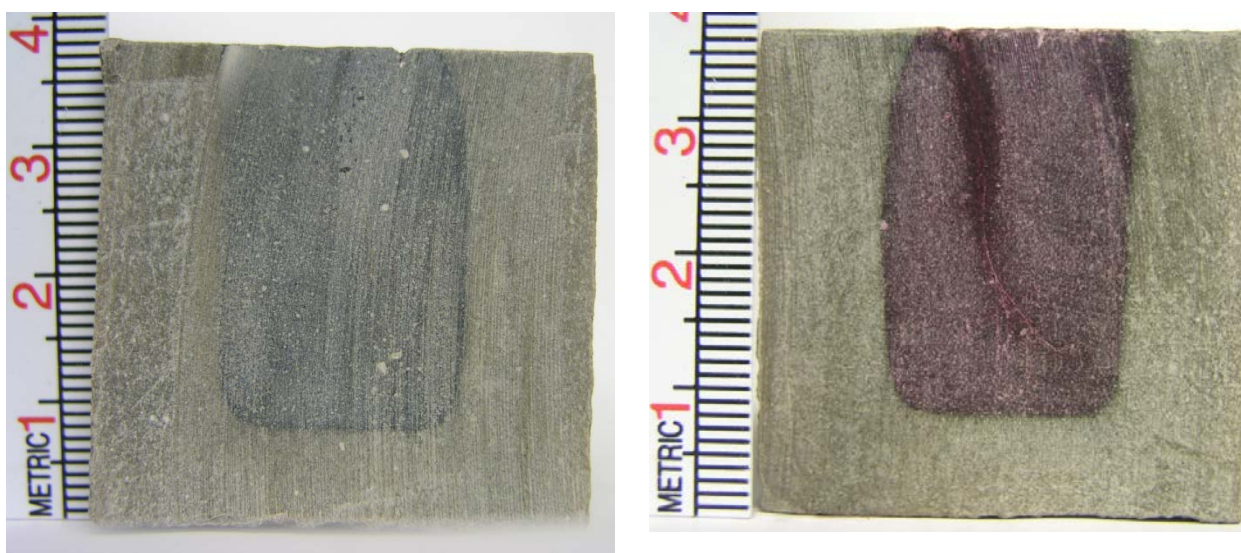


Figure 1. Fmix1, 1 week cure in Ormat brine/CO₂ showing the altered zones including natural state (left) and treated with phenolphthalein (right)



Figure 2. Fmix1, 3 week cure in Ormat brine/CO₂. Right sample is treated with phenolphthalein. No color change indicates pH < 10.

Table 1. Summary of properties of Fmix1 cured at 300°F for 1 week.

		1 week		3 week
	Initial	Ormat brine/CO ₂	Control	Ormat brine/CO ₂
q _u (psi)	6484	3968	5091	3233
E (ksi)	1243	831	933	828
v	0.33-0.38	~0.28	~0.38	~0.40
mass gain		5.5%	1.3%	~6.0%
Permeability (mD)	0.005	0.0055	0.0016	n/a

Ferrierite & NM2 at 27.5% with MINUSIL and lime

The quantity of Ca^{+2} ions was increased by decreasing the amount of zeolites and adding an additional amount of hydrated lime. The rate of alteration is decreased, however, significant alteration still occurs. Unlike the Fmix1, the cement shows a significant increase in 1 week permeabilities.

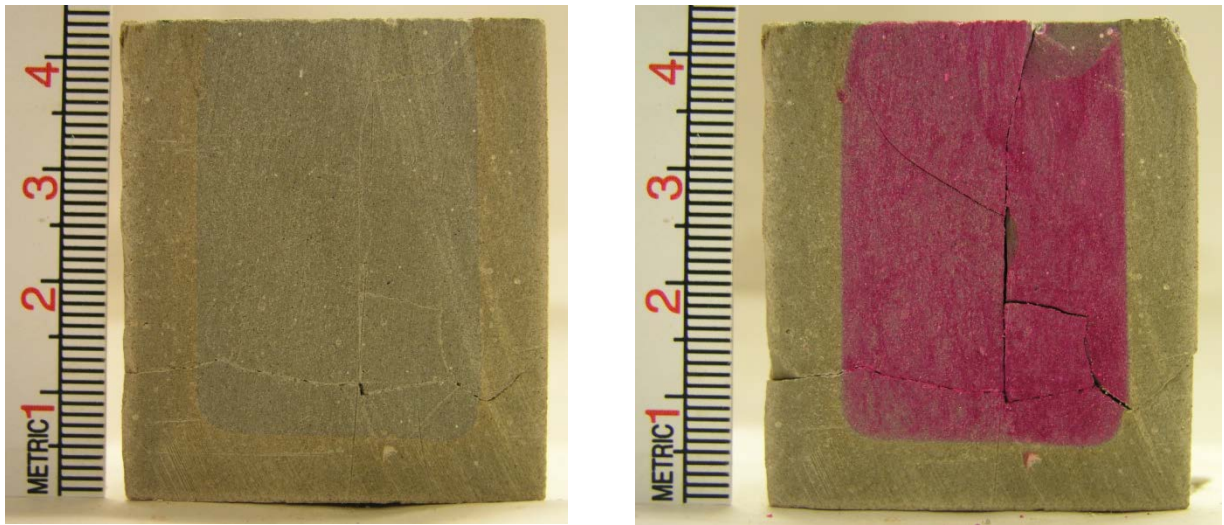


Figure 3. Ferrierite_5_27.5%_MINUSIL20%_Lime20%_13.5ppg_H. One week cure in Ormat brine/ CO_2 showing the altered zones including natural state (left) and treated with phenolphthalein (right)

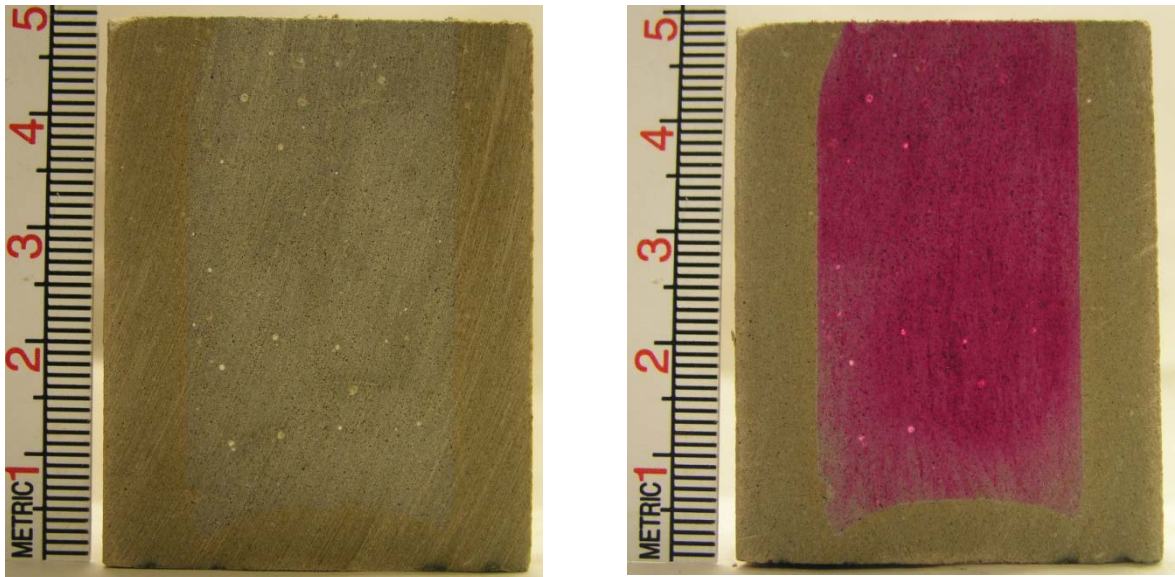
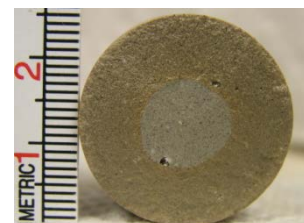


Figure 4. NM2_5_27.5%_MINUSIL20%_Lime20%_13.5ppg_H. One week cure in Ormat brine/CO₂ showing the altered zones including natural state (left) and treated with phenolphthalein (right)

Table 2. Carbonation characteristics for ferrierite and NM2 using 5 μ m_27.5%_MINUSIL20%_lime20%_H_13.5ppg

	Ferrierite		NM2	
	Initial	1 week	Initial	1 week
Permeability (mD)	0.0031	0.010	0.003	0.012
% alteration (area)	--	57.7%	--	63.0%
% alteration (linear)	--	37.0%	--	38.6%
mass gain	--	7.1%	--	7.4%



Cement Development

Fmix1 Properties

Pipe Bond Strength

Using standard grade A56/A106 carbon steel, the pipe-cement bond was determined for the Fmix1 blend as presented in the June 2013 report. Communications with a pipe supplier in Bakersfield, CA, indicate that standard carbon steel is the most widely used alloy. The test equipment and typical sample conditions are shown in Figure 1. The testing apparatus is designed to precisely accommodate 1.5" schedule 40 pipe. The actual inner diameter of the pipe is approximately 1.63 inches. The push out rod is aligned using an alignment sleeve. A typical test profile is shown in Figure 2. The average pipe-cement bond was 126 psi. As consistent with interface bonds, the bond fails at small displacements.



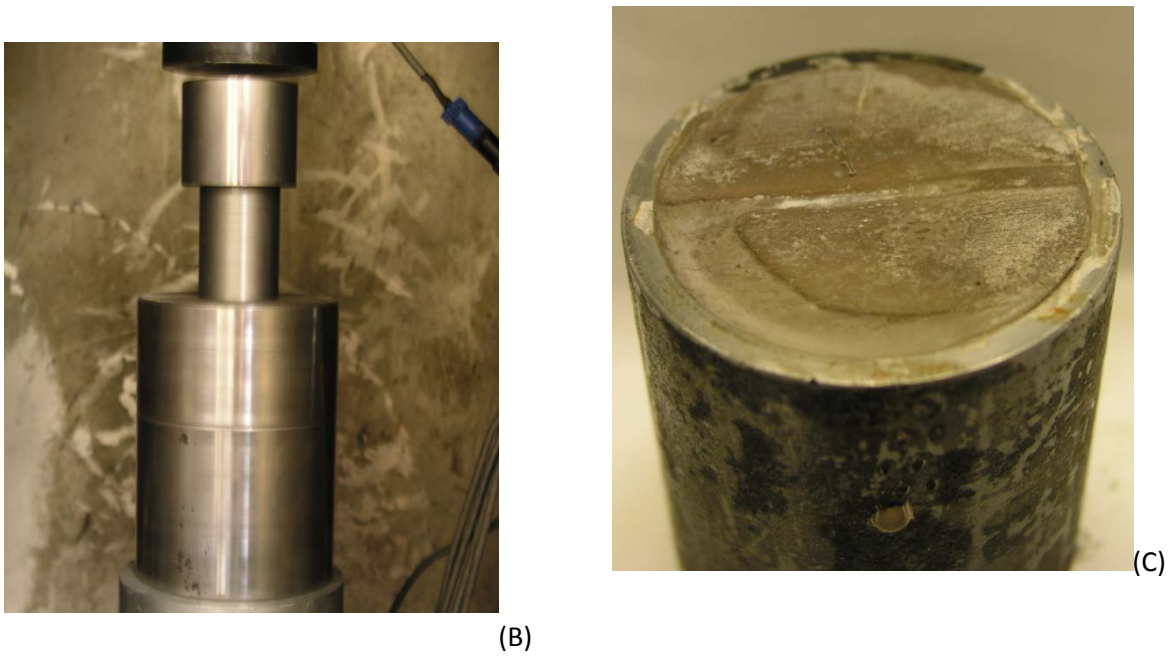


Figure 1. Test equipment and typical samples for pipe-cement bond strength measurements. (A) and (B): test apparatus. (C): Cured cement in steel pipe.

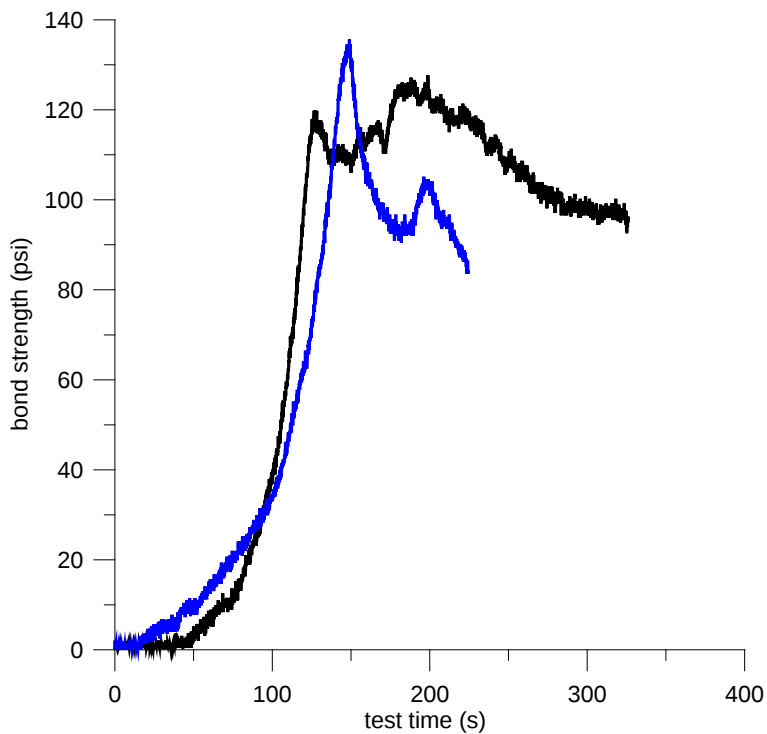


Figure 2. Typical test profile for pipe-cement bond test for Fmix1.

Fmix1 retarder influence

An inconsistency was discovered in Table 2 from the June 2013 report. The table has been updated to reflect the correct retarder concentration and is supplied below as Table 1.

Table 1. Influence of retarders on consistency and thickening times for base Fmix1.

Additives: retarders and fluid loss				time (min)		
Na GluHep	TA	FL-17	FL-24	30 Bc	70 Bc	100 Bc
0.5%	0.5%	0.75%	0.75%	166	168	168
1.0%	1.0%	0.75%	0.75%	679	715	715
0.8%	0.8%	0.50%	1.50%	448	485	485

Notes:

- 1) Na GluHep is a RussTech sodium glucoheptonate in liquid form with 51% actives.
- 2) TA: tartaric acid
- 3) FL-17 and FL-24 are fluid loss additives by Fritz Oilfield Products
- 4) Additive quantity based on weight of blend of zeolite and cement, does not include MDE or MINUSIL.

Retardation and Consistency of NM2 clinoptilolite

In this section, the response of NM2 clinoptilolite to retarders at 300°F is presented. Sodium glucoheptonate and tartaric acid were used for retardation. The results are summarized in Table 2, and Figures 3 and 4. For 40% replacements, 10 µm is used, due to high viscosity from using 5 µm particle size. As expected, as the amount of cement decreases relative to the blend volume, the effectiveness of the retarder is reduced. Typical of both replacement levels is the high level of fluctuations within the first 50 minutes. This obviously represents a zone of distinct reactivity. This will be referred to as zone 1. Depending on the retarder concentration, there will be a period of fairly stable consistency. The length of this stable zone increases with increasing retarder concentration. This stable region will be referred to as zone 2. Following zone 2, the consistency shows an initial jump in followed by a very slow, nearly linear increase. This is referred to as zone 3. The third zone represents approximately half of the total test time. Note that the consistency profiles in Figures 3 and 4 have been smoothed by using a running average with a window width between 5 and 11. This smoothing primarily is applied to the third zone as significant fluctuations were observed in the consistency. These fluctuations are interpreted as shearing of the developing gel. Zone 3 differs from the trends exhibited by the ferrierite based blends. In zone 3, the consistency tends to increase exponentially as the gel begins to develop for the ferrierite blends. Generally, the effective retardation zone in terms of pumpability will be the first two zones for the NM2 clinoptilolite.

In Table 2, the influence of the individual application of sodium glucoheptonate and tartaric acid were tested as a comparison to the combination of the two retarders. This was performed for a total retarder concentration of 0.4%. The concentration is based on the weight of the zeolite/cement blend and does not include the weight of the MINUSIL or other additives. The zeolite/cement is considered the "base blend". The sodium glucoheptonate appears to offer slightly better retardation characteristics as

compared to the tartaric acid or sodium glucoheptonate-tartaric acid combination. In Figure 3, no gelation peak was observed for the sodium glucoheptonate which is a distinct contrast to the other retardation trials. Further tests will be conducted to verify this result. If the results are verified, this suggests that the gelation peaks and fluctuations within zone 1 are triggered by a reaction with the tartaric acid.

The UCA setting profile for NM2_5µm_27.5%_MINUSIL 20%_RussTech 0.2%_TA 0.2% is shown in Figure 5. Using the transit time, the onset of strength development can be estimate to occur between six and seven hours. The mix reached 70 Bc just under four hours. Figure 5(B) shows the extended trend. Upon termination of the test, the sample was removed and the unconfined compressive strength was determined as 2552 psi. As is consistent with the zeolite cements, the measured compressive strength is approximately 2 times larger than that predicted by the "cooled" UCA compressive strength estimate. The sample likely reaches acceptable strength values by eight to ten hours.

Table 2. Retarder response for NM2 clinoptilolite.

Sample	RussTech	TA	Consistency		
			30 Bc	70 Bc	100 Bc
NM2_5µm_27.5%_MINUSIL 20%	0.1%	0.1%	65	68	79
"	0.2%	0.2%	122	228	228
"	0.3%	0.3%	243	344	353
"	0.4%	0%	143	243	267
"	0%	0.4%	108	195	217
NM2_10µm_40%_MINUSIL 20%	0.2%	0.2%	66	106	140
"	0.3%	0.3%	5, 83*	198	198
"	0.5%	0.5%	264	419	439
NM2_10µm_40%_MDE 20%_MINUSIL 20%_FL17 0.5%_FL24 1.5%	0.5%	0.5%	Note 1	94	94

RussTech: liquid form of sodium glucoheptonate

TA: tartaric acid

note 1: 30 Bc is commonly exceeded during fluctuations.

* note values of 5 and 83 min are given here as 30 Bc was exceeded at both times.

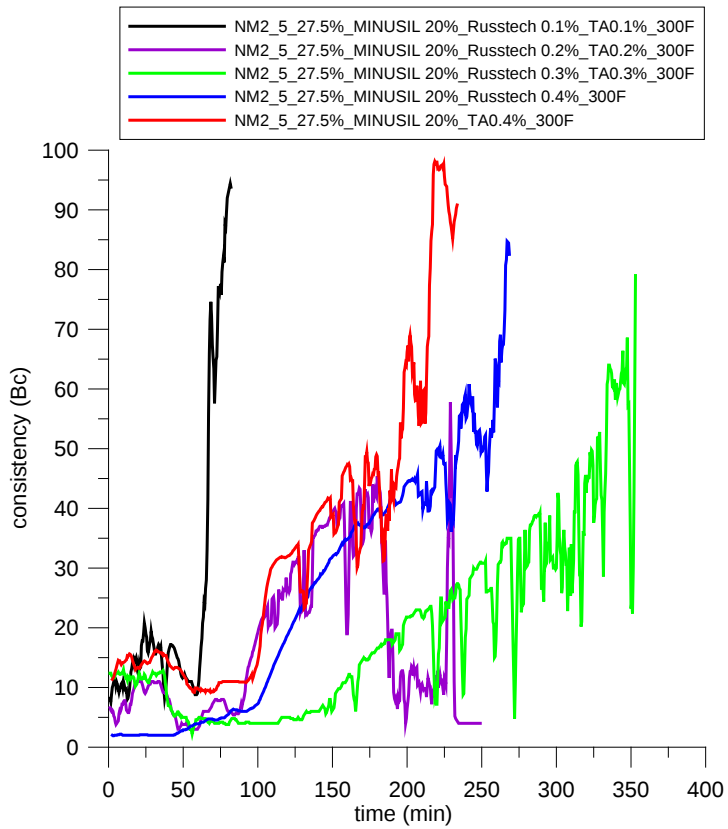


Figure 3. NM2 clinoptilolite consistency profiles at the 27.5% replacement level.

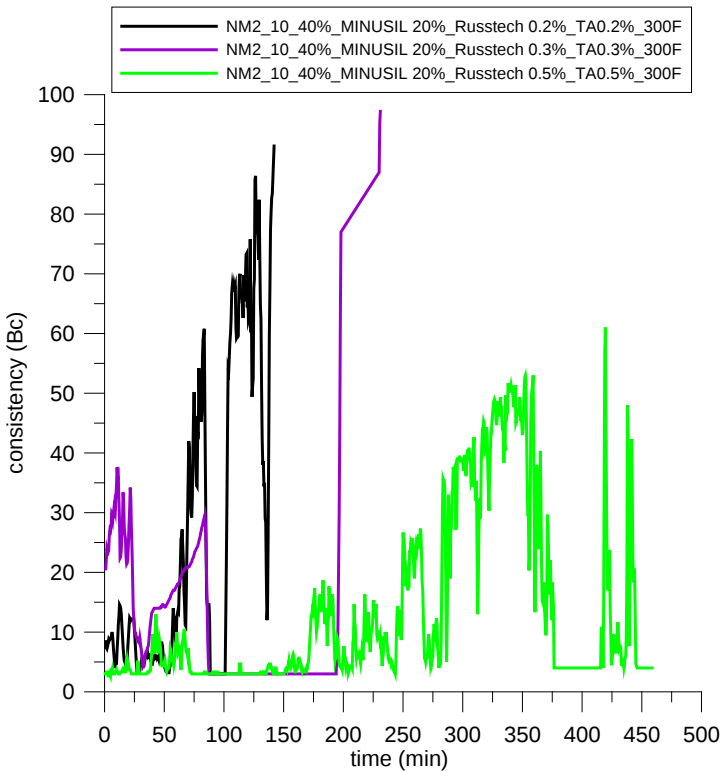


Figure 4. NM2 clinoptilolite consistency profiles at the 40% replacement level.

Lower Density Variations

As a preliminary investigation at 300°F, four simple mixes were tested at slurry density ranging between 11.5ppg and 12.0 ppg. Past experience indicates that slurries with low viscosities do not yield good strength characteristics. Based on this experience, four blends were tested which had consistencies between 10 to 25 Bc. This was achieved by high levels of zeolites, Moltan diatomaceous earth, and MINUSIL silica flour. The NM2_ferrierite blend contained a zeolite replacement of 60%. The cure time was short at 2 days. Long term results may vary significantly. The short term strength and elastic parameters show encouraging results. The samples show an increased ductile behavior as compared to the 13.5 ppg samples tested previously. Note that the blends contained no retarders or fluid loss additives. Even if the mechanical properties are encouraging, it may not be possible to obtain acceptable retardation or fluid loss characteristics. No UCA data is available at this time as the high pressure pump for the UCA needs to be repaired. After the UCA comes online, real time development of strength can be monitored. A sample of each of the blends listed in Table 3 has been placed in the Ormat/CO₂ brine for a 1 week analysis of alteration trends.

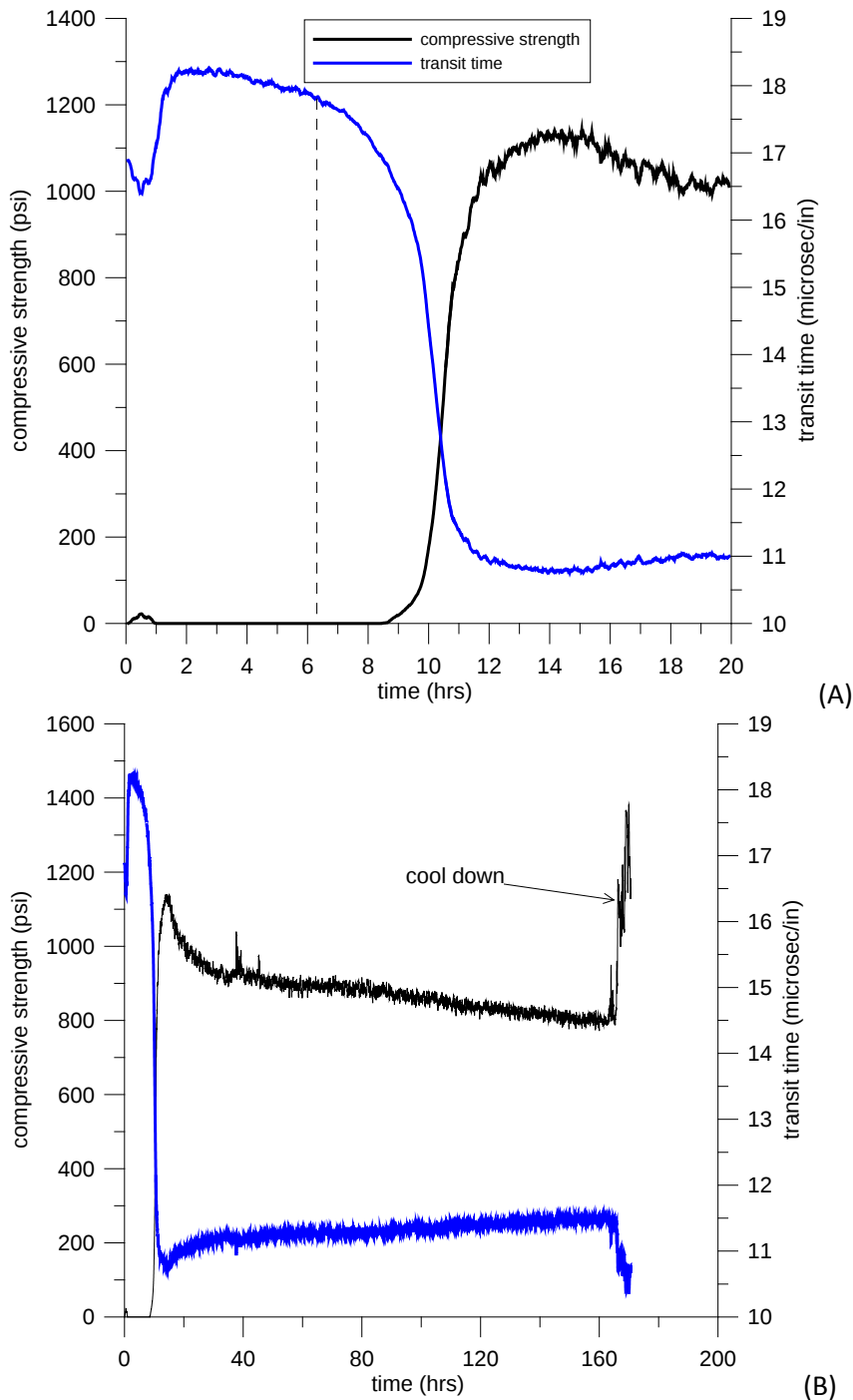


Figure 5. Setting characteristics for NM2_5_27.5%_MINUSIL 20%_RussTech 0.2%_TA 0.2%_300F. (A) First 20 hours. (B) extended trend.

Table 3. Elastic properties of high zeolite replacement test samples at 300°F for 2 days.

Sample	Density	q _u (psi)	E	ν
Ferrierite_10μm_40%_MDE 40%_MINUSIL 40%	12.0 ppg	1693	565	0.34
Ferrierite_10μm_50%_MDE 40%_MINUSIL 40%	11.5 ppg	1402	515	0.33
NM2_5μm_30%_ferrierite_5μm_30%_MINUSIL 40%	12.0 ppg	1887	665	0.33
NM2_5μm_30%_ferrierite_5μm_30%_MINUSIL 40%	11.5 ppg	1289	448	0.47

Bear River Zeolite (Clinoptilolite)

A series of tests was conducted on a clinoptilolite produced by the Bear River Zeolite company. The Bear River Zeolite company maintains a website at <http://www.bearriverzeolite.com>. The zeolite is a pale green sodium, calcium, potassium clinoptilolite a generic formula of $(\text{Na}, \text{K}, \text{Ca})_{2-3}\text{Al}_3(\text{Al}, \text{Si})_2\text{Si}_{13}\text{O} \cdot 12\text{H}_2\text{O}$. The deposit is approximately 85% clinoptilolite with the remaining amount composed of opaline (non crystalline) silica. The deposit is produced commercially for a wide range of industries. Trabits Group provided UAF with two small samples of crushed zeolite. One is referred to as "60 Cycle" Raymond Mill and other referred as Ultra Fine Mesh. The "60 Cycle" has mean particle size of 23 μm and will be referred to as BRZ60CRM. The Ultra Fine Mesh has mean particle size of 10 μm and will be referred to as BRZUFM.

The testing purpose was to perform as a small run of trial tests to obtain data regarding its general behavior. Four mixes were tested using both particle sizes at 27.5% and 40% replacement levels. An additional 20% BWOC MINUSIL (fine silica flour) was added to each mix. Sodium glucoheptonate (RussTech) was added at 0.6% BWOB for the 27.5% and 0.8% BWOB for the 40%. No fluid loss additive was added, and the samples were mixed at 13.5 ppg (1.61 g/cm³). The samples were cured in the HPHT curing chamber at 300°F and 5000 psi for 6 days. For each mix, two samples for strength and elastic properties were run, one sample for permeability tests, and one sample to be placed in the Ormat/CO₂ fluid for additional curing at 300°F. One thermal conductivity test was performed on the BRZUFM_40% mix.

Results are summarized in Table 1. Figure 1 provides images of the 1.5" cores used for strength and elastic testing along with images of the molded samples. Each one of the mixes is discussed individually below.

1) BRZ60CRM_27.5%: BRZ60CRM_27.5% shows good strength and permeability results. From Figure 1, it can be seen from the mold image that significant settling of the sample has occurred. This resulted in samples with an increased density of 1.83 g/cm³. This also indicates potential free water issues. This mix was most consistent in terms of repeatability of unconfined compressive strength and elastic modulus. The stress strain behavior was also very similar. No obvious cracking of the sample was

noticed during the curing process. The slurry was very thin and fluid which is consistent with the coarser particle size of other tested zeolites.

2) BRZ60CRM_40%: As a result of the increased zeolite content, the sample showed less settling than the BRZ60CRM_27.5%. Initial observations suggested no apparent cracking during the curing process. However, some settling did occur which also suggest potential free water issues. The density decreased to 1.71 g/cm³. The two samples showed a compressive strength range of 4538 psi to 5654 psi. The lower strength sample did develop a horizontal split during instrumentation of the sample, which may account for the lower strengths. The elastic modulus and Poisson's ratio are based on one sample. The slurry was also thin and fluid.

3) BRZUFM_27.5%. With the decrease in particle size, the degree of settling decreases as compared to the BRZ60CRM samples. This suggests lower free water issues. The smaller particle size has a higher water demand as would be expected. The density decreased to 1.68 g/cm³. With the BRZUFM particles size, micro-cracking of the molded samples was noticed. The cracking is characterized by very thin cracks. The cracks tended to be dominated by one well developed crack. Both samples tested for strength and elastic properties show a longitudinal and or a diagonal crack. The lower strength sample failed abruptly along this diagonal crack as the crack was oriented towards maximum shear. This cracked failed at approximately 1750 psi based on the stress-strain plot. The other sample also failed along the longitudinal crack. Despite the cracking, the elastic modulus appeared to be fairly consistent. Poisson's ratio was taken from the sample with the longitudinal crack. The presence of the longitudinal crack can be seen in Figure 1 by the slight dark line running along the long axis of the core.

4) BRZUFM_40%: At the 10 µm particle size and increased replacement level, increased micro cracking within the cured samples was noticeable. The density of the cracks appeared to have increased. Only one sample was tested for strength and elastic properties. The resulting elastic modulus and Poisson's ratio data were poor and hence, are not provided. The cracks were primary expressed in the sample as small wedge shaped cracks from which an example can be seen in Figure 1. The sample failed along preexisting micro cracks as well as in a tensile spalling mode. From the mold image, it can be seen that the settling of the cement slurry was minimal, which suggest minimal free water issues. The density was the lowest of the four mixes at 1.64 g/cm³. The strength is comparable to the other three mixes. A thermal conductivity test was conducted on this sample. It yielded a value of 1.39 W/m°C. For comparison the Fmix1 (ferrierite) sample had a thermal conductivity of 1.11 W/m°C at a density of 1.61 g/cm³.

Table 1. Summary of preliminary test results for the Bear River Zeolite clinoptilolite.

Sample/mix	Density (g/cm ³)	q _u (psi)	E (ksi)	ν	Permeability (mD)	Thermal cond. (W/m°C)
BRZ60CRM_27.5%	1.83	4187	1602	0.40- 0.60	0.0013	n/a
BRZ60CRM_40%	1.71	5096	1536	0.33	0.0004	n/a
BRZUFM_27.5%	1.68	2447- 4433	926	0.33	0.0020	n/a
BRZUFM_40%	1.64	4500	n/a	n/a	0.0014	1.39

The general trend indicates increased settling and free water concerns with the coarser particle size (BRZ60CRM). This is intuitive considering the coarser particle size. This same trend is observed for the ferrierite and NM2 clinoptilolite. However, the settling issues may be fixable with the right fluid loss additive or addition of a high water demand component. The BRZ60CRM samples as a whole showed less micro-cracking than the BRZUFM samples. This may result from the higher densities of the samples. Conversely, the decreasing particle size of the BRZUFM allows for the zeolites to exhibit enhanced pozzolanic activity. This potential cracking at very fine particle size and high replacement levels is not confined to the Bear River clinoptilolite. Small micro-cracks can also be observed for the ferrierite and NM2 clinoptilolite. Despite the presence of micro-cracks, the permeabilities of the cements are initially very low. It is not conclusive at this point if the micro-cracks are a characteristic of the cement, or the result of the curing process in the HPHT curing chamber. In general (i.e. with other zeolites), the same prevalence of micro cracks was not observed for UCA samples. The elastic modulus of the Bear River clinoptilolite is similar to the ferrierite mixes. This may suggest a fairly strong pozzolanic reaction during the curing process.

Initial impressions suggest that the Bear River clinoptilolite performs as well as the ferrierite and NM2 clinoptilolite. As this time we do not have data regarding the retardation characteristics of the Bear River clinoptilolite. If the economic characteristics of the deposit are appropriate, it may represent a viable alternative to the ferrierite or NM2 clinoptilolite.

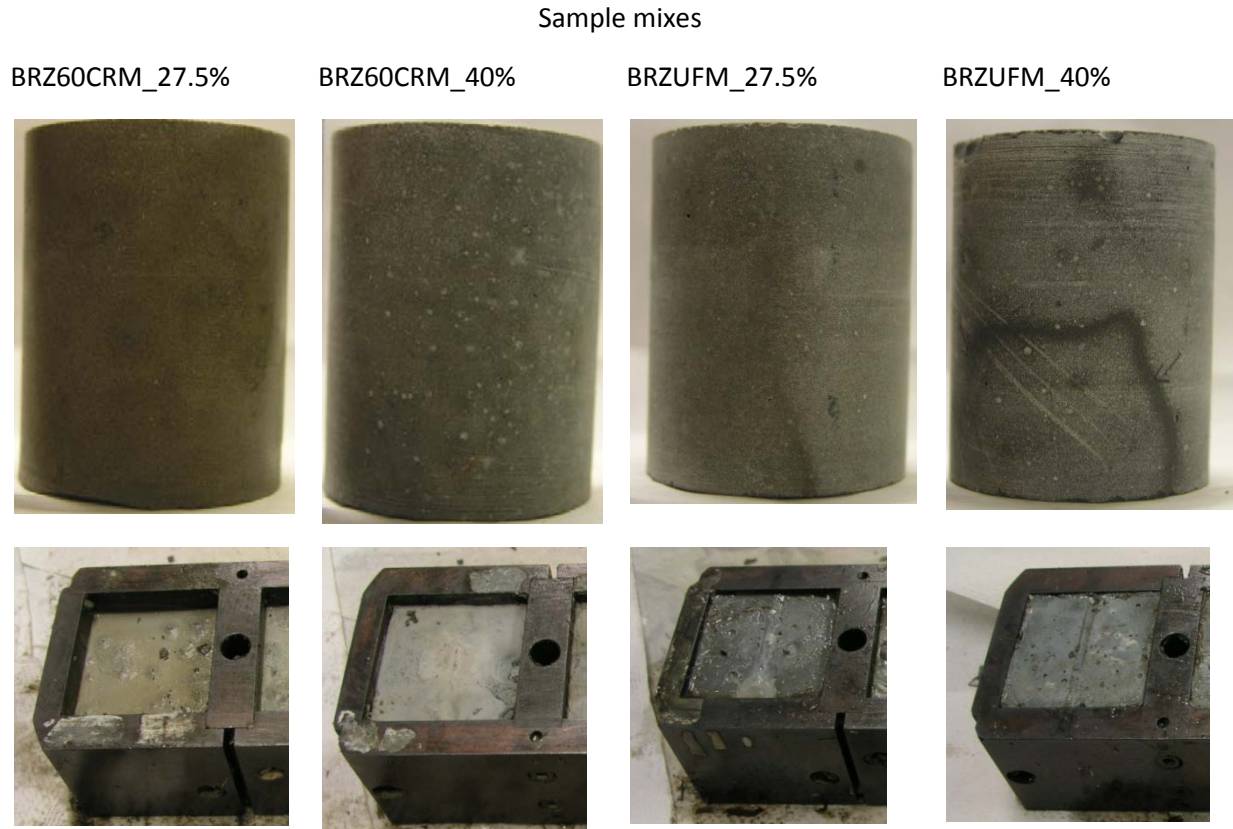


Figure 1. Images of the Bear River Zeolite trial mixes for 1.5" cores and mold characteristics.

Fmix1 400F

A batch of the Fmix1 at 400°F was prepared to define a wide range of material properties for comparison to the results obtained at 300°F. Recall that Fmix1 is defined as ferrierite_5 μ m_30%_44 μ m_10%_MDE20%BWOC_MINUSIL 20%_BWOC with retarder concentrations of 0.8%BWOB of sodium glucoheptonate (RussTech) and tartaric acid and fluid loss additives of 0.5%BWOB FL-17 and 1.5%BWOB FL-24. The results are provided in Table 2 along with a comparison to the results for 300°F. The results show a decrease in the unconfined compressive strength and tensile strength. Notice the slightly longer cure times. Past trends in the UCA suggest a peak strength early on followed by lower strengths by days 3-5. Also, trends at 400°F show lower strengths in general. Permeability is low at 0.003 mD. The other major difference is the thermal conductivity increase to 1.66 W/m°C. High silica minerals (especially quartz) are known to have a higher thermal conductivity than other minerals. The increased thermally conductivity may be related at an increased silica phase within the cement. The higher temperatures may increase the silica solubility resulting in enhanced silica reactions. Samples from this run were also placed in the Ormat/CO₂ fluid for permeability and alteration observations.

Table 2. Mechanical and material properties for mix Fmix1 at 300°F and 400°F.

Temp (°F)	Cure time (days)	Density (ppg)	Density (g/cm ³)	q _u (psi)	E (ksi)	ν	Tensile strength (psi)	Thermal conductivity (W/m°C)	Permeability (mD)
300	2	13.5	1.61	6484	1243	0.33- 0.38	990	1.11	0.005
300	3	13.5	1.61	5533	1112	n/a	572	n/a	n/a
400	5	13.5	1.62	3205	1185	n/a	341	1.66	0.003

* Many of the samples showed micro cracks likely resulting from sub-sampling.

Consistency Reaction to Polyvalent Salts

Quaternary gelation peaks are fairly common for the ferrierite and NM2 clinoptilolite retardation consistency profiles. The use of polyvalent metal salts was briefly investigated to see if they had any impact on the formation of quaternary gelation peaks (QP) or thickening time profiles. In the tests, sulfate salts were used while varying the primary cation. In each case, the cations are +2 valence charge. Using NM2_10µm_40% as base at 300°F, the retarder concentration of RussTech sodium glucoheptonate at 0.3% BWOB and tartaric acid at 0.3% BWO B was held constant while the type of polyvalent metal salt was varied. The results are shown in Table 3 and Figure 2. When compared to the 0.2%BWOB polyvalent cation additions, the base sample showed a significantly larger QP magnitudes. The addition of polyvalent cations changed the magnitude and timing of the QP. The addition of the MgSO₄ 0.2% reduce the QP to below 30 Bc. Above 30 Bc, pumping issues may arise. However the addition lowered the overall working time of the slurry. The addition of MgSO₄ 1.0% resulted in a strong QP of 49 Bc at 33 min. At 0.2% the QP was reduced. At 1.0% the QP was increased. At the 1.0% addition, the overall thickening time was significantly reduced. The addition of Zn⁺² in the form of ZnSO₄ at 0.2% significantly reduced the QP to 15Bc @ 20 min. The thickening time was extended as compared to the base and Mg⁺² additions. Physical observations as well as consistency profiles show that the ZnSO₄ addition reduced the consistency of the slurry and appeared to act as a dispersant. ZnO is known to be a strong retarder. It appears that ZnSO₄ also acts to enhance retardation ability. The last salt to be tested was ferrous sulfate (FeSO₄) in which the Fe was in Fe⁺² form instead of the common Fe⁺³ form. The QP was also reduced to 20Bc at 47 min. The ferrous salt extended the location of QP noticeably as compared to the other polyvalent salts. They slightly enhanced the overall working time. The addition or higher concentration of the zinc and ferrous sulfates was not explored at this time to see if the trend is similar to that of the magnesium sulfates.

The influence of sodium glucoheptonate (RussTech) concentration and polyvalent salt addition to ferrierite_10µm_40% are briefly presented. It was observed that in some instances, the addition of only sodium glucoheptonate (RussTech) instead of combining it with tartaric acid can help reduce quaternary

gelation peaks. Figure 3 and Table 4 present consistency data for test runs at 400°F. The use of 1.0% sodium glucoheptonate (RussTech) resulted in the presence of a strong QP. The thickening time is reduced as compared to sodium glucoheptonate (RussTech) 0.7% and tartaric acid 0.7% however. Looking to match the total retarder concentration of the combination retarder, a concentration of sodium glucoheptonate (RussTech) of 1.4%BWOB was tested. The results do not suggest a QP, however, the working time is reduced to 67 minutes from 377 minutes. This result was a bit surprising. The addition of $MgSO_4$ at 0.2%BWOB did not mitigate the QP. The QP increased to 55 Bc at 58 min. Post QP, the consistency drops to a lower level with the time. The thickening time (70 Bc) increased to 529 min or by 40%. The addition of the small amount of polyvalent metal salt greatly increased the overall thickening time. It may be possible that changing the type of cation may reduce the magnitude of the gelation peak as was observed for the NM2 clinoptilolite presented earlier.

Table 3. Consistency data in response to the addition of polyvalent metal salts.

	Quaternary gelation peak	30 Bc (min)	70 Bc (min)	100 Bc (min)
Base	42 Bc @ 13 min	103	194	216
$MgSO_4$ 0.2%	25 Bc @ 21 min	88	151	172
$MgSO_4$ 1.0%	49 Bc @ 33 min	72	118	149
$ZnSO_4$ 0.2%	15 Bc @ 20 min	120	214	244
$FeSO_4$ 0.2%	20 Bc @ 47 min	106	207	243

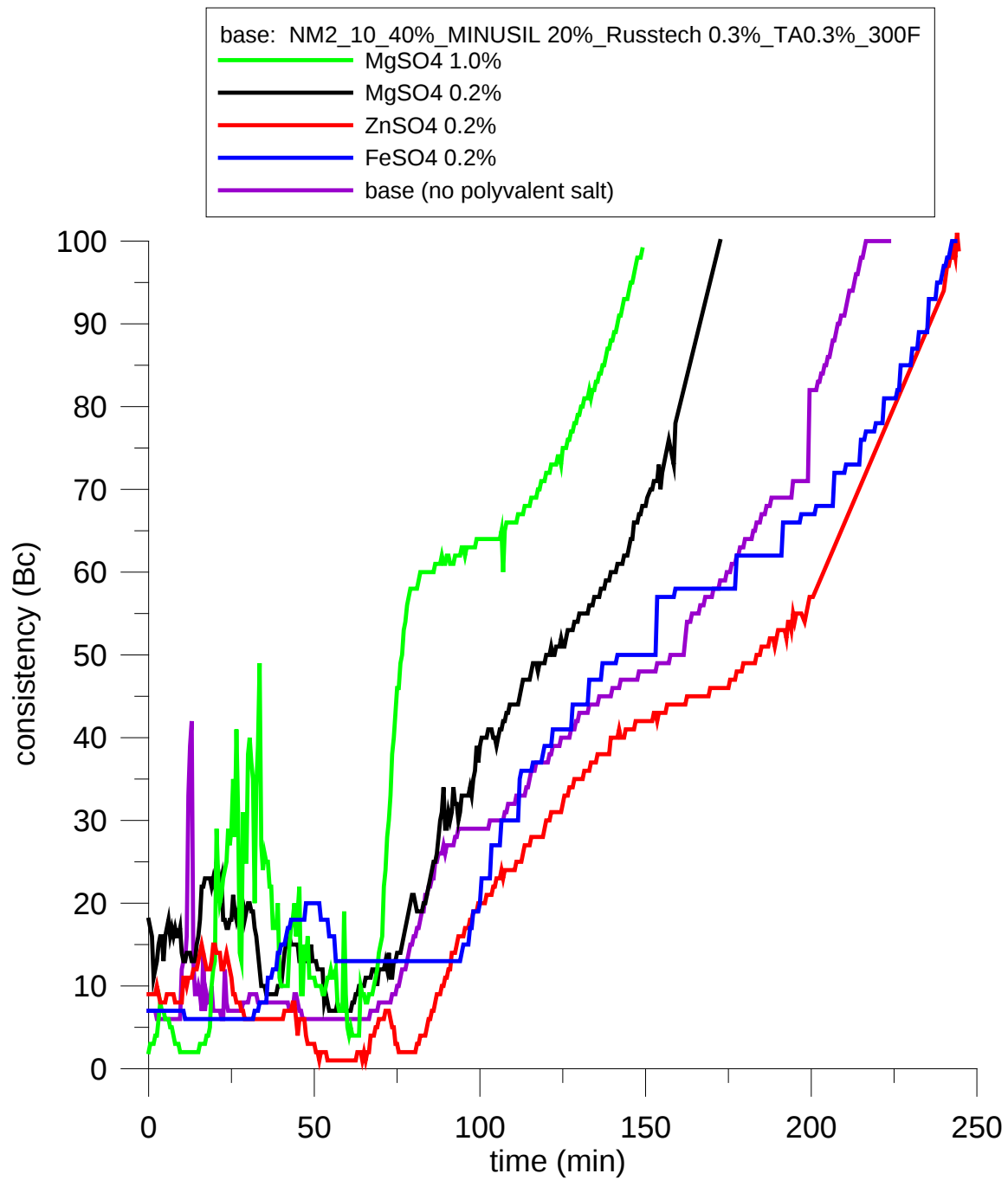


Figure 2. Consistency profiles in response to the addition of polyvalent metal salts.

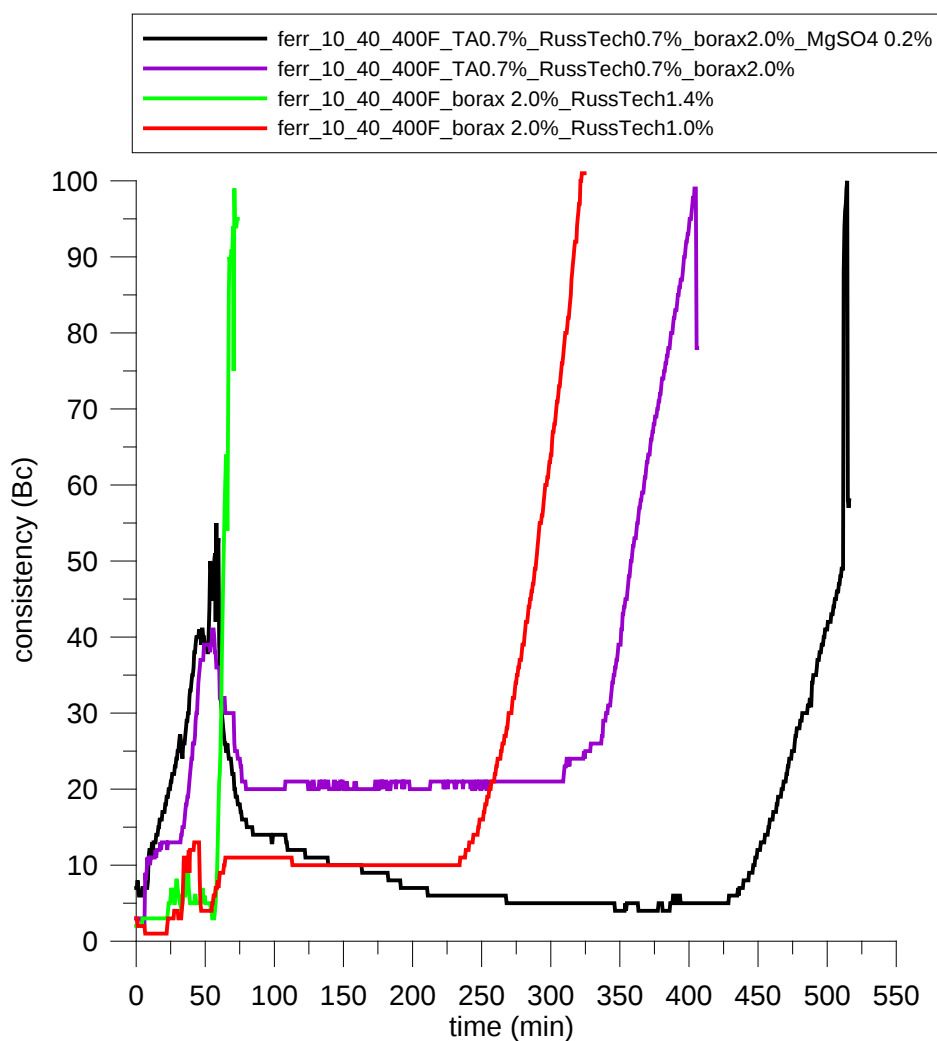


Figure 3. Influence of variations in sodium glucoheptonate and MgSO_4 on the consistency of ferrierite_{10μm_40%} at 400°F

Table 4. Consistency data for retarder variation and influence of polyvalent salts for ferrierite_{10μm_40%} at 400°F. Retarder concentration BWOB.

RussTech	TA	Borax	MgSO ₄	QP	30 Bc (min)	70 Bc (min)	100 Bc (min)
0.7%	0.7%	2.0%	0.2%	55 @ 58 min	485 min	529	547
0.7%	0.7%	2.0%	0%	41@ 55 min	340	377	404
1.4%	0%	2.0%	0%	None	61	67	71
1.0%	0%	2.0%	0%	None	270	304	322

Consistency of NM2 clinoptilolite at 400°F

Several retarder concentrations were tested for NM2 clinoptilolite at 400°F. Using the ferrierite results as a base value, retarders were applied to the NM2 clinoptilolite. Consistency profiles are shown in Figure 4. Quaternary gelation peaks are observed for both cases presented. The timing of the peaks suggest that the same reaction is responsible. The consistency predictably decreases following the QP. The profile with RusTech and tartaric acid shows that in intermediate period consistency fluctuates between 30 and 40 Bc. This is not ideal. The ferrierite samples without MINUSIL show the QP at approximately the same time period, however, they fall to a low stable consistency post QP. Also shown in Figure 4 is a ferrierite sample with diatomaceous earth, MINUSIL, and fluid loss additives. As can be seen, the ferrierite post QP consistency profiles vary from the NM2 clinoptilolite consistency profiles.

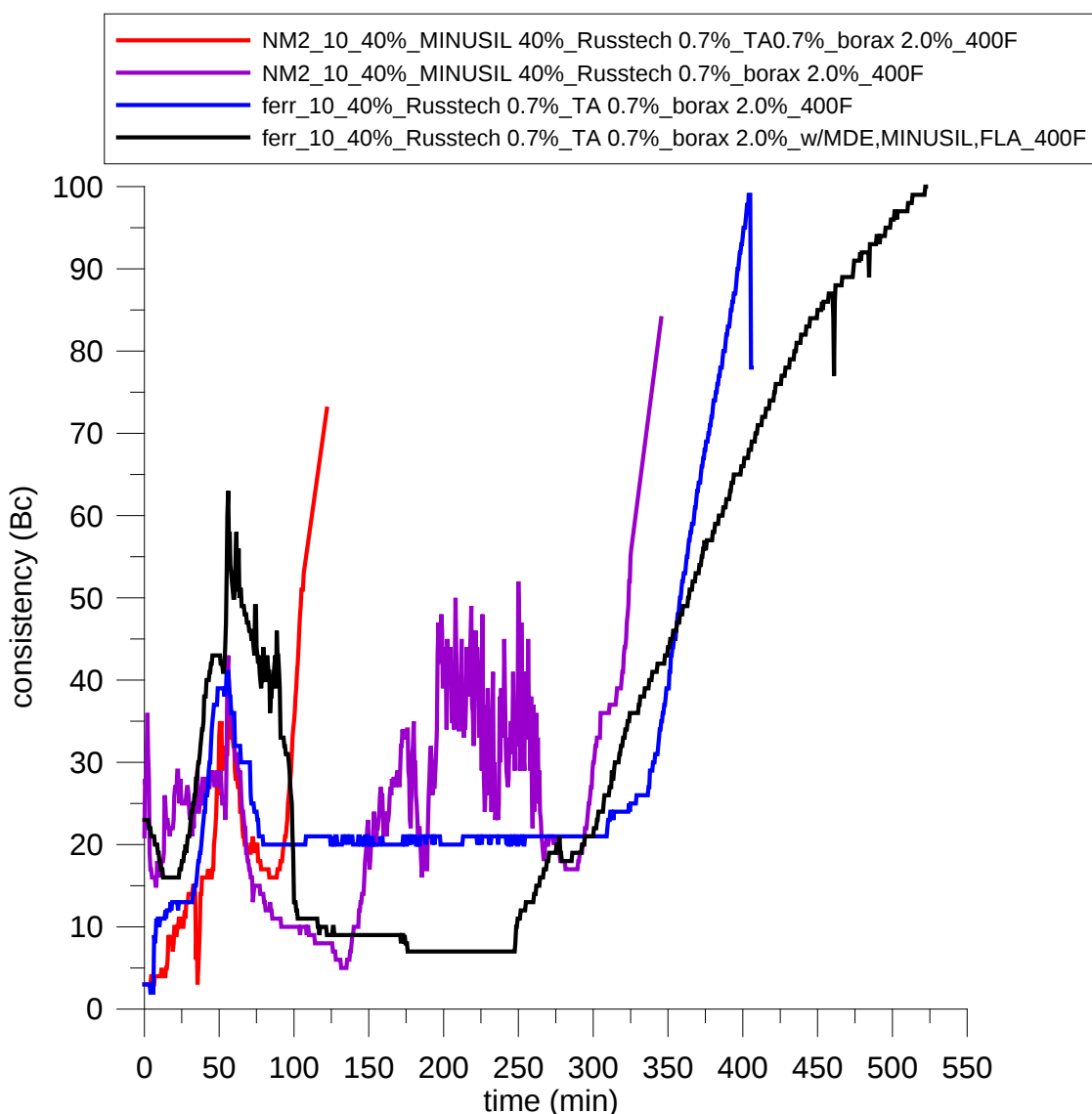


Figure 4. Consistency profiles for NM2 retardation at 400°F.

Peer Review

For Final Stage Cement Development research findings are submitted for Peer Review. The Peer Reviewer for the Project is Dr. Karen Luke. Dr. Luke's Peer Review comments during the reporting period were as follows:

"The effect of the Ormat/CO₂ is as I would expect and is similar to what we have observed with Portland cement based systems in the past. The initial reaction at 300°F. I would expect is conversion of the Ca(OH)₂ (formed on hydration of cement) to react with the carbonic acid formed on the dissolution of the CO₂ to give CaCO₃. This is what lowers the pH of the cement, from around 13, to below 10 as indicated by the phenolphthalein test. XRD would definitely show the presence of CaCO₃ in the sample. The addition of more silica flour may react with the Ca(OH)₂ in the cement to form more C-S-H binder though I doubt if it would be significant at this temperature in short time interval and also it just delays the carbonation effect. CO₂ attack start with the conversion of the Ca(OH)₂ and then it will go for the calcium in the C-S-H binder phase. One of the benefits of the ferrierite system is the reduced permeability that should stop the ingress of CO₂ though this does not appear to be happening in this case, and the second is that it forms a C-A-S-H (calcium-aluminum-silicate-hydrate) binder that may be less susceptible to attack. I would not expect to see α-C₂SH forming in short times at 300°F.

The other comment I have is on the free water, the API standard of 5.9% is purely as a QC method for the manufacturer and is based on neat cement slurries using a conical flask method as compared to a 250 mL cylinder that is used for cement blends which gives significantly less volume and the typical limit is in that case is less than 2%. They used to use a 250 mL cylinder but the volume of free water was so small that any minor differences obtained give a big difference in percentage so they adopted the conical flask method which gives larger volume of free water but more accuracy. In terms of the cement blends for use in the field the 250mL cylinder is the recommended method and values are typically less than 2.0% and preferably 0% - depends on customer and type of well, well conditions etc."

"The Ormat brine/CO₂ data definitely look good for the Fmix 1 sample cured at 300°F and it will be interesting to see how this proceeds with time. The increase in strength of the NM2_10_40%_MDE30%_SF30% with time both in the O/CO₂ and control is probably a result of the slower reaction of the SF and MDE in comparison to the MINUSIL though it is unexpected that the strength would improve in the O/CO₂ system."

"The results do show that the Bear River Clinoptilolite is a potential alternative to the ferrierite and NM2 clinoptilolite, and it would at some point be worthwhile finding out why these three have similar properties from a scientific viewpoint."

Element 1 - Laboratory Scale Demonstration

Carbonation

The influence of curing at 300°F in Ormat brine/CO₂ has been explored for the Fmix1 (ferrierite blend 40% replacement), NM2 clinoptilolite and ferrierite at the 27.5% replacement level with MINUSIL silica flour and dolomitic lime, and NM2 at the 27.5% replacement level with 20% to 40% MINUSIL silica flour. The data set for the Fmix1 is the most complete with data up to 3 weeks. Basic data for the 27.5%

replacement levels is also presented for 1 week cures. Each group of samples will be presented independently. The samples are placed in the brine from the Ormat Brawley geothermal field and pressured with CO₂. The pH of the fluid with additional CO₂ at room temperature varies from 5.8 to 6.0

Fmix1

The Fmix1 properties are summarized in Table 4. No control exists for the 3 week measurement as the initial samples cracked requiring initiation of a second run. Figures 6 and 7 depict the amount of alteration at 1 week and 3 weeks respectively. The Fmix1 at 300°F shows significant alteration when cured in a high brine/CO₂ fluid. By 3 weeks, the entire core has undergone alteration (Figure 7). The 1 week permeability is still low, despite the alteration. The 3.5 week permeability shows an increase to 0.01 mD from 0.005 mD. The permeability still meets general requirements of 0.1 mD. The strength and elastic properties are taken from 1.5" diameter cores. Permeability measurements are conducted on 1" diameter cores. The larger cores show an increase in mass at 3 weeks. On the smaller permeability cores, a 5.08% mass gain is observed at 1 week and a 3.39% mass gain at 3.5 weeks. Mass gain is based on the initial mass after 2 days of cure at 300°F. The data suggests that possible corrosion of the cement has also occurred. Likewise, the difference in mass gains may result from slight losses of material during testing of the core.

Table 4. Summary of properties of Fmix1 cured at 300°F for 1 week.

	Initial	1 week		3 week
		Ormat brine/CO ₂	Control	Ormat brine/CO ₂
q _u (psi)	6484	3968	5091	3233
E (ksi)	1243	831	933	828
v	0.33-0.38	~0.28	~0.38	~0.40
mass gain		5.5%	1.3%	~6.0%
Permeability (mD)	0.005	0.0055	0.0016	0.010

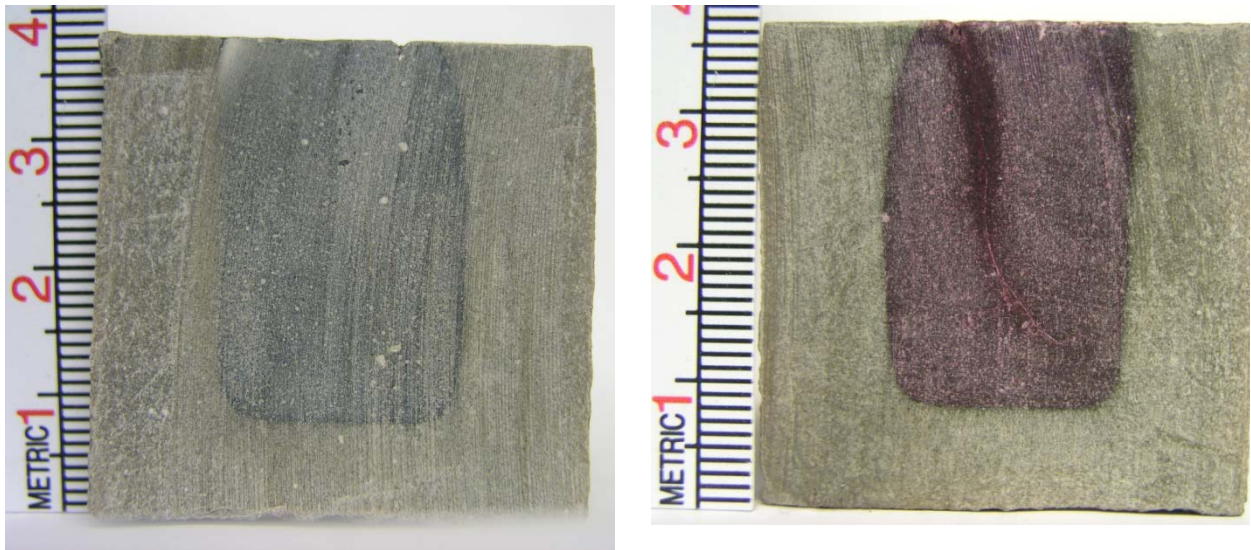


Figure 6. Fmix1, 1 week cure in Ormat brine/CO₂ showing the altered zones including natural state (left) and treated with phenolphthalein (right)



Figure 7. Fmix1, 3 week cure in Ormat brine/CO₂. Right sample is treated with phenolphthalein. No color change indicates pH < 10.

Ferrierite & NM2 at 27.5% with MINUSIL and lime

The quantity of Ca⁺² ions was increased by decreasing the amount of zeolites and adding an additional amount of hydrated lime. The rate of alteration is decreased, however, significant alteration still occurs. Unlike the Fmix1, the cement shows a significant increase in 1 week permeabilities. Basic properties are provided in Table 5. Images of the alteration characteristics at 1 week are shown in Figures 8 and 9. Only permeability measurements were taken at the 3.5 week time interval. No significant permeability increases were seen from the 1 week and 3.5 week periods. It should be noted the permeability cores contained horizontal splits, however vertical cracking was not present and therefore should not heavily influence the resulting permeability as the flow was perpendicular to the splits.

Table 5. Carbonation characteristics for ferrierite and NM2 using
5µm_27.5%_MINUSIL20%_lime20%_H_13.5ppg

	Ferrierite			NM2		
	Initial	1 week	3.5 week	Initial	1 week	3.5 week
Permeability (mD)	0.0031	0.010	0.012	0.003	0.012	0.010
mass gain	--	7.1%	--	--	7.4%	7.4%

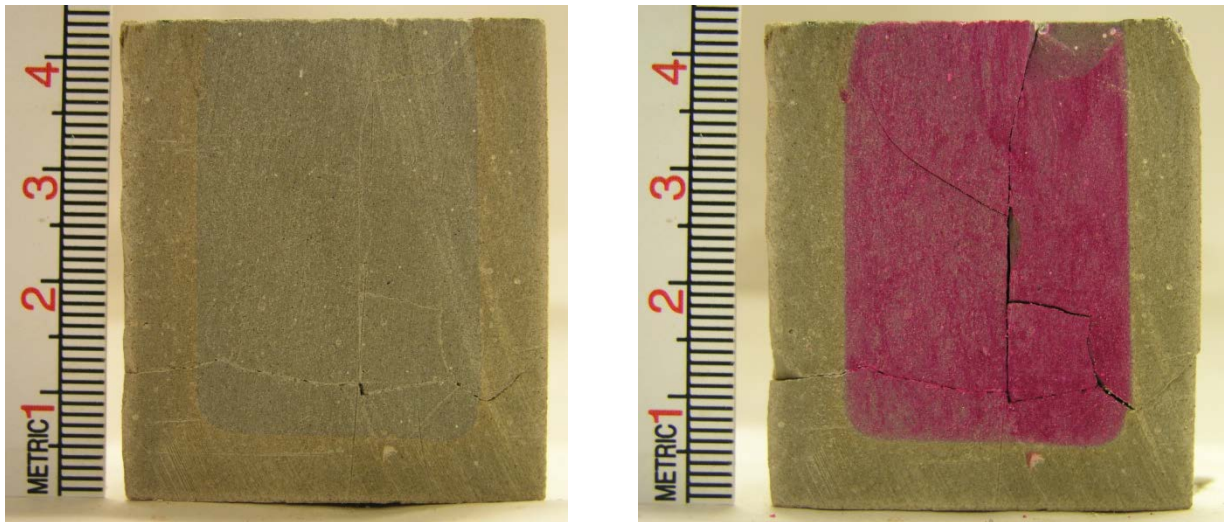


Figure 8. Ferrierite_5_27.5%_MINUSIL20%_Lime20%_13.5ppg_H. One week cure in Ormat brine/CO₂ showing the altered zones including natural state (left) and treated with phenolphthalein (right)

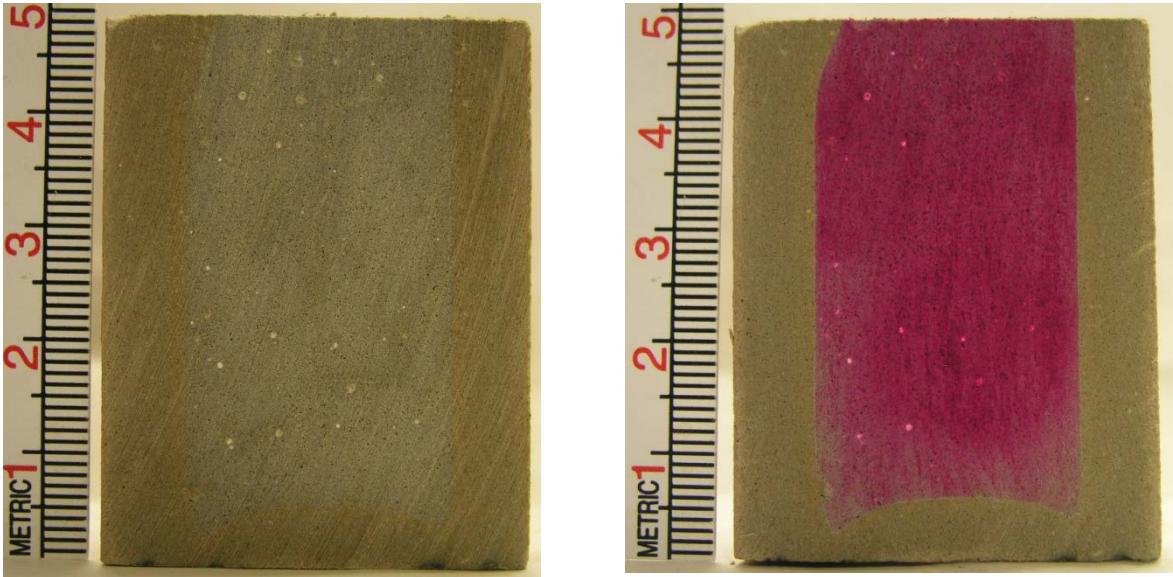


Figure 9. NM2_5_27.5%_MINUSIL20%_Lime20%_13.5ppg_H. One week cure in Ormat brine/CO₂ showing the altered zones including natural state (left) and treated with phenolphthalein (right)

NM2 at 27.5% with MINUSIL

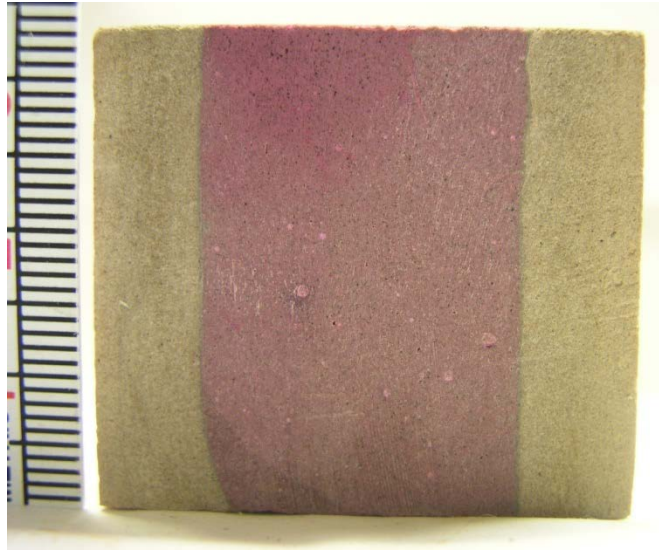
Samples of NM2_5_27.5% with MINUSIL silica flour amounts of 20% and 40% were tested at 1 week in the Ormat/CO₂ brine. Three-week data is not available. Permeability and alteration data is provided in Table 6. The degree of alteration is higher as compared to the sample with lime. The thickness of the altered rim with lime was 7.20 mm. The mass gain is less suggesting the amount of CaCO₃ formed in the lime free sample is reduced. A significant increase in permeability is seen for the 1 week sample cured in the Ormat/CO₂ fluid. The samples are still below the 0.1 mD value typically provided as an upper limit. Figures 10 and 11 provide images of the alteration of the samples.

Table 6. Carbonation characteristics for NM2_5 μ m_27.5% with variable MINUSIL silica flour at 13.5 ppg.

	NM2_5 μ m_27.5%_MINUSIL 20%	NM2_5 μ m_27.5%_MINUSIL 40%
Initial permeability (mD)	0.003	0.002
Permeability control , 1 week (mD)	0.004	0.007
Permeability Ormat/CO ₂ 1 week (mD)	0.036	0.032
Thickness of alter rim (mm)	7.85	9.00
Non altered center diameter (mm)	19.61	21.86
Mass gain (%)	5.7%	5.1%



(A)

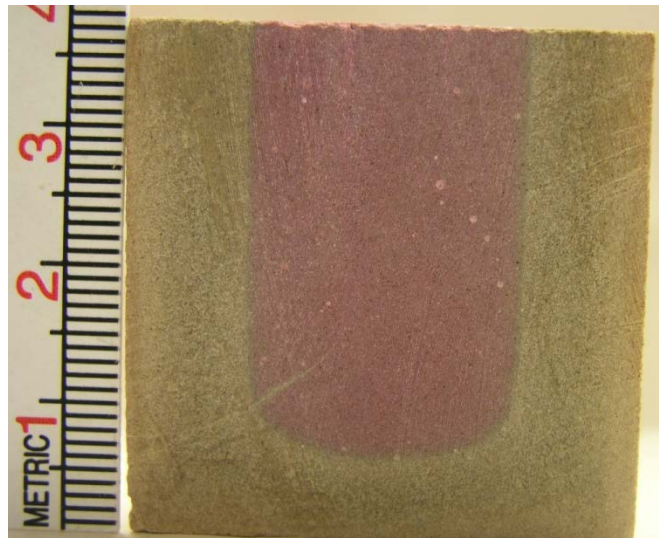


(B)

Figure 10. NM2_5 μ m_27.5%_MINUSIL 20%. (A) initial core. (B) Core cured 1 week in Ormat/CO₂ brine. Sample treated with phenolphthalein.



(A)



(B)

Figure 11. NM2_5 μ m_27.5%_MINUSIL 40%. (A) initial core. (B) Core cured 1 week in Ormat/CO₂ brine. Sample treated with phenolphthalein.

Permeability

Permeability data up to two months for sample mixes cured in Ormat/CO₂ brine and control fluids are presented in Table 5. Fmix1 is the only ferrierite based mix and contains retarders and fluid loss additives. The NM2_5_27.5% blends contain retarders, but no fluid loss additives. The NM2_10_40% blends contain retarders and fluid loss additives. The permeability along with mass gain is presented. The measurements are taken on the same cores at the specified time periods. All samples in Table 5 were initially cured for 2 days at 300°F. The samples were then placed in the Ormat/CO₂ fluid or the control fluid. Sample Fmix1_400°F was cured for 5 days at 400°F and then transferred to the Ormat/CO₂ fluid for further curing at 300°F

For Fmix1_300°F, the permeability magnitudes are on the same order for both the Ormat/CO₂ brine and the control fluid up to 2 months. The two NM2_5_27.5% mixes permeability for Ormat/CO₂ brine change little from 1 week to 2 months. Initially the 1 week control shows significantly lower permeabilities, however by 3 weeks up to 2 months, the permeabilities are on the same order of magnitude. NM2_10_40%_MINUSIL40% shows much higher permeabilities for the samples cured in the Ormat/CO₂ brine as compared to the control. The overall magnitude is similar to the other mixes cured in the Ormat/CO₂ brine. No Ormat/CO₂ brine permeability data is available for NM2_10_40%_MDE30%_SF30% as the sample was excessively soft after the initial two day cure and physically crushed during the initial permeability measurements. This sample contains diatomaceous earth and a fine silica sand (SF) rather than the micro silica flour characteristic of the MINUSIL. What is interesting about this blend is the low permeability of the 1 and 3 week control samples. The control noticeably hardened when compared to the samples cured in Ormat/CO₂ brine for alteration observations.

NM2_10µm_40% Observations

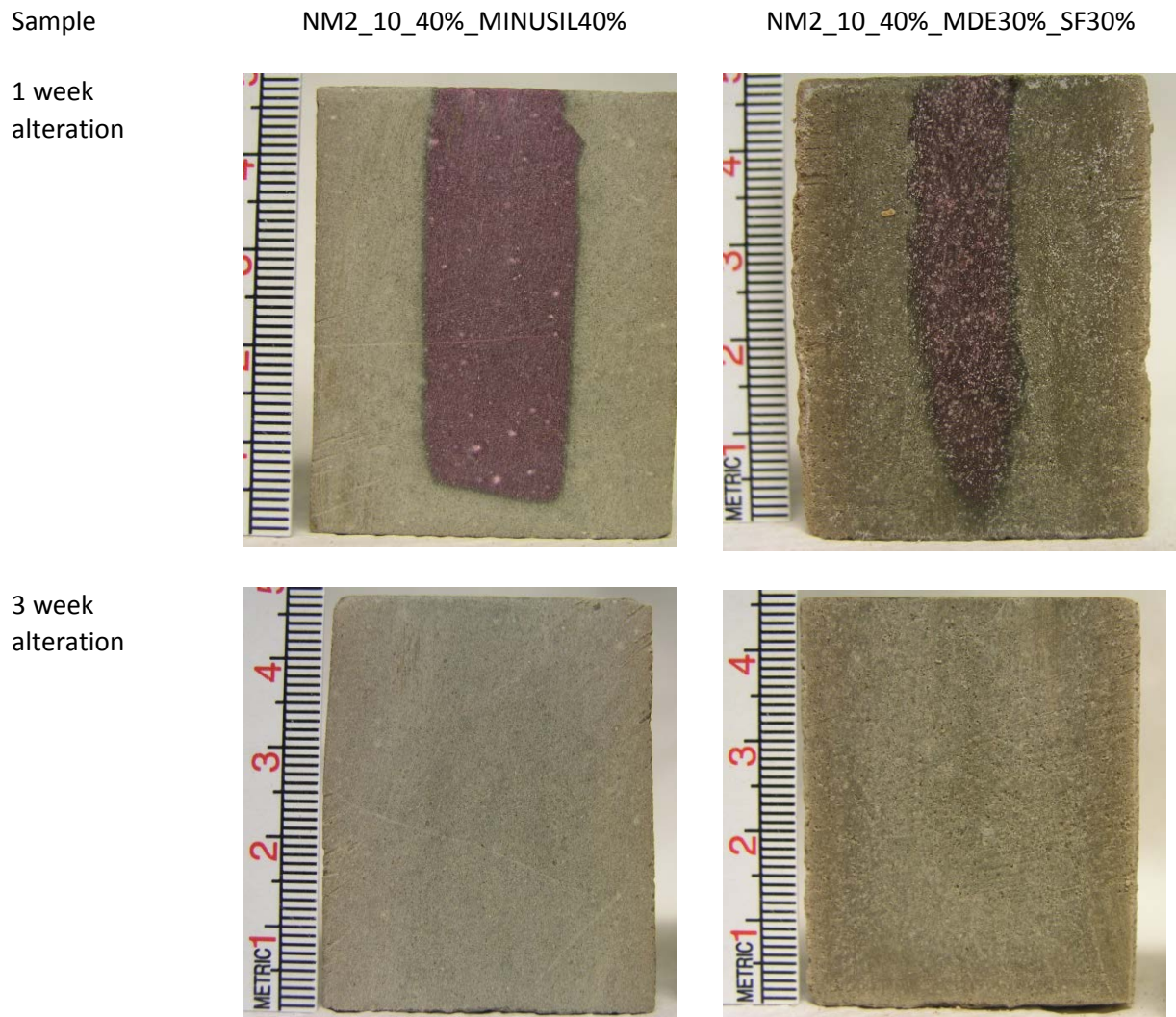
Two mixes using NM2_10µm_40% replacements were tested with varying sources of additional silica. For one sample, 40% MINUSIL BWOC was added. For the other sample, 30% diatomaceous earth (MDE) and 30% fine silica sand (SF) were added. Samples were cured at 300°F for two days. Retarders and fluid loss additives were added to each mix. The permeability data was presented earlier for these samples. In this section alteration observations and strength properties are discussed.

Table 5. Permeability and mass gain data for samples cured in Ormat/CO₂ brine and controls.

		Base	1 week		3 week		2 months	
			O/CO ₂	control	O/CO ₂	control	O/CO ₂	control
Fmix1_300°F	k (mD)	0.005	0.006	0.002	0.010	0.048	0.036	0.016
	Mass gain (%)	--	5.08	0.68	3.39	1.14	1.46	1.05
NM2_5_27.5%_MINUSIL20%	k (mD)	0.003	0.036	0.004	0.028	0.016	0.036	0.016
*	Mass gain (%)	---	5.94	0.32	1.86	-0.11	0.81	0.03
NM2_5_27.5%_MINUSIL40%	k (mD)	0.002	0.032	0.007	0.025	0.043	0.033	0.013
	Mass gain (%)	--	6.66	0.70	6.09	0.72	6.53	0.45
NM2_10_40%_MINUSIL40%	k (mD)	0.002	0.012	0.002	0.021	0.0003	n/a	n/a
	Mass gain (%)	--	5.19	1.23	2.98	0.94	n/a	n/a
NM2_10_40%_MDE30%_SF30%	k (mD)	0.016	n/a	0.002	n/a	0.0004	n/a	n/a
	Mass gain (%)	--	--	0.82	--	0.64	--	--
Fmix1_400°F	k (mD)	0.003	0.013	--	--	--	--	--
	Mass gain (%)		3.89	--	--	--	--	--

note: k is the permeability in milliDarcies. * mass gain for NM2_5_27.5%_MINUSIL20% for 3 week and 2 months are likely underestimates due to loss of small portion of core due to chipping.

Images of the alterations for the NM2_10 μ m_40% blends are shown in Figure 5. Both blends shown significant alteration by 1 week. NM2_10_40%_MINUSIL40% alteration zones extends approximately 10.8 mm into the sample. The alteration zone for NM2_10_40%_MDE30%_SF30% extends approximately 12.2 mm. Along the outer edge of this sample, a 0.6mm zone exists which is light tan in color. The 3 week post crushing photo shows that this zone distinctly separates from the rest of the sample. The thickness of this zone at 3 weeks is approximately the same as at 1 week. This zone is consistent with carbonation sheath. We see a slight alteration on the outer most portion of the core for NM2_10_40%_MINUSIL40%, however it shows not distinct mechanical weakness. This is typical of the other samples tested. Only NM2_10_40%_MDE30%_SF30% blend has shown this detachment layer. By 3 weeks, the entire core shows alteration as is consistent with previous samples. Permeability data does not change significantly from 3 weeks to 2 months for other blends. This may suggest that this alteration becomes stable.



3 week post
crushing.



Figure 5. One to three week alteration images. The alteration photos for 1 and 3 week samples are treated with phenolphthalein.

Strength data for the two blends are provided in Table 6. The data was taken as the base two-day cure and the 3-week cure in the Ormat/CO₂ fluid and the control fluid. Initially the NM2_10_40%_MINUSIL40% show high strengths. A significant reduction in strength is observed for the Ormat/CO₂ fluid as compared to the control. The post deformation photo in Figure 5 shows the brittle failure tendencies for the blend. The NM2_10_40%_MDE30%_SF30% blend initially after 2 days was extremely weak and easily deformable. This same blend crushed during permeability testing with a confining pressure of 400 psi. This agrees fairly well with the unconfined compressive strength of 642 psi, which is an average value. One of the samples failed at 406 psi. Significant strength gains are observed by three weeks for both the Ormat/CO₂ fluid and the control. The Ormat/CO₂ fluid cured sample showed lower strengths than the control. The post deformation photo in Figure 5 shows that the sample fails in a more ductile mode than the NM2_10_40%_MINUSIL40% sample. The 3 week strength and elastic properties are based off of one sample. The presence of discontinuities can potentially skew the results. NM2_10_40%_MINUSIL40% samples occasionally exhibit micro cracks. These micro cracks may also influence the resulting behavior.

Table 6. Strength and elastic properties for NM2_10µm_40% blends cured at 300°F.

	NM2_10_40%_MINUSIL40%			NM2_10_40%_MDE30%_SF30%		
	2 day (base)	3 week O/CO ₂	3 week control	2 day (base)	3 week O/CO ₂	3 week control
q _u (psi)	4701	1436	3829	642	1688	3036
E (ksi)	905	423	753	224	492	1389
ν	?	0.34	0.42 ?	0.29	0.23	?

? Indicates unrealistic Poisson's ratio values or questionable values.

Fmix1 300°F

Table 7 updates the strength and elastic properties through 3 weeks. The control for 3 weeks was added. The data suggest that minimal difference in terms of strength is observed between the 3 week Ormat/CO₂ cured sample and the control. The permeability data also suggest a similarity between the two curing mediums.

Table 7. Summary of properties of Fmix1 cured at 300°F for 1 week.

		1 week		3 week	
	Initial	Ormat brine/CO ₂	Control	Ormat brine/CO ₂	Control
q _u (psi)	6484	3968	5091	3233	3652
E (ksi)	1243	831	933	828	556
ν	0.33-0.38	~0.28	~0.38	~0.40	0.27

NM2_10µm_40%_MINUSIL 20%_SF20%: Properties

A mix using New Mexico 2 clinoptilolite was tested to define a wide arrange of material properties. The basic mix is defined as NM2_10µm_40%_MINUSIL 20%BWOC_ SF20%BWOC. MINUSIL is a 40µm silica flour. SF is a coarse silica flour with an average particle size of 150µm. Sodium glucoheptonate (RussTech) was at added as a retarder at 0.8%BWOB. Fluid loss additives FL-17 and FL-24 were added at 1.0%BWOB each. This quantity is sufficient to limit the API fluid loss <100 cc/30 min for the zeolite blends at 300°F. The results are shown in Table 1. The results for the ferrierite mix with a 40% replacement with similar retarder and fluid loss additive quantities (@ 300°F) are reproduced in Table 2 for comparison.

The coarse silica flour (SF) when added to a blend, acts to as a thinner as it has a minimal water demand. The mix was visually less thick then the other 40% replacements that have been tested to date. However, settling and free water do not appear to be an issue. Images of the cored cement and mold are shown in Figure 1. The primary purpose of testing this mix was to see if the addition of extra water and slower reacting silica would help with the development of micro-cracks during the curing process. No obvious micro-cracks were observed in the cured cubes or during the sub sampling process. The samples were noticeably "softer" than the ferrierite and NM2 clinoptilolite at 40% replacement levels containing the MINUSIL silica source. In the August 2013 report, results for NM2_10µm_40%_MDE30%BWOC_SF30%BWOC. This mix is similar to the mix presented in this section. That mix was initially fairly soft, however, the sample continue to gain strength (based on hardness) up to 2 months in the control curing environment. The control cure is conducted in water with no heavy brine or CO₂ added. It is anticipated this mix will also continue to gain strength. In a heavy brine/CO₂ environment, the slower curing nature of the blend may lead to a distinct separation rim as occurred with NM2_10µm_40%_MDE30%BWOC_SF30%BWOC. Visually, the coarser silica flour was readily apparent within the cement paste matrix. The increased thermal conductivity is likely due to the increased crystalline silica content.

Table 1. Mechanical and material properties for NM2_10µm_40%_MINUSIL 20%_SF20% at 300°F.

Temp (°F)	Cure time (days)	Density (g/cm ³)	q _u (psi)	E (ksi)	ν	Tensile strength (psi)	Thermal conductivity (W/m°C)	Permeability (mD)	Pipe bond (psi)
300	6	1.61	2035	980	n/a	248	1.52	0.005	409

Table 2. Mechanical and material properties for mix Fmix1 at 300°F and 400°F.

Temp (°F)	Cure time (days)	Density (g/cm ³)	q _u (psi)	E (ksi)	ν	Tensile strength (psi)	Thermal conductivity (W/m°C)	Permeability (mD)
300	2	1.61	6484	1243	0.33-0.38	990	1.11	0.005
300	3	1.61	5533	1112	n/a	572	n/a	n/a
400	5	1.62	3205	1185	n/a	341	1.66	0.003

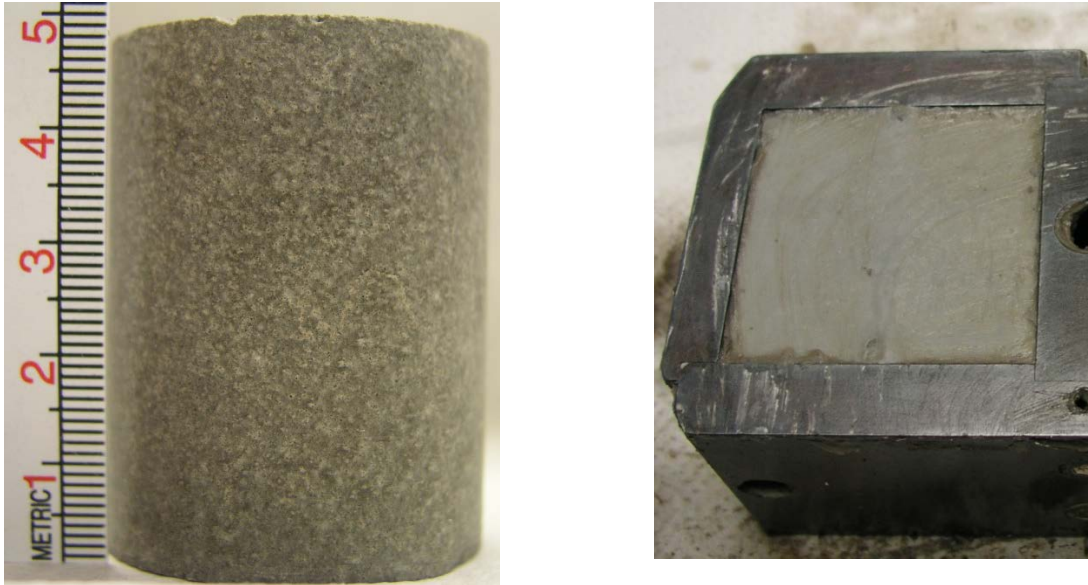


Figure 1. Images depicting a cored sample and the characteristics of the cured cube within the mold.

Permeability

The final updated permeability data is provided in Table 3. Several observations have been extended to 3 months. For Fmix1_300°F (i.e. a ferrierite 40% blend) the permeability changed little through 3 months. By three months, the control sample showed low permeability. The NM2_5_27.5%... blends show a slight increase in permeability by 3 months. The control shows a progressive decrease. The permeability for NM2_10_40% ... and Fmix1_400°F blends are consistent with previous mixes for samples cured in the Ormat/CO₂ and control. Permeability data up to 3 weeks for the Bear River Zeolites (BRZ) cured in the Ormat Brawley brine/CO₂ is provided. Through 3 weeks the permeability is consistent with the other blends for the 40% replacements. For BRZ60CRM_27.5%.. the permeability remained fairly high at 0.097 mD despite being the most dense of the mixes.. The adopted criterion for the lower limit on permeability is 0.1 mD.

Fmix1 Mechanical Properties (Update)

Recall Fmix1 is a ferrierite based blend at 40% replacements levels containing diatomaceous earth and MINUSIL. Samples for long term testing of 3 months were placed in three curing environments. Two samples were placed in the Ormat Brawley brine/CO₂ (i.e. O/CO₂) fluid, two samples were placed in water/CO₂ fluid, and two samples were placed in water and pressured with nitrogen gas (i.e. control). Attempts were made to measure the unconfined

compressive strength (q_u), modulus of elasticity, and Poisson's ratio. Added to this section is Fmix1 cured at 400°F for 5 days and transferred to the O/CO₂ fluid and cured for an additional month at 300°F. The results for all cases are shown in Tables 4 and 5. By one week through three months, the unconfined compressive strength for the samples cured in the O/CO₂ fluid remained fairly constant with a slight progressive decrease in the elastic modulus. As discussed later, the overall phases are fairly consistent throughout that time period. The permeability data also indicates fairly stable properties over that time period. The control shows a drop in strength from the initial cure through three weeks. Through 3 months, a noticeable strength gain is observed back to the one week level. This same trend can also be observed from the permeability data. The one week and 3 month control permeability is lower than those measured at three weeks and 2 months. The sampled cured in water/CO₂ shows a slightly smaller compressive strength and modulus of elasticity than that cured in the brine based O/CO₂ fluid. However, the results are within normal testing variability and therefore are not significant. Visual observations do indicate that the outer surface of the water/CO₂ cured samples is softer than the O/CO₂ cured samples. The soft layer is approximately 1 mm in thickness. From the XRD data presented later in the report, the sample cured in the water/CO₂ fluid contains more calcite. It is likely this outer rim is a calcite based rim. The Fmix1_400°F cured initially at 400°F for 5 days and then transferred to the O/CO₂ fluid shows significantly greater strength loss than the Fmix1_300°F samples. This must relate to the initial cure time at 400°F. The reason for this variability is not well known.

Table 3. Permeability and mass gain data for samples cured in Ormat/CO₂ brine and controls.

			Base	1 week		3 week		2 months		3 months	
				O/CO ₂	control	O/CO ₂	Control	O/CO ₂	contro l	O/CO ₂	contr ol
Fmix1_300°F	k (mD)	0.005	0.006	0.002	0.010	0.036	0.016	0.016	0.014	0.0004	
	Mass gain (%)	--	5.08	0.68	3.39	1.46	1.05	1.05	1.61	0.91	
									2.5 months		
NM2_5_27.5%	k (mD)	0.003	0.036	0.004	0.028	0.036	0.016	0.016	0.043	0.014	
— MINUSIL20%	Mass gain (%)	---	5.94	0.32	1.86	0.81	0.03	0.03	0.43	0.16	

*										
NM2_5_27.5%	k (mD)	0.002	0.032	0.007	0.025	0.033	0.013	0.013	0.048	0.009
MINUSIL40%	Mass gain (%)	--	6.66	0.70	6.09	6.53	0.45	0.45	6.08	0.45
							1.5 months			
NM2_10_40%	k (mD)	0.002	0.012	0.002	0.021	0.0003	0.023	0.0008	--	--
MINUSIL40%	Mass gain (%)	--	5.19	1.23	2.98	0.94	2.01	0.81		
NM2_10_40%	k (mD)	0.016	n/a	0.002	--	0.0004	--	0.0005	--	--
MDE30%_SF30%	Mass gain (%)	--	--	0.82	--	0.64	--	0.75	--	--
					1 month					
Fmix1_400°F	k (mD)	0.003	0.013	--	0.021	--	--	--	--	--
	Mass gain (%)		3.89	--	2.54	--	--	--	--	--
			2 week		3 week					
BRZ60CRM_27.5%_MINUSIL20%	k (mD)	0.0013	0.083	--	0.097	--	--	--	--	--
	Mass gain (%)		5.31	--	6.63	--	--	--	--	--
BRZ60CRM_40%_MINUSIL20%	k (mD)	0.0004	0.017	--	0.006	--	--	--	--	--
	Mass gain (%)		5.47	--	6.08	--	--	--	--	--
BRZUFM_27.5%_MINUSIL20%	k (mD)	0.002	0.055	--	--	--	--	--	--	--
	Mass gain (%)		7.23	--	--	--	--	--	--	--

BRZUFM_40	k (mD)	0.001	0.013	--	0.01	--	--	--	--	--
%_MINUSIL		4			4					
20%	Mass gain (%)		5.32	--	4.10	--	--	--	--	--

notes:

- 1) k is the permeability in milliDarcies.
- 2) mass gain for NM2_5_27.5%_MINUSIL20% for 3 week and 2 months are likely underestimates due to loss of small portion of core due to chipping.
- 3) Base measurements for Bear River Zeolite (BRZ...) were taken at 6 days cure.

Table 4. Summary of mechanical properties of Fmix1 cured at 300°F

Cure medium/time	q _u (psi)	E (ksi)	v
Initial cure; 2 days (medium water)	6484	1243	0.33-0.38
1 week; Ormat Brawley Brine/CO ₂	3968	831	~0.28
1 week; control	5091	933	~0.38
3 week; Ormat Brawley Brine/CO ₂	3233	828	~0.40
3 week; control	3652	556	0.27
3 month; Ormat Brawley Brine/CO ₂	3696	654	0.29
3 month; water/CO ₂	3494	642	0.24
3 month; control	4817	1553	? (data high, structural control on results)

Table 5. Summary of mechanical properties of Fmix1 cured initially at 400°F.

Cure medium/time	q_u (psi)	E (ksi)	ν
Initial cure; 5 days (medium water)	3205	1185	n/a
1 month; Ormat Brawley Brine/CO ₂	1523	n/a*	n/a*

* transducer malfunction.

Bear River Zeolites: Carbonation Observations

In this section, we provide a brief discussion of carbonation characteristics for the Bear River Zeolites (BRZ). Mechanical properties of the four tested BRZ samples were reported in August 2013 report. Recall the BRZ was tested at two particle size. The "60 Cycle" has mean particle size of 23 μm and will be referred to as BRZ60CRM. The Ultra Fine Mesh has mean particle size of 10 μm and will be referred to as BRZUFM. To each replacement, an additional 20% BWOC MINUSIL (fine silica flour) was added to each mix. Sodium glucoheptonate (RussTech) was added at 0.6% BWOB for the 27.5% and 0.8% BWOB for the 40%. No fluid loss additives were added. The samples were cured in the HPHT curing chamber at 300°F and 5000 psi for 6 days. One sample of each mix was placed in a cylinder containing Ormat Brawley brine and pressurized with CO₂. The samples were allowed to cure for an additional 11 days at 300°F. No mechanical property data was obtained for the BRZ cured further in the Ormat/CO₂ system.

Figures 2 and 3 show the extent of alteration of the BRZ60CRM and BRZUFM blends. The images on the right are treated with phenolphthalein. Coloration indicates $\text{pH} > 10.0$. Note that due to settling affects, the measured density of the different blends was 1.83 g/cm³, 1.71 g/cm³, 1.68 g/cm³, 1.64 g/cm³ for BRZ60CRM_27.5%, BRZ60CRM_40%, BRZUFM_27.5%, and BRZUFM_40% respectively. The target density was 1.61 g/cm³.

The depth of alteration and corresponding permeability are provided in Table 6. The depth of alteration appears to be strongly controlled by sample density. The data does not allow for isolation of the impacts of density, particle size, and replacement level. It would be expected that the 27.5% replacement levels would have lower overall alteration depths due to the increased Ca⁺² content. The BRZUFM samples have a similar overall density. The depth of alteration is higher for the 40% replacement as compared to the 27.5% replacement. The permeability data does show trends when comparing the replacement levels. The 27.5% replacement level for both particle sizes show permeabilities which are 4 to 5 times higher than the 40% replacement level. This appears to be an effect of the replacement level rather than density and depth of alteration. BRZUFM_27.5% has a significantly higher permeability than BRZ60CRM_40% despite showing a lower density and increased alteration depth. The highest density sample shows the highest permeability (i.e. BRZ60CRM_27.5%). The initial permeability was similar for all four blends (See Table 3). The measured permeabilities are relative in that they represent the alteration zone and the non-altered core. Each core has a diameter of

~25 mm. The differences in permeability are likely due to the non altered core of each sample. XRD data does indicate that the alteration is primarily characterized by various phases of CaCO_3 .

Overall, the carbonation characteristics of the Bear River Zeolites (clinoptilolite) are very consistent with the ferrierite and NM2 clinoptilolite. This consistency applies to alteration depths, permeability, and mass gains.

Table 6. Summary of carbonation effects for BRZ (Bear River Zeolite)

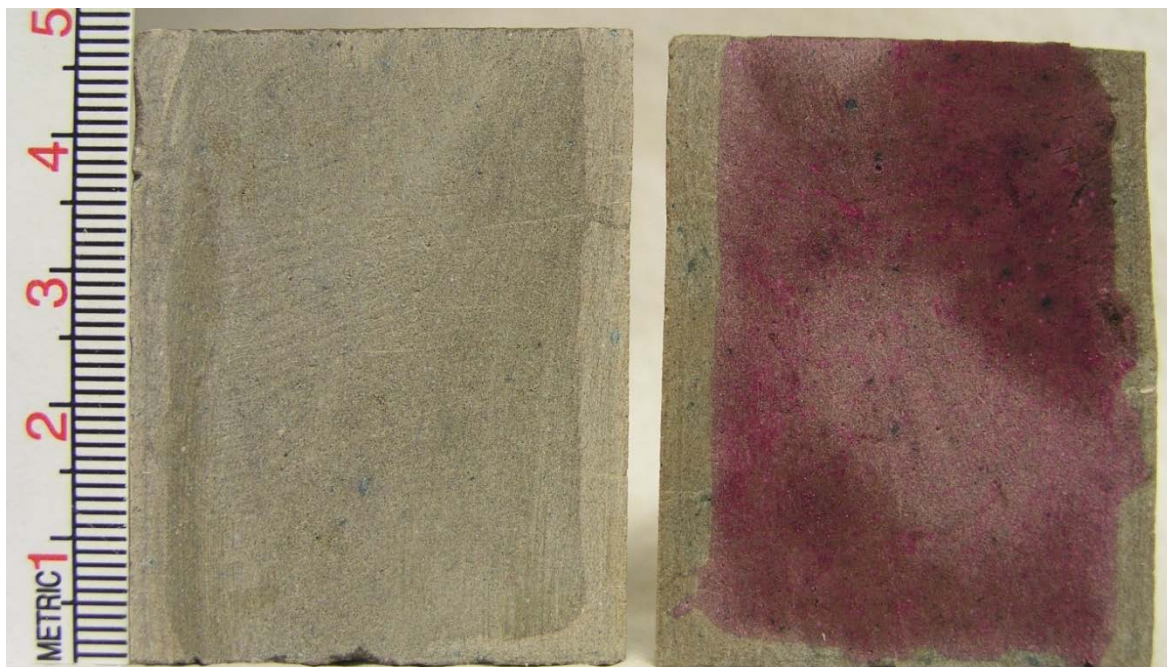
	Density (g/cm^3)	Depth of alteration (mm)	Permeability (mD)
BRZ60CRM_27.5%_MINUSIL20%	1.83	3.31	0.083
BRZ60CRM_40%_MINUSIL20%	1.71	5.15	0.017
BRZUMF_27.5%_MINUSIL20%	1.68	5.92	0.055
BRZUFM_40%_MINUSIL20%	1.64	7.42	0.013

Powdered X-Ray Diffraction: Phase Analysis

Powdered x-ray diffraction (pxrd) tests were conducted on cement pastes at various cure intervals. Each cement paste was crushed and soaked in acetone to cease hydration. The samples were then oven dried at 45°C and stored in sealed containers. Each sample was then crushed with a mortar and pestle and separated through a $125\ \mu\text{m}$ sieve to insure uniform particle size. The samples were run on PANalytical X'Pert MRD devise. Diffraction patterns were made using Cu k-alpha radiation. In this section, we will present a cross section of the pxrd results with a focus on Fmix1_300°F in which 2 day, 1 week, 3 week, and 3 month observation were made.

Cement pastes from 2 days, 1 week, 3 week and 3 months were tested for samples cured in the Ormat Brawley brine/ CO_2 medium and the control (water). The results are shown in Figure 4. Figure 4 shows both the pxrd patterns for the control samples and the samples cured in the O/ CO_2 . Also shown is the pxrd pattern for 3 months in a water/ CO_2 fluid for comparison to the samples cured in the O/ CO_2 fluid.

The pxrd results for the control samples or non altered portions of samples are shown in Table 7. The dominant phases tend to be fairly consistent from 2 days through 3 months. In the two day cure, initially there appears to be more tobermorite in the sample in relation to aluminum tobermorite. The amount of aluminum tobermorite increases with time. Little change is observed from 3 weeks to 3 months. After 1 week, the amount of crystalline silica used seems to stabilize. In all stages it is likely that some non aluminum substituted tobermorite exists. If xonotlite exists, it does not appear to be a major phase.



BRZ60CRM_27.5%_MINUSIL20%

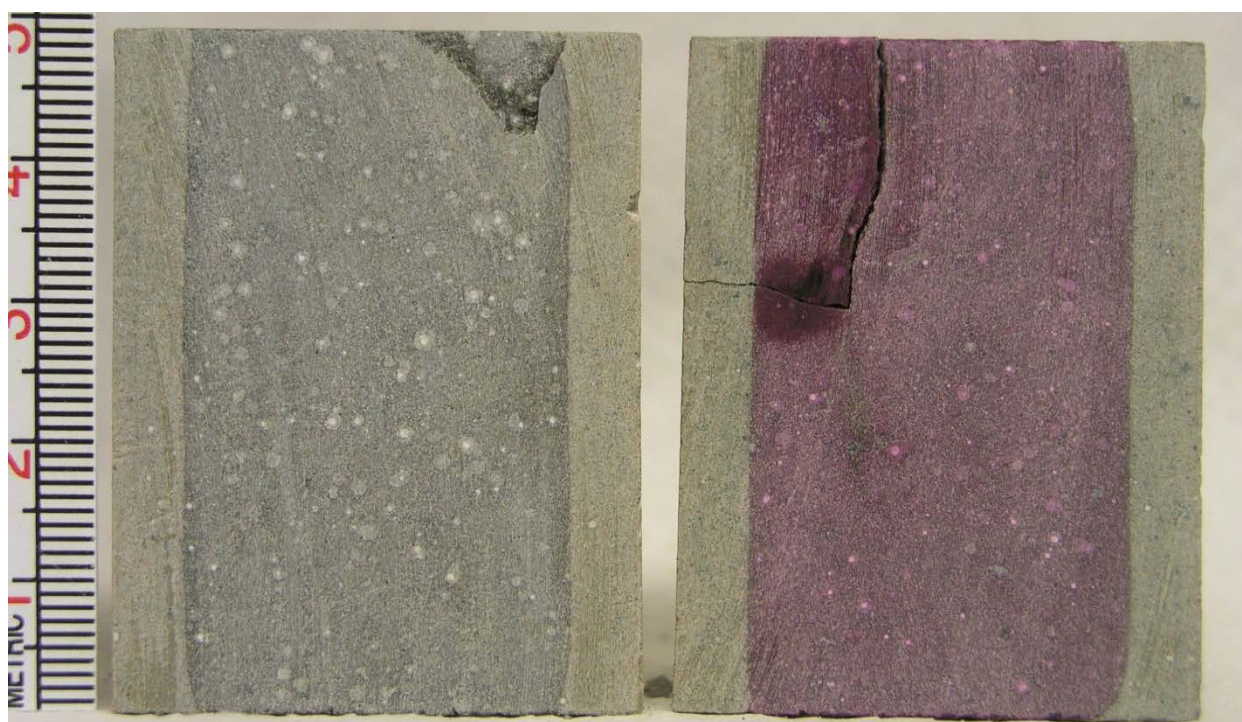
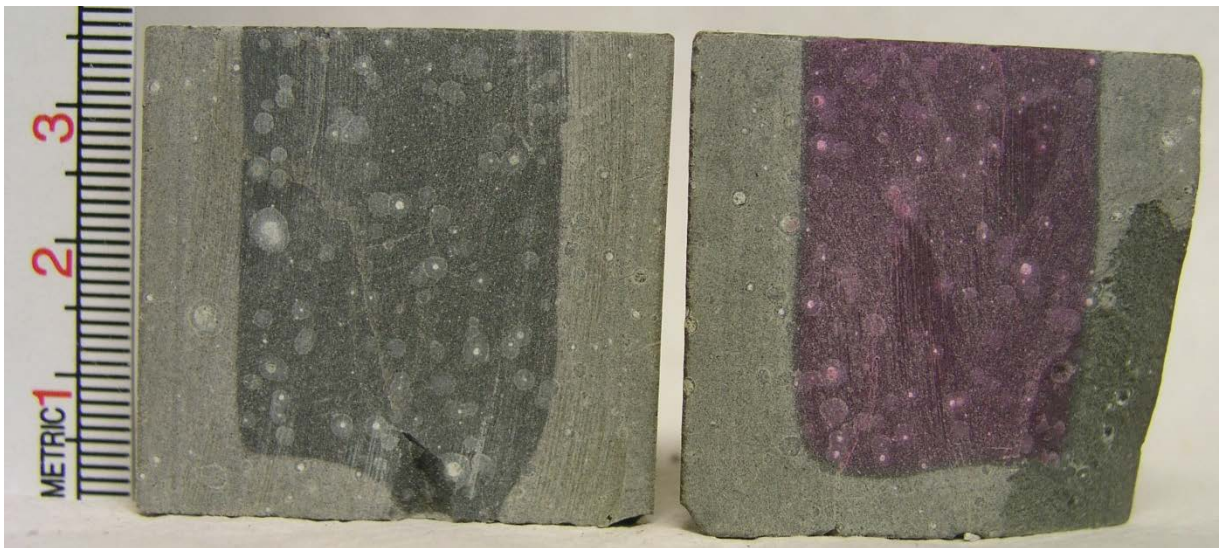


Figure 2. BRZ60CRM_40%_MINUSIL20%



BRZUFM_27.5%_MINUSIL20%



BRZUFM_40%_MINUSIL20%

Figure 3. Alteration observations for BRZUFM blends.

Table 7. Phase description for Fmix1_300°F for control or non altered cement pastes.

cure time	comments
2 days (initial cure)	The primary phases identified are aluminum tobermorite, tobermorite, and quartz. There are a few minor phases which may include xonotlite, and unreacted zeolite, C3S, C2S. The plots suggest greater possibility of tobermorite at this stage than the longer cured samples.
1 week	Primary phases: aluminum tobermorite, quartz
3 week	Primary phases: aluminum tobermorite, quartz. Additional phases could include tobermorite and xonotlite.
3 months	Primary phases: aluminum tobermorite, quartz.

The phase characteristics of the samples cured in the Ormat Brawley brine/CO₂ fluid are shown in Table 8 and Figures 4 and 5. Figure 5 shows an enlarged portion of the pxd patterns in which the major diagnostic peaks exist. After the initial 2 day cure, the aluminum tobermorite to tobermorite peaks are easily seen. After 1 week in the O/CO₂ fluid, the aluminum tobermorite phase signatures tend to disappear. The quartz peaks are very intense as they are very crystalline in nature. The relative amounts of the four primary phases (minor phases not included) are provided in Table 8. The highly crystalline nature of the quartz particles may result in an over representation of the relative amount of quartz. What we do know is that the crystalline quartz persists through 3 months. The primary component is calcium carbonate (CaCO₃) and is present as three phases including calcite, vaterite, and aragonite. As evidenced by Table 8 and Figure 5, the amount of calcite increased at the expense of vaterite and aragonite as the sample cures up to 3 months. The amount of calcite is higher in the sample cured in the a water/CO₂ fluid at three months as compared to the sample cured in the O/CO₂ fluid. The powdered x-ray diffraction data clearly indicates that the alteration in the samples is indeed carbonation of the cement.

For a quick comparison, pxd patterns are provided for Bear River Zeolite (BRZ) and NM2 clinoptilolite and are shown in Figure 6 for non altered cement pastes and Figure 7 for altered cements. The BRZ are represented by BRZUFM_40%_Minusil 20% at 2 week cure. NM2 clinoptilolite is represented by NM2_10_40%_SF20%_MINUSIL 20% at 6 day cure. The material and mechanical properties for this mix were presented in Table 1. For the non altered cement pastes (Figure 6), the pxd patterns are very similar. The primary phases are aluminum tobermorite and quartz. There appears to be some minor phases of aluminum based calcium silicates or oxides. The aluminum tobermorite is slightly more pronounced than in the Fmix1_300°F.

Table 8. Phase description for Fmix1_300°F for samples cured in the Ormat Brawley brine/CO₂ fluid.

time	comments
2 days (initial cure) non brine/CO ₂ fluid	The primary identified phases are aluminum tobermorite, tobermorite, quartz. There are a few minor phases which may include xonotlite, and unreacted zeolite, C3S, C2S. The plots suggest greater possibility of tobermorite at this stage than the longer cured samples.
1 week	Primary phases: Quartz 40%, Calcite 20%, Vaterite 27%, Aragonite 13%. Possible minor phases may include tobermorite and xonotlite.
3 week	Primary phases: Quartz 34%, Calcite 20%, Vaterite 15%, Aragonite 31%.
3 months, O/CO ₂	Primary phases: Quartz 27%, Calcite 44%, Vaterite 12%, Aragonite 17%.
3 months, water/CO ₂	Primary phases: Quartz 21%, Calcite 58%, Vaterite 11%, Aragonite 10%.

* The phase percentage is on semi-quantitative analysis from pxrd based on the four primary phases.

The pxrd patterns for the samples cured in the O/CO₂ represent altered cement pastes are shown in Figure 7. Mixes shown are BRZUFM_40%_Minusil 20% cured for 3 weeks, NM2_5_27.5%_Minusil 20% cured for 3 months, Fmix1_400°F cured at 400°F for 5 days and transferred to the 300°F for an additional month, and Fmix1_300°F. As with Fmix1_300°F, the main components are various phases of CaCO₃ and non reacted quartz. The BRZ and Fmix1_400°F are dominated by aragonite but also contain calcite and vaterite. The NM2 blend is has strong aragonite and calcite signatures.

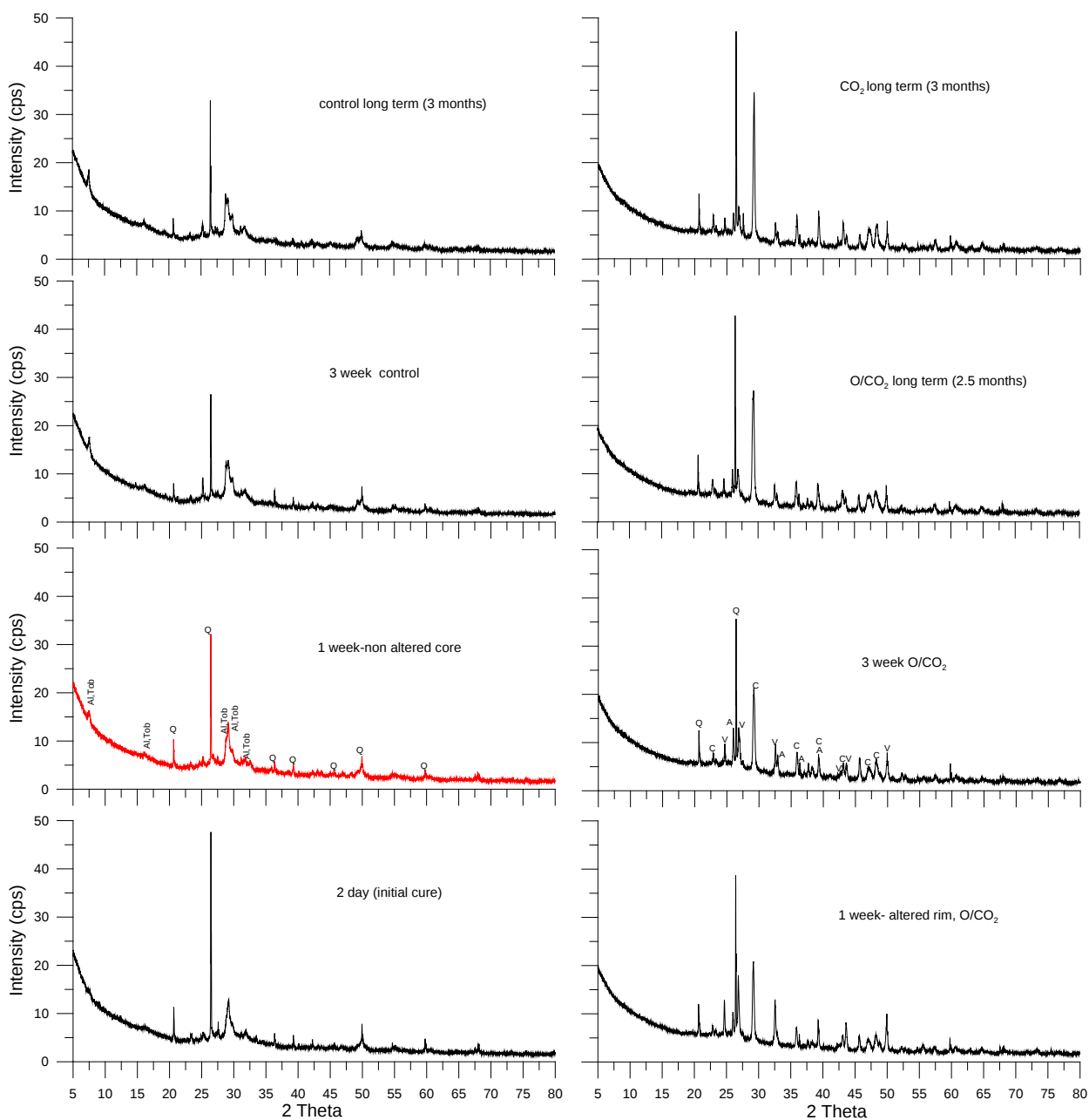


Figure 4. Powder x-ray diffraction for Fmix1_300°F. The left hand plots show the control or non altered portion of the core. The right hand plots show the samples which showed altered pastes after curing in the Ormat Brawley brine/CO₂ medium or water/CO₂.

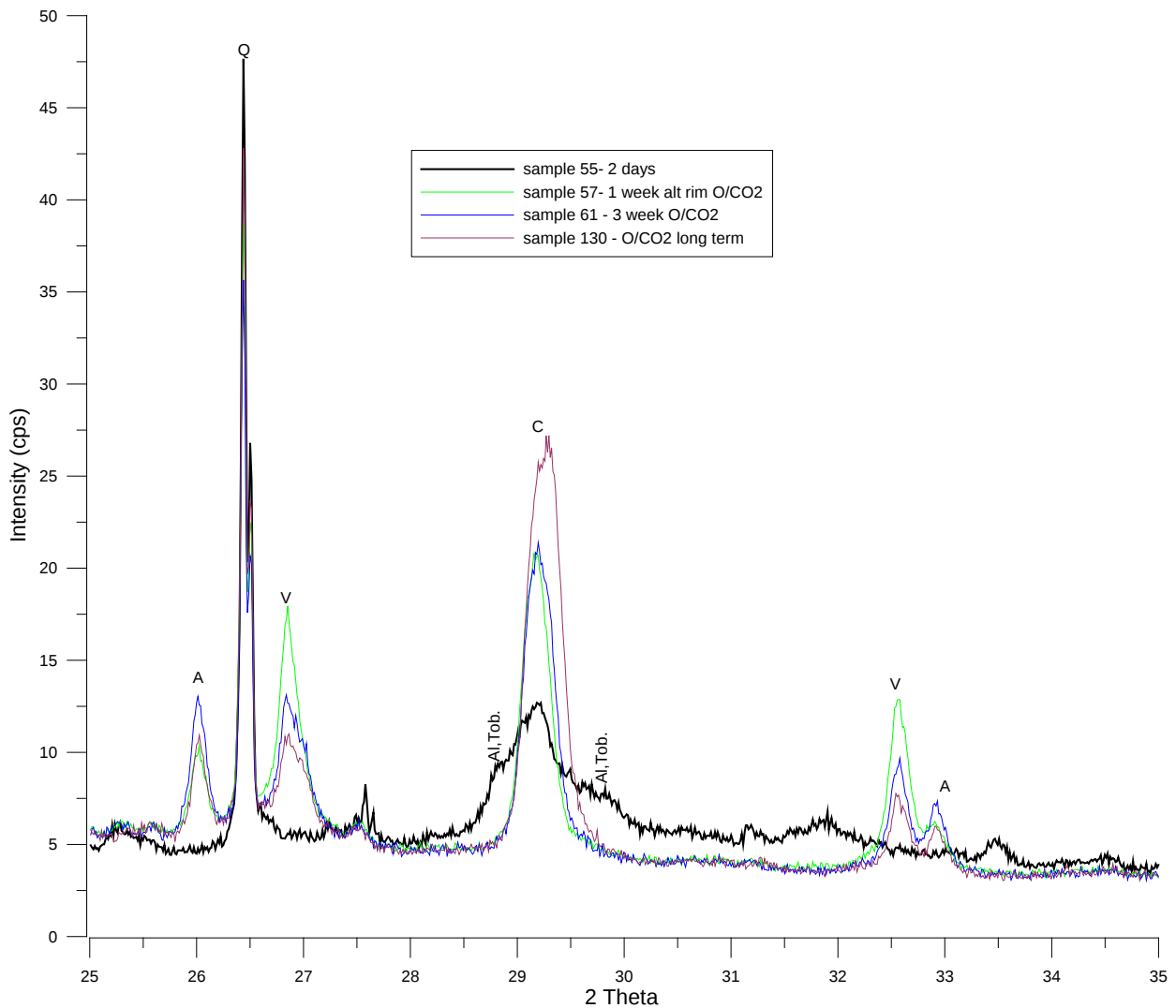


Figure 5. Powder x-ray diffraction for Fmix1_300°F. The pxrd pattern are shown for cement paste characteristics extending from 2 days (initial cure) through 3 months for samples cured in the Ormat Brawley brine/CO₂ fluid.

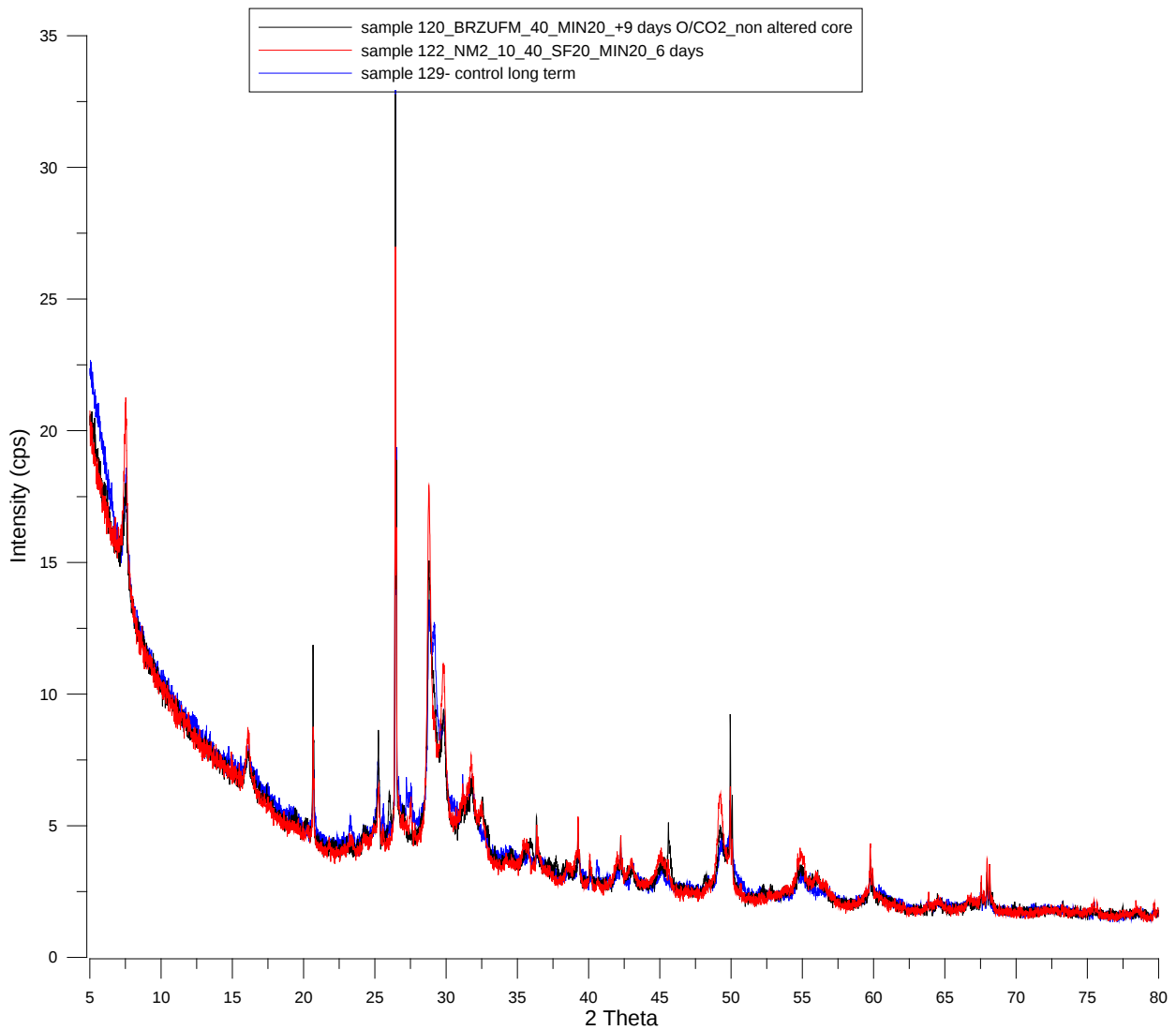


Figure 6. Powder x-ray diffraction patterns comparing BRZ (Bear River Zeolite), NM2 clinoptilolite, and Fmix1 at 300°F for non-altered cement pastes.

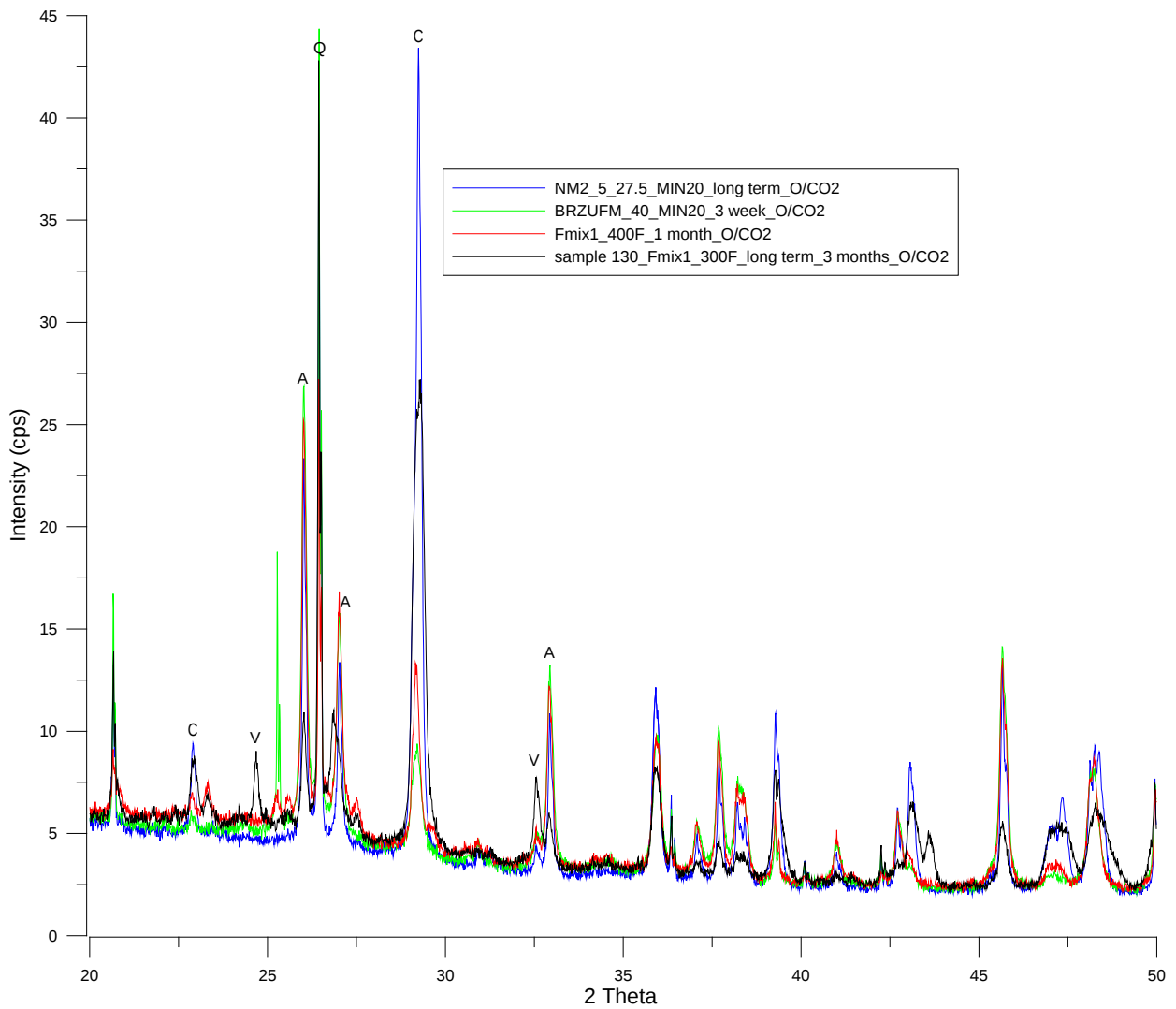


Figure 7. Powder x-ray diffraction patterns comparing BRZ (Bear River Zeolite), NM2 clinoptilolite, Fmix1_400°F, and Fmix1 at 300°F for altered cement pastes.

FY2014 Q1

Task 5 Element 3

Trabits Group worked with Gloria Colmenares and Jodi King of Baker Hughes on the cement blend to be used for the Ormat Brawley, California demonstration well. Previous cement blends had used small amounts of zeolite as an additive. After testing it was determined to use the zeolite as a replacement for cement rather than an additive.

The following pages are the test reports for the Brawley cements. These are:

- 15 ppg / 75% Class G cement and 25% Clinoptilolite – BHST 175°F
- 15 ppg / 75% Class G cement and 25% Clinoptilolite – BHST 250°F
- 13 ppg / 60% Class G cement and 40% Clinoptilolite - BHST 175°F
- 13.5 ppg / 60% Class G cement and 40% Clinoptilolite – BHST 250°F



West Coast Area Laboratory Report

Rev.
5-20-

Report #: CMT046113H

Client/Well Information:

Company:	Ormat	District:	Santa Fe Springs	Depth MD:	500
Field:	Lawley Geothermal Field	Job Type:	Intermediate	Depth TVD:	500
Well:	84-22	Hole Size:	12.25 in	BHST:	175
Prepared for:	Jodi King	Casing Size:	9 5/8 in	BHCT:	135
Submitted by:	Gloria Colmenares	Cement:	Class G	Water:	Fresh - Tap
Tested by:	Yarbrough	Lot #:	61-198-13	Date:	10/2/13

Slurry Design:

Base	Class G	75	%	Additives	Silica Flour	35	% BWOC
	Clinoptilolite	25	%		FP-6L	1	gal/100sack
					CD-32	0.6	% BWOC
					FL-62	1.2	% BWOC

Slurry Properties:

Density:	15	ppg	Yield:	1.47	ft ³ /sack	Mix Water:	6.183	gal/sack
----------	----	-----	--------	------	-----------------------	------------	-------	----------

Rheology:	600 rpm	300 rpm	200 rpm	100 rpm	60 rpm	30 rpm	6 rpm	3 rpm
Ambient	0	146.5	114	72.5	55.5	54.5	19	8
135 F	0	92.5	63	32.5	21	11	2.5	1

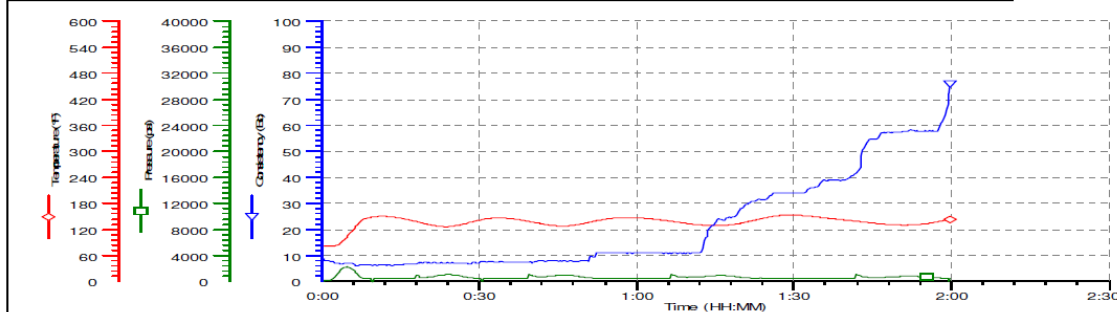
Bingham Plastic	PV	YP
	129	26
	92	1

Gel Strength	10 sec	10 min	100 lb/sqft	500 lb/sqft

Free Water:	90 deg	0
Fluid Loss:	48	cc/30min

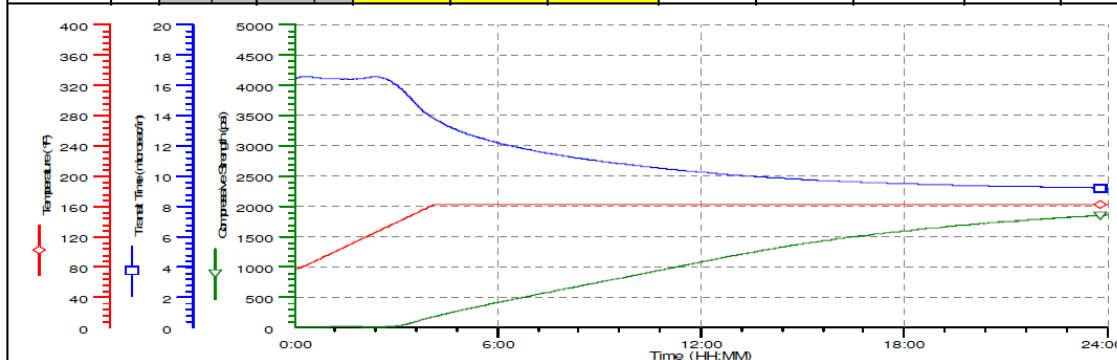
Consistometer Recording of Bearden Consistency (Time is in hrs:min):

Machine:	Jack	30 bc:		50 bc:		70 bc:	1:59	100 bc:	
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Compressive Strength Data:

Temp	3:18	6:48	8 hr	12 hr	24 hr	48 hr	72 hr	96 hr		
163	F	50 psi	500 psi	634	1077	1850				



Comments:

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West Coast Area Laboratory Report

Rev. D
 5-20-13

Report #: CMT049513C

Client/Well Information:

Company:	Ormat	District:	Santa Fe Springs	Depth MD:	2050
Field:	Lawley Geothermal Field	Job Type:	Production	Depth TVD:	2050
Well:	84-22	Hole Size:	8.5 in	BHST:	250
Prepared for:	Jodi King	Casing Size:	7 in	BHCT	160
Submitted by:	Gloria Colmenares	Cement:	Class G	Water:	Fresh - Tap
Tested by:	John H Yarbrough	Lot #:	61-235-13	Date:	10/2/13

Slurry Design:

Base	Class G Clinoptilolite	75 25	%	Additives	Silica Flour	35	% BWOC
					FP-6L	1	gal/100sack
					CD-32	0.8	% BWOC
					A-7 (CaCl ₂)	0.75	% BWOC
					FL-62	1.2	% BWOC

Slurry Properties:

Density:	15	ppg	Yield:	1.48	ft ³ /sack	Mix Water:	6.179	gal/sack
----------	----	-----	--------	------	-----------------------	------------	-------	----------

Rheology:	600 rpm	300 rpm	200 rpm	100 rpm	60 rpm	30 rpm	6 rpm	3 rpm
Ambient	0	138	99.5	59	38	31.5	28.5	22.5
160 F	0	103	78.5	50.5	36	28.5	23	20

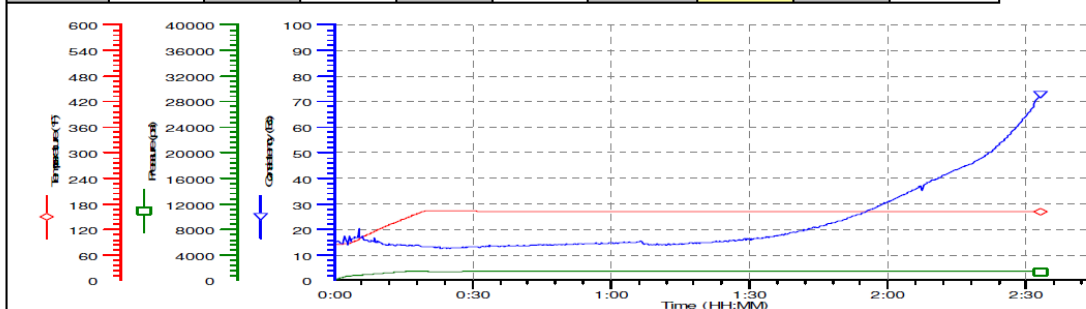
Bingham Plastic	PV	YP
	116	22
	84	22

Gel Strength	10 sec	10 min	100 lb/sqft	500 lb/sqft

Free Water:	90 deg	0
Fluid Loss:	84	cc/30min

Consistometer Recording of Bearden Consistency (Time is in hrs:min):

Machine:	Nemo	30 bc:		50 bc:		70 bc:	2:32	100 bc:	
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Compressive Strength Data:

Temp		8 hr	12 hr	24 hr	48 hr	72 hr	96 hr		
F	50 psi	500 psi							

Comments:

23 micron Clinoptilolite was used for testing.

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West Coast Area Laboratory Report

Rev.
5-20-1

Report #: CMT049213A

Client/Well Information:

Company:	Ormat	District:	Santa Fe Springs	Depth MD:	500
Field:	Lawley Geothermal Field	Job Type:	Intermediate	Depth TVD:	500
Well:	84-22	Hole Size:	12.25 in	BHST:	175
Prepared for:	Jodi King	Casing Size:	9 5/8 in	BHCT:	135
Submitted by:	Gloria Colmenares	Cement:	Class G	Water:	Fresh - Tap
Tested by:	John H Yarbrough	Lot #:	61-235-13	Date:	10/3/13

Slurry Design:

Base	Class G	60	%	Additives	Silica Flour	35	% BWOC	FL-62	1.2	% BWOC
	Clinoptilolite	40	%		FP-6L	1	gal/100sack			
					CD-32	0.6	% BWOC			
					A-7 (CaCl ₂)	2	% BWOC			
					BA-90	15	% BWOC			

Slurry Properties:

Density:	13	ppg	Yield:	2.11	ft ³ /sack	Mix Water:	10.477	gal/sack
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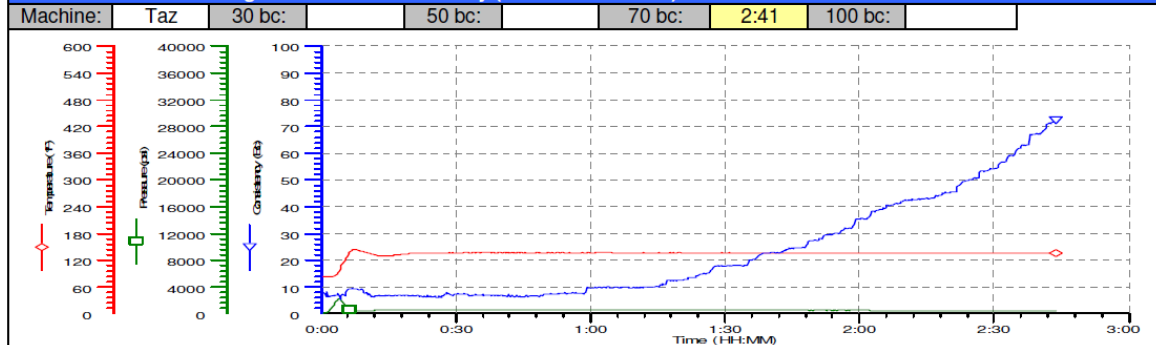
Rheology:	600 rpm	300 rpm	200 rpm	100 rpm	60 rpm	30 rpm	6 rpm	3 rpm
Ambient	0	29.5	25	19	23	22	13	6.5
135 F	0	31.5	28	25.5	24	22	20	14

Bingham	PV	YP
Plastic	16	15
	14	20

Gel Strength	10 sec	10 min	100 lb/sqft	500 lb/sqft

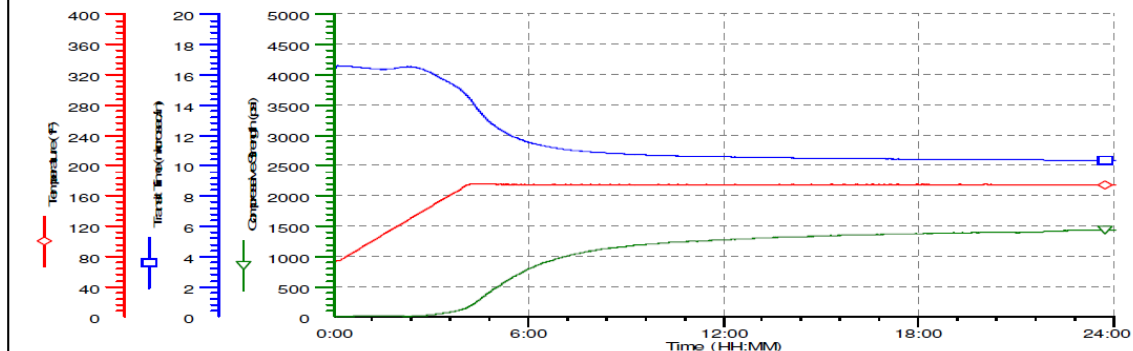
Free Water:	90 deg	0
Fluid Loss:	60	cc/30min

Consistometer Recording of Bearden Consistency (Time is in hrs:min)



Compressive Strength Data:

Temp	3:21	5:03	8 hr	12 hr	24 hr	48 hr	72 hr	96 hr
175 F	50 psi	500 psi	1085	1261	1428			



Comments:

23 micron Clinoptilolite was used for testing.

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West Coast Area Laboratory Report

Rev.
5-20-

Report #: CMT049413C

Client/Well Information:

Company:	Ormat	District:	Santa Fe Springs	Depth MD:	2050
Field:	Lawley Geothermal Field	Job Type:	Production	Depth TVD:	2050
Well:	84-22	Hole Size:	8.5 in	BHST:	250
Prepared for:	Jodi King	Casing Size:	7 in	BHCT:	160
Submitted by:	Gloria Colmenares	Cement:	Class G	Water:	Fresh - Tap
Tested by:	John H Yarbrough	Lot #:	61-235-13	Date:	10/2/13

Slurry Design:

Base	Class G	60	%	Additives	Silica Flour	35	% BWOC	FL-62	1.2	% BWOC
	Clinoptilolite	40	%		FP-6L	1	gal/100sack			
					CD-32	0.8	% BWOC			
					R-3	0.2	% BWOC			
					BA-90	15	% BWOC			

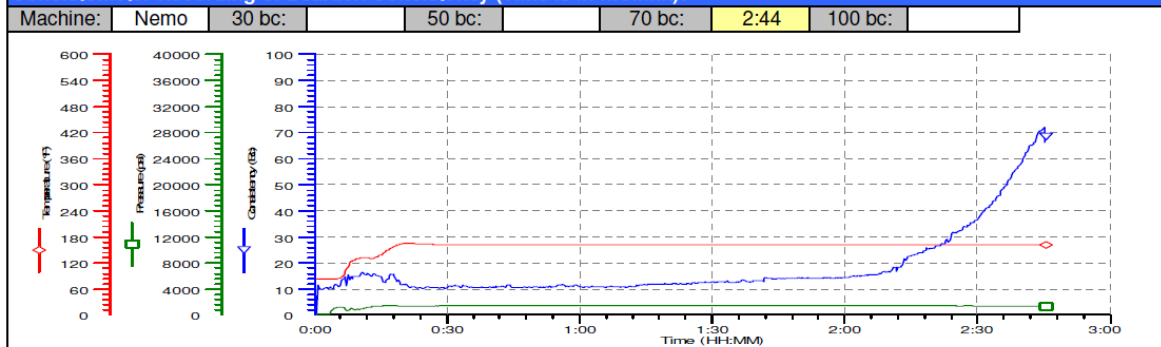
Slurry Properties:

Density:	13.5	ppg	Yield:	1.89	ft ³ /sack	Mix Water:	8.883	gal/sack
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Rheology:	600 rpm	300 rpm	200 rpm	100 rpm	60 rpm	30 rpm	6 rpm	3 rpm	Bingham Plastic	PV	YP
Ambient	0	48.5	37	29	30	32.5	17	14		28	22
160 F	0	28	18	11.5	9.5	9	7	4.5		21	6

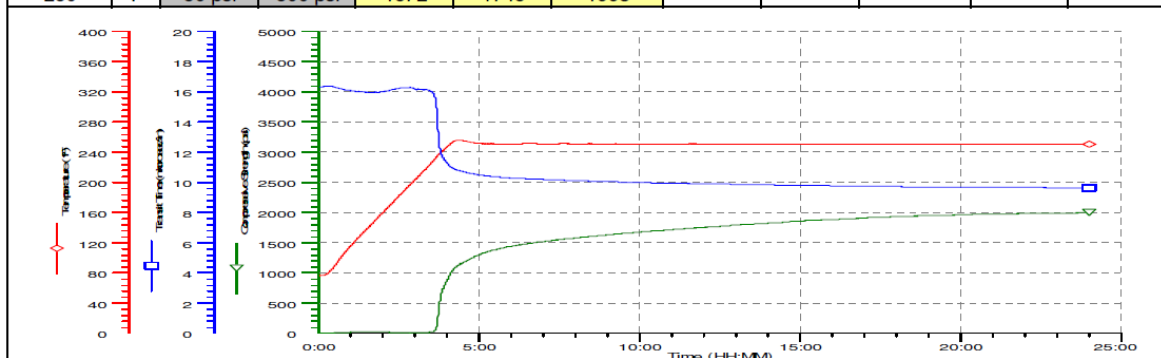
Gel Strength	10 sec	10 min	100 lb/sqft	500 lb/sqft	Free Water:	90 deg	0
					Fluid Loss:	165	cc/30min

Consistometer Recording of Bearden Consistency (Time is in hrs:min):



Compressive Strength Data:

Temp	3:37	3:45	8 hr	12 hr	24 hr	48 hr	72 hr	96 hr		
250	F	50 psi	500 psi	1572	1745	1993				



Comments:

23 micron Clinoptilolite was used for testing.

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FY2014 Q2

Intergrinding Cement Clinker and Zeolite

Texas Lehigh Cement Meeting

On February 5th Trabits Group met with Mr. Jim Jarl, Quality Control Manager, Texas Lehigh Cement, at the plant in Buda, Texas. Texas Lehigh supplied all of the Class H cement that was used in the Project screening and development testing. The purpose of the meeting was to learn how a special interground product would be handled by a plant and what tonnage requirements would be necessary to be economic.

Mr. Jarl explained that a switch over from one cement product to another was never a “clean” change over in that there was always overlap product between, as an example, a well cement and a construction cement. This change over product is then not a well cement or a construction cement and the plant has to find a use to blend this back into some other product. Runs could not be expected to be small. It would take several hundred tons to make a complete switch over and steady state for the new product. In the case of a zeolite intergrind, the plant would gain the benefit of saving clinker for other products. In other words, a 60% clinker and 40% zeolite would free up 40% clinker for other product.

The plant would also have to install additional product silos for storage of the new interground product while the product was being made and before it was shipped from the plant. Plants often experience “slow” periods when construction cement product is low like during the winter and there could be plant optimization with running a special interground product during such slow periods. Not all cement plants produce a well cement that could be used in the intergrind. For example, the Nevada Cement plant makes a Type II clinker which is not used as a well cement. This may or may not be a problem given that many states allow well completions with something other than an API well cement. The new interground product would be classified by API as a Composite Cement and not like a Class H or Class G anyway. Accordingly, the performance as demonstrated by testing would be the control and not the API class of the cement. Mr. Jarl pointed out that there would be a carbon credit for the new interground cement and that should appeal to the environmental sensitivity of geothermal or oil and gas operators. This lower carbon results from the zeolite in the interground product that is an ingredient that was not manufactured using fossil fuels as is the case with cement clinker.

Lehigh Hanson Tehachapi Cement Plant

Working through Texas Lehigh Cement Trabits Group was introduced to the Heidelberg Technology Center (HTC) and Lehigh Hanson, Inc. The parent company of both of these is Heidelberg Cement Group. Lehigh Hanson is very interested in the intergrind method and has supplied the services of the HTC lab in Doraville, Georgia. The HTC lab has the capability to make bench scale intergrind composites.

On March 25th, Trabits Group and Baker Hughes met with personnel representing Lehigh Southwest Cement Co, Lehigh Hanson Inc. and Heidelberg Technology Center. The meeting took place at the Lehigh Southwest Cement plant located near Tehachapi, California.

Present for the meeting were:

Lori Tiefenthaler, Lehigh Hanson/Heidelberg Cement

Craig Mifflin, Lehigh Southwest Cement

Jean-Claude Royer, Lehigh Southwest Cement

Steve Lewis, Lehigh Southwest Cement

Anthony Mattei, Lehigh Cement

David Melcher, Heidelberg Technology Center

Matt Hummel, Heidelberg Technology Center

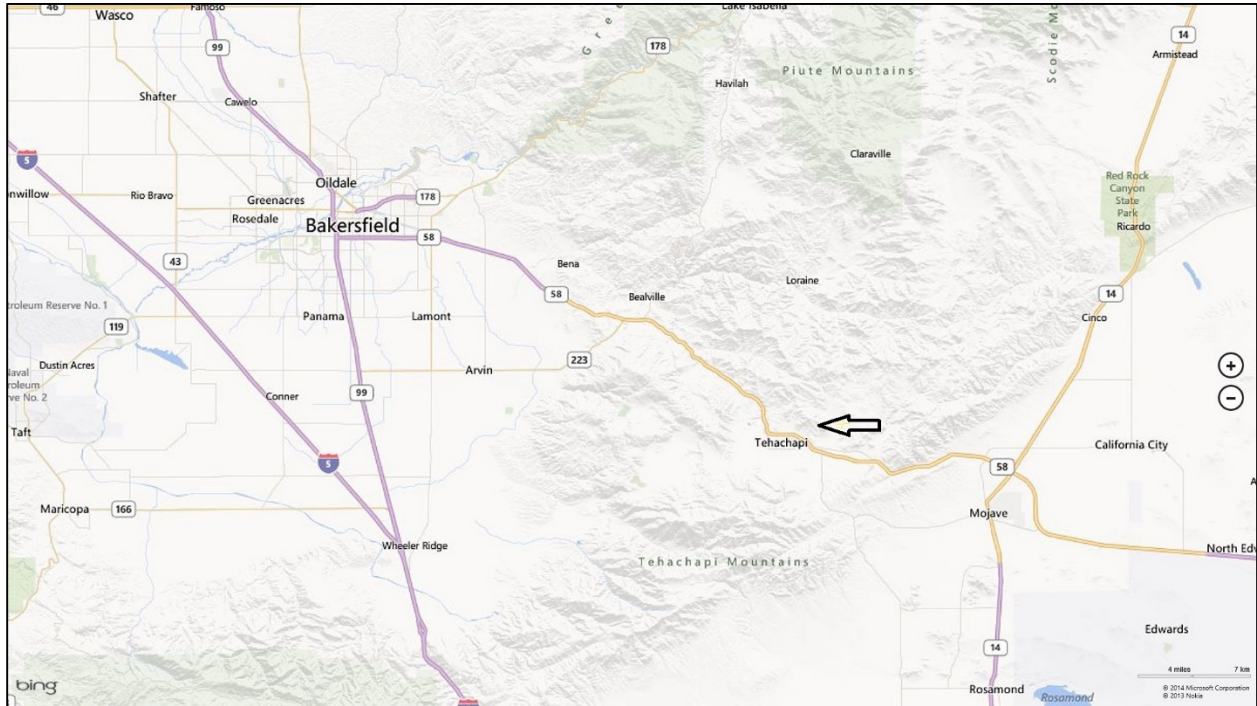
Gloria Colmenares, Baker Hughes

George Trabits, Trabits Group

Geoff Trabits, Trabits Group

Dorwin Smith, Trabits Group

John Lawrence, US Antimony/Bear River Zeolite



Location Map: Tehachapi is 40 miles Southeast of Bakersfield, California



Aerial Image: The cement plant is in the lower center of the image. The plant limestone source is in the upper left of the image.

Discussion

Lori Tiefenthaler opened the meeting with a presentation on Heidelberg Cement Group. Heidelberg is a global company operating in more than 40 countries. Heidelberg has 52,500 employees in more than 2,500 locations. Heidelberg's core activities include the production of cement and aggregates.

Lehigh Hanson is one of the largest construction materials companies in North America. Lehigh Hanson companies produce cement, aggregates, ready mixed concrete, asphalt and a range of building materials including precast concrete products, roof tiles and clay bricks.

Lehigh Hanson – West Region operates three cement plants in California located at Tehachapi, Cupertino and Redding. In addition they have import terminals at Stockton and Long Beach along with distribution terminals at Springfield, Oregon; Phoenix, Arizona; Sparks, Nevada and Union City, California.

Trabits Group followed Ms Tiefenthaler's presentation with an overview of the Geothermal Technologies Program and the development of the high temperature/high pressure geothermal cement.

Gloria Colmenares followed with a discussion on zeolite-containing cement development for the planned Ormat Steamboat Geothermal Technologies demonstration well. Ms Colmenares explained that development had focused on dry blending Bear River 23 micron Clinoptilolite with Class G cement for the lead and tail. She continued that the lead cement was challenging given Ormat's working time constraints at relatively high temperatures. She continued that Baker Hughes was interested in the intergrind concept given the potential of cement quality improvement and low cost of production.

Craig Miffilin and Jean-Claude Royer provided the history of the Tehachapi plant and gave an overview of the operation. The Tehachapi plant is uniquely suited to the intergrind with zeolite given that there is a large source of Clinoptilolite located on the plant property. In 1912 Tehachapi Clinoptilolite was used in a 25% replacement for Portland cement in the construction of the 240 mile-long Los Angeles aqueduct.



Tufa Quarry

The Tufa Quarry zeolite deposit has been extensively drill explored and was a permitted mining area in the past. Given its location on plant property it is expected that new mining permits could be obtained at reasonable time and expense to support the production of an intergrind product.

David Melcher and Matt Hummel then lead a detailed discussion on how Heidelberg was approaching the preparation of bench scale intergrind samples. Baker Hughes requested at the very minimum one 5 gallon bucket of each intergrind to be tested. Two Intergrinds are planned. These are:

60% Tehachapi Class G Clinker interground with 40% Tehachapi Tufa Quarry zeolite.

60% Tehachapi Class G Clinker interground with 40% Bear River Clinoptilolite.

Making each 5 gallon sample is a long process given that lab scale grinders are relatively small which requires multiple runs. Each run must create the same conditions as the previous run for the entire sample to be representative. Additionally, full scale grinding conditions are different than those in a lab so care must be taken to closely simulate expected full scale grinding conditions.



Primary Participants: Pictured left to right, Geoff Trabits, Craig Mifflin, George Trabits, Gloria Colmenares, Lori Tiefenthaler and David Melcher

Plant Tour Images



Primary crusher next to mine is an impact crusher. Feed is conveyed 1.5 miles to plant. Mining is up to 7,000 tpd,



Main plant. Cement plant is about 850,000 tpy.



Ball Mill (Finish Mill)



Cement testing quality control.



Cement testing quality control.



Two operators run the plant using computerized process controls.

FY2014 Q3

Intergrinding Cement Clinker and Zeolite Bench Scale Development

During the reporting period Trabits Group began evaluating using intergrinding of cement clinker and zeolite as a more cost effective method of making the actual geothermal cement. During the period the Heidelberg Technology Center (HTC) completed work on the first two bench scale intergrinds. These intergrinds are:

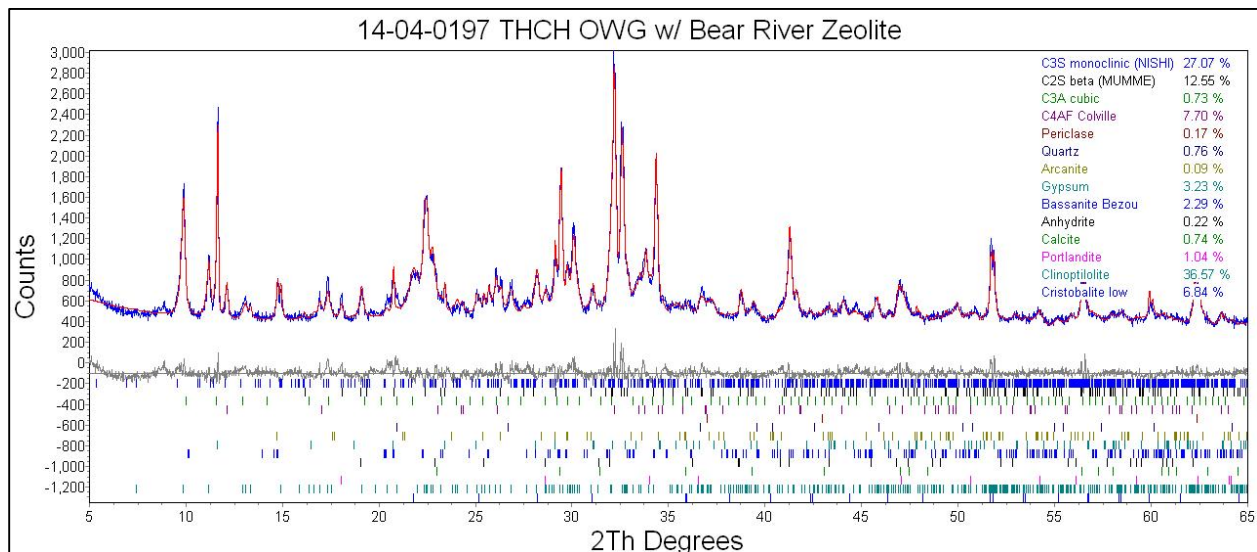
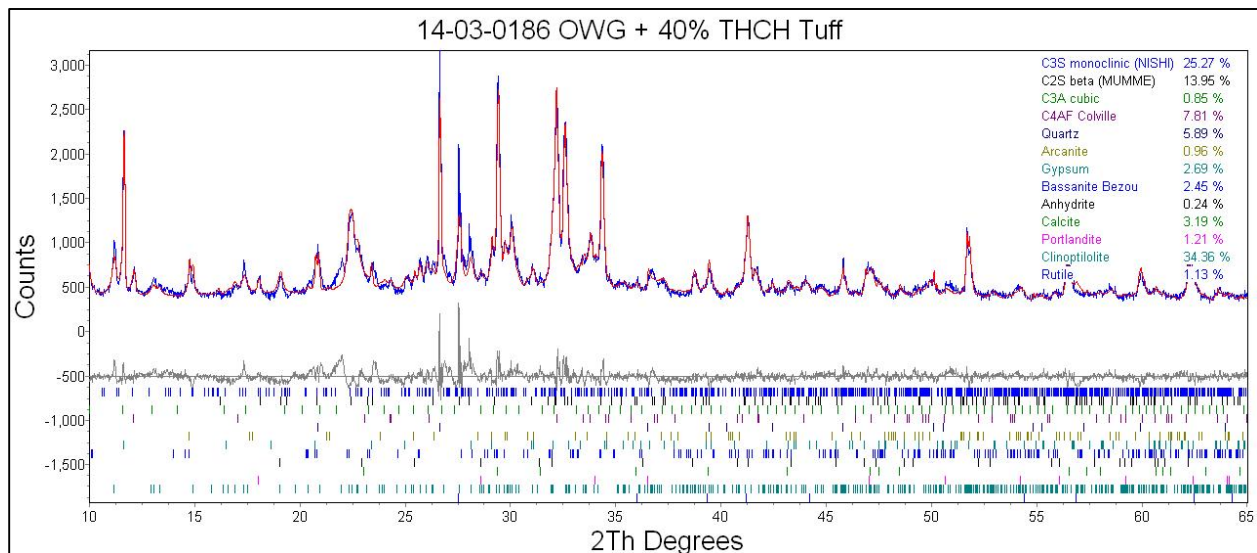
- A) Tehachapi Class G clinker 60% / Tehachapi Clinoptilolite 40% (THCH)
- B) Tehachapi Class G clinker 60% / Bear River Clinoptilolite 40% (BRZ)

Following is a summary of the HTC observations:

- 1) The specific gravities are 2.70 for the THCH and 2.67 for the BRZ
- 2) The Blaine for THCH is 7925 cm²/g and BRZ 8350 cm²/g
- 3) The retain on 45 micron sieve is 18.5% for THCH and 16.1% for BRZ

For general reference, these are well within a manufacturing tolerance for a product like this.

- 4) As shown below, are the quantitative XRD patterns for both grinds. HTC used 40% by weight (dry) of each zeolite. You can see that the clinoptilolite % is nearly the same. Gypsum phases are equal. The main difference between the two cements is that THCH lightweight cement has 6% quartz and the BRZ lightweight cement appears to have 6% cristobalite. That shouldn't be a big difference since we are only dealing with different modifications of SiO₂.



- 5) The XRF data shows very similar results on the main oxides. One thing HTC did note is that the Tuff must be a Na substituted zeolite compared to BRZ. All else is the same.

14-03-0186

THCH OWG Clinker + 40% THCH Tuff + 2.5% Gyp + 2.5% Plaster

		Ignited	Unignited
LOI			6.17
SiO ₂	%	41.39	38.84
Al ₂ O ₃	%	7.65	7.18
Fe ₂ O ₃	%	3.78	3.55
CaO	%	40.15	37.67
MgO	%	0.68	0.64
SO ₃	%	2.77	2.60
Na ₂ O	%	1.336	1.254
K ₂ O	%	1.813	1.701
P ₂ O ₅	%	0.109	0.102
TiO ₂	%	0.172	0.161
SrO	%	0.074	0.069
Mn ₂ O ₃	%	0.055	0.052
Cr ₂ O ₃	%	0.009	0.008
ZnO	%	0.022	0.021

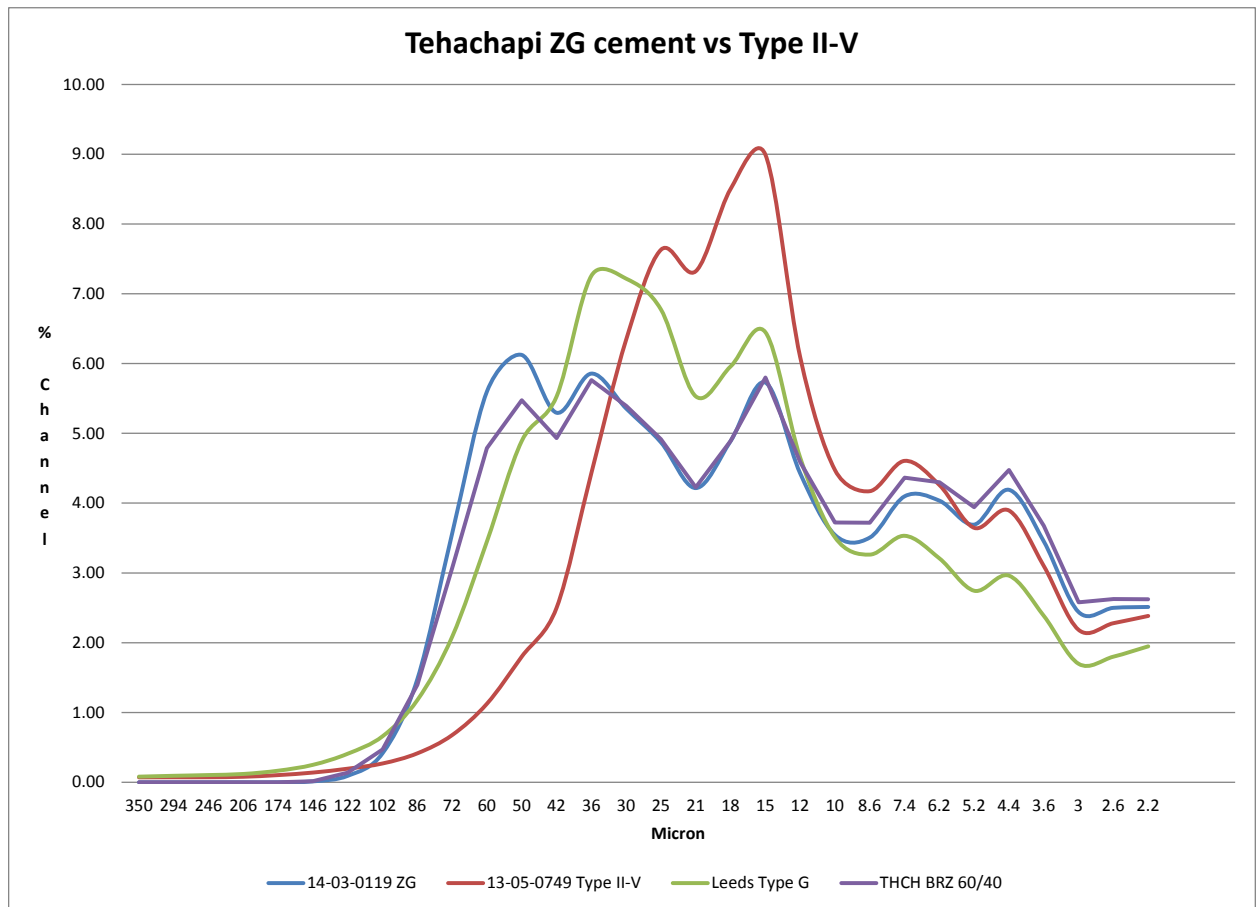
14-04-0197

THCH OWG Clinker + 40% Bear River Zeolite + 2.5% Gyp + 2.5% Plaster

		Ignited	Unignited
L.O.I.	%		7.00
SiO ₂	%	41.79	41.03
Al ₂ O ₃	%	7.03	6.90

Fe ₂ O ₃	%	4.11	4.04
CaO	%	40.37	39.64
MgO	%	0.83	0.81
SO ₃	%	2.91	2.86
Na ₂ O	%	0.325	0.319
K ₂ O	%	2.131	2.092
P ₂ O ₅	%	0.111	0.109
TiO ₂	%	0.26	0.255
SrO	%	0.069	0.068
Mn ₂ O ₃	%	0.045	0.044
Cr ₂ O ₃	%	0.009	0.009
ZnO	%	0.021	0.021

- 6) Below is a PSD comparison between the two intergrinds, a normal Type II/V construction cement and a normal type G cement. What HTC notes is that there are more coarse and more fine particles in the intergrind than compared to the type G. This means that the Zeolite is finer than the average 20-21 micron that these samples are. How much finer HTC cannot speculate without a huge margin of error.



HTC's summary comment on particle size distribution was:

"What I can tell you for certain is that this cement is going to be much easier and repeatable for the plant to do. Going coarser than this with the Tuff in the mix has in the past (personal experience with) caused many issues in the grinding circuit. I don't want to represent a product that is not possible to make in a real world setting."

Intergrinding Cement Clinker and Zeolite Full Scale Pilot Run

On May 5th the first full scale pilot production run was completed at the Lehigh Southwest Cement plant located at Tehachapi, California.

The zeolite used for the intergrind is located on the Tehachapi plant property. This zeolite was used in the 1912 construction of the Los Angeles aqueduct.



Tehachapi Clinoptilolite Deposit

Preparation of the Clinoptilolite for intergrinding required loading and hauling shot zeolite from the quarry pictured above to the primary crusher. At the primary crusher the Clinoptilolite was crushed and screened to a minus 2 inch for cement mill feed. From there the now sized mill feed was trucked to the cement plant.



Stockpiled minus 2 inch Clinoptilolite Mill Feed

Production samples were taken at the ball mill (finish mill) during the run. The plant reported that the material ground somewhat slower than expected but well within economic parameters. Steady state was achieved after two hours of switch over operation.



Ball Mill (Finish Mill)



Intergrind Production Run Samples

The plant was able to capture 8 five gallon buckets during steady state operation. Given the scale of production it is difficult to capture small samples during actual operation.

FY2014 Q4

Element 3 - High Temperature EGS Well Demonstration

Ormat Demonstration/Steamboat Cement Design

Baker Hughes reported that Ormat had concerns with the Lead slurry. For the Lead Ormat stated that they need 500 psi at 8 hours and 1500 psi at 72 hours. There were no problems with the Tail slurry design.

Ormat elected to use Halliburton for the Steamboat well. Halliburton proposed to use ThermaLock for both lead and tail cement. On July 8th Paul Spielman reported to Trabits Group that Halliburton was rigging up at the well. On July 9th Halliburton reported “currently drilling, at 180 feet”. In August, Ormat

reported that the Halliburton job for the Steamboat well was satisfactory. Ormat further reported that Halliburton had problems with ThermaLock and completion required 3 squeezes and 2 top jobs.

Alternate Well

During the reporting period, Jodi King met with Bill Ragle, partner, of TBR Well Services in Bakersfield. Mr. Ragle is interested in the technology and stated he may have a hot well for a demonstration.

The current TBR facility is located on Downing Street in Bakersfield sitting on five acres. A new facility is currently under construction on Norris Road and is expected to be completed mid-September. The new facility is on 10 acres and has rail access. There are two shops each at 2500 sq ft. The new silo capacity will have 4 or 5, 4000 cft., 4 or 5, 2500 cft., and several 1400 cft. Field silos. TBR has a complete fleet of bulk trucks, pump trucks and ancillary equipment. The new facility will also include a blending capability.

Interground Cement Clinker and Zeolite Full Scale Pilot Run / Testing

Dr. Luke completed testing to characterize the 60:40 Tehachapi interground composite lightweight cement. Following are Dr. Luke's results:

Physical Characteristics

Water requirement (12.73 ppg) 7.214 gal/sk
Yield 1.468 ft³/sk
Bulk density 79.7 lb/sk

Performance Characteristics

Thickening Time:

40Bc: 1:19
70Bc: 2:05
100Bc: 2:29
Initial Bc: 17Bc

Compressive Strength:

3.5MPa: 11:31:00
8hrs: 2.2MPa = 319.08 psi
12hrs: 3.7MPa = 536.64 psi
24hrs: 8.7MPa = 1261.83 psi
48hrs: 10.9MPa = 1580.91 psi

Rheology data:

300 rpm - dial reading 102
200 rpm - dial reading 97.5
100 rpm - dial reading 82.5
6 rpm - dial reading 32.5
3 rpm - dial reading 16.5

All tests were performed at 52°C, with a 28mins ramp time following API Schedule 5 standards.

FY2015 Q1

Trabits Group reported discussions with Nevada Cement Company located at Fernley, Nevada about doing a second intergrind using Ferrierite. From the cement development work Ferrierite exhibited the best strength characteristics at high temperatures. Unlike Tehachapi which had a Class G clinker that was used for the first intergrind, Nevada Cement makes a Type I/II clinker and does not make any oilfield cement products.

On December 16th Trabits Group personnel met with management and technical staff at Nevada Cement.

Present for the meeting were:

Joe Sells, President, Nevada Cement
Ben Bufmack, Plant Manager, Nevada Cement
Eddie Chantaniyom, Production Manager, Nevada Cement
George Trabits, Trabits Group
Dorwin Smith, Trabits Group
Geoff Trabits, Trabits Group

Nevada Cement has been manufacturing and distributing bulk and sack cement in Northern Nevada and Northern California since 1964. The cement plant is located thirty-five miles east of Reno off Interstate 80 in Fernley, Nevada. Nevada Cement manufactures an all-purpose Type I/II low alkali moderate sulfate resistant cement and a Type II/V low alkali high sulfate resistant cement. Nevada Cement is an Eagle Materials company.



Nevada Cement Plant

The Nevada Cement plant is ideally suited for the interground clinker / zeolite technology. The plant has the ability to dry zeolite before the intergrinding takes place. Zeolite moisture around 2% provides the best results. Moisture at Tehachapi and Bear River has run as much as 9%.



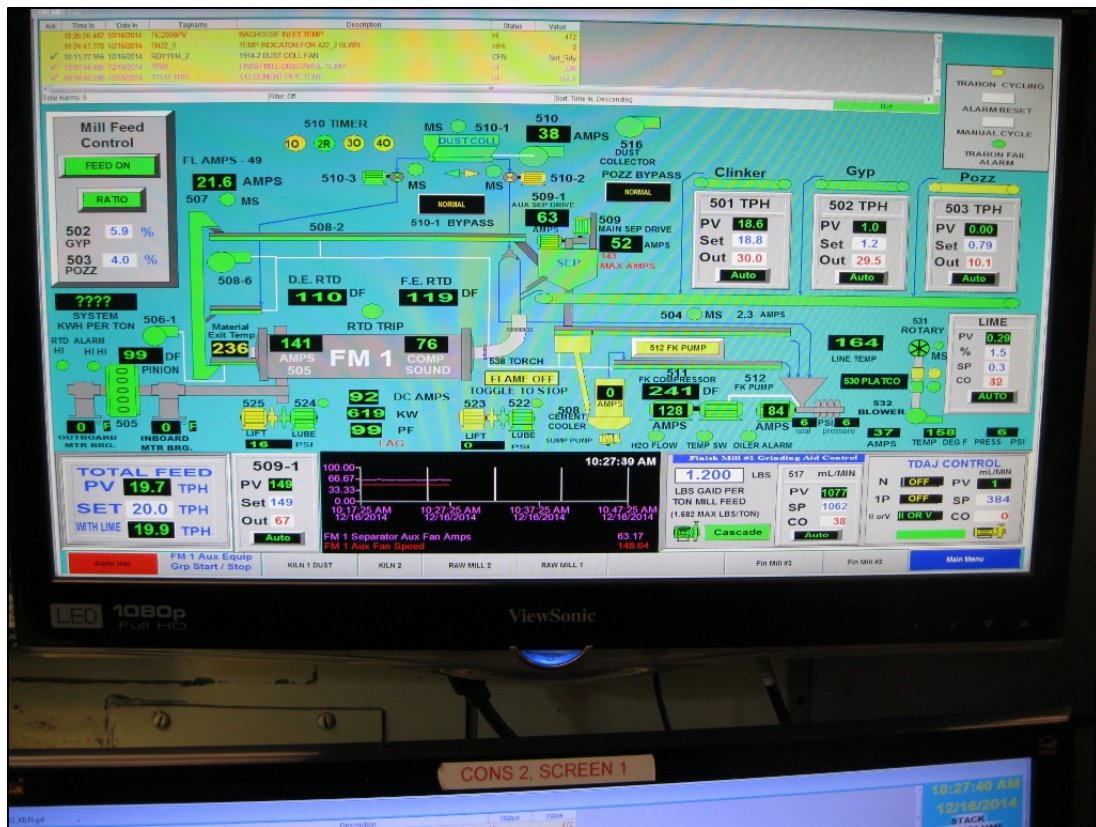
Nevada Cement Long Kiln



Dorwin Smith Inspects the kiln flame



Nevada Cement Control Room



The intergrind feed can be programed to track Clinker, Gypsum and zeolite (Pozz)

Following the plant tour the Trabits Group team and Eddie Chantaniyom, Production Manager, had a lengthy meeting on how to conduct a full scale intergrind using Ferrierite. The group considered the amount of Ferrierite that would be required to reach a steady state consistent production. There was also discussion on the clinker/zeolite ratio that would be targeted. The plant does not have excess silo capacity for storage so the production run will have to loaded out to offsite storage as soon as it is produced. The group discussed possible storage facilities and methods that could be available. The group then looked at schedule. The plant is taking the long kiln that would be used down for a rebuild and re-bricking in January. After comparing schedules the group targeted mid-February for the production scale intergrind.

Products

News Releases

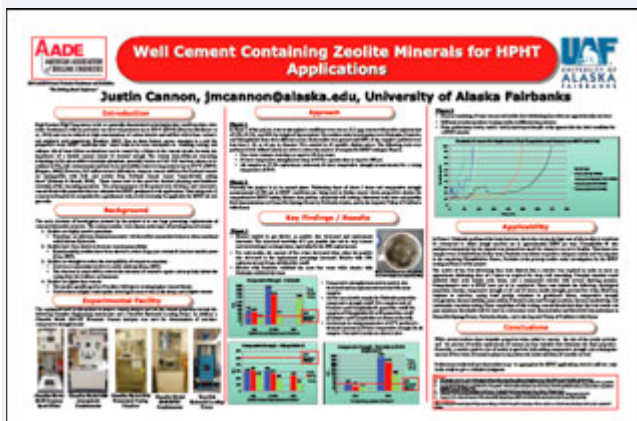
Justin Cannon, UAF Petroleum Development Laboratory student, awarded Third Place in Student Poster Competition



Justin Cannon, with his poster award.

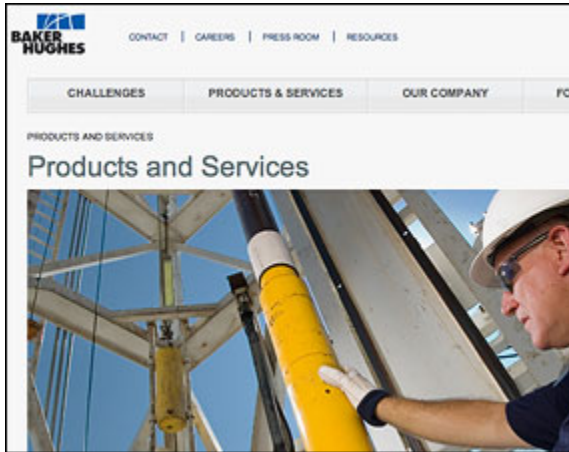
Justin Cannon, UAF Petroleum Development Laboratory student, was awarded Third Place in the Student Poster Competition at the 2013 National Technical Conference of the [American Association of Drilling Engineers](#). Mr. Cannon's poster details the development of the Project's HPHT cement. The National Technical Conference was held at Oklahoma City, Oklahoma.

Congratulations from the Project Team to Mr. Cannon.



Baker Hughes is participating as the primary industry partner with Trabits Group and University of Alaska, Fairbanks

As primary industry partner, Baker Hughes has provided more than \$130,000 in In-Kind Cost Share testing of trial cement blends at its Bakersfield, California testing facility. Additionally, Baker Hughes has supported the project by providing training in well cement testing procedures at Bakersfield.



Baker Hughes web site



*UAF student Justin Cannon in training,
Bakersfield, California*

From the Trabits Group Press Release: August 24th, 2012



Pictured are left Dr. Santanu Khataniar, center Dr. Abhijit Dandekar and right George Trabits. Equipment is Chandler 8340 Consistometer and Chandler 1910 Curing Chamber.

Petroleum engineering students at the University of Alaska Fairbanks will now enjoy access to cutting edge well cement testing technology, thanks in part to Trabits Group.

The new equipment, installed this summer at UAF's Petroleum Development Laboratory (PDL) brings to Alaska cement testing technology that previously existed only in the Lower 48, providing not only the ability to conduct cementing research in Alaska but training for Alaska's future oil, gas and geothermal resource workforce. It also plays a key role in promoting and advancing the science of cementing, a crucial component of safe and responsible drilling practices.

The new well cement testing equipment installed at UAF includes:

- High-temperature, high-pressure consistometers to measure cement's thickening time under extreme conditions.
- An ultrasonic cement analyzer (UCA) system that helps to continuously monitor cement composition development trends during the curing process. Testing takes place inside a pressure- and-temperature-controlled curing chamber and is completed without destroying the cement sample.
- A fluid loss cell to measure the loss of water from cement slurry, ensuring cement strength is not compromised when set.
- A six-speed viscometer, which measures viscosity of cement slurries.

Web Site

Early in the project Trabits Group established webpages associated with the Trabits Group website that provided detail on the Geothermal Cement Development.

<http://trabitsgroup.com/geocement.html>

The Geothermal Cement webpages are divided into six tabs:

Intro

Grant Details

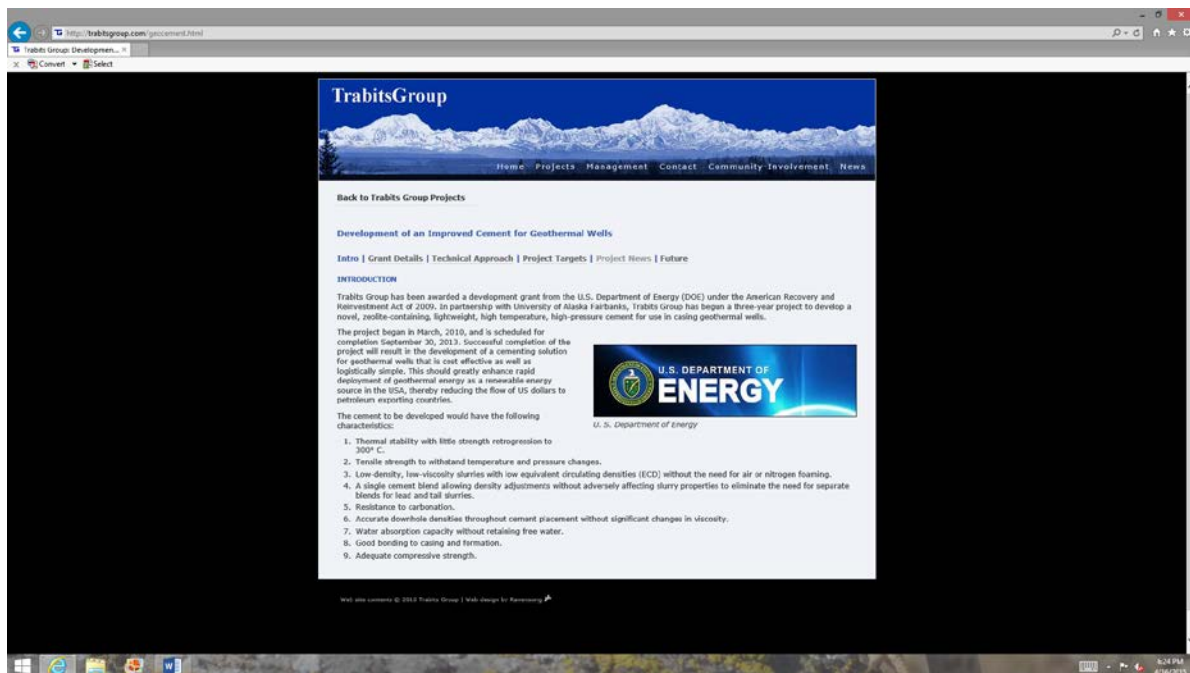
Technical Approach

Project Targets

Project News

Future

The webpages contain not only project information but a number of downloadable PDF documents to assist the reader in understanding the developing technology. Each webpage, as well as downloadable documents, contained an embedded code that allowed for tracking of the number of visitors to the site and also what content was viewed as well as country of origin. Website statistics were reported to GTO on a monthly basis.



Screen Capture Trabits Group Geothermal Cement Development Website

Technologies/Techniques

Two approaches were developed during the project with both meeting the stated goals of the new geothermal cement. These approaches were:

1. Dry blending of micronized zeolite with finished API Class cement.
2. Intergrinding cement clinker and whole rock zeolite at the cement plant in the final grinding mill.

Of these two methods the intergrinding of cement clinker and whole rock zeolite has the greatest benefit from both a performance perspective and for a lower manufacturing cost.

Intergrinding Benefits

- Economic gain of replacing a higher cost clinker with a lower cost zeolite.
- Lowering the resulting interground cement environmental cost associated with greenhouse gases during Portland manufacture.
- Interground cement allows for density adjustments within a single blend without adversely affecting slurry properties.
- Eliminates the need for separate blends for lead and tail slurries.
- Maintains accurate downhole densities throughout the cement placement without significant changes in viscosity.
- Extends water-absorption capacity without retaining free water.
- Provides thermal stability with little or no strength retrogression.
- Provides resistance to carbonation to maintain compressive strength and low permeability.