Monthly Research Performance Progress Report
Protected Data

Federal Agency and Organization: DOE EERE – Geothermal Technologies Program

Recipient Organization: Trabits Group, LLC
DUNS Number: 829739395

Recipient Address: PO Box 870404
Wasilla, AK 99687-0404

Award Number: DE-EE0002785
Project Title: Development Of An Improved Cement For Geothermal Wells
Project Period: 1/29/2010 through 9/30/2013

Principal Investigator: George Trabits
Trabits Group, LLC

Report Submitted by: Dr. Santanu Khataniar
University of Alaska Fairbanks

Reporting Period: January 2012

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This material is based upon work supported by the Department of Energy under Award Number DE-EE0002785

Project: Development of novel geothermal well cement using zeolite

Progress:

Free water tests were performed on Clinoptilolites from New Mexico Mine 2, and Mudhill. Both Clinoptilolites were tested using 10µm sizes at 15% replacement of Class H cement, to complement the previous results of 5µm and 44µm.

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 and then poured into the graduated cylinders and placed at an angle of 45° for measuring free water.

The free water results are shown in the Table below. The 10µm Clinoptilolites showed slightly higher free water than their 5µm counterparts.

Table 1: Free water test results for 13.5 ppg, 10µm Mudhill and New Mexico Mine 2 Clinoptilolites at 15% replacement of Class H cement

Clinoptilolite		
10µm		
Free Water, ml	Total Slurry, ml	Free Water, %
Mud Hill		
3.0	250	1.20
New Mexico #2		
2.8	250	1.12

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Principal Investigator: George Trabits
Trabits Group, LLC

Report Submitted by: Dr. Santanu Khataniar
University of Alaska Fairbanks

Reporting Period: February 2012

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Project: Development of novel geothermal well cement using zeolite

Progress:

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 will have to be conducted again due to increased amount of water required to make the 13.5ppg slurry.

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.

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Project Period: 1/29/2010 through 9/30/2013

Principal Investigator: George Trabits
Trabits Group, LLC

Report Submitted by: Dr. Santanu Khataniar
University of Alaska Fairbanks

Reporting Period: March 2012

Protected Data

This material is based upon work supported by the Department of Energy under Award Number DE-EE0002785

Project: Development of novel geothermal well cement using zeolite

Progress:

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 1 Damaged Ferrierite samples while de-molding

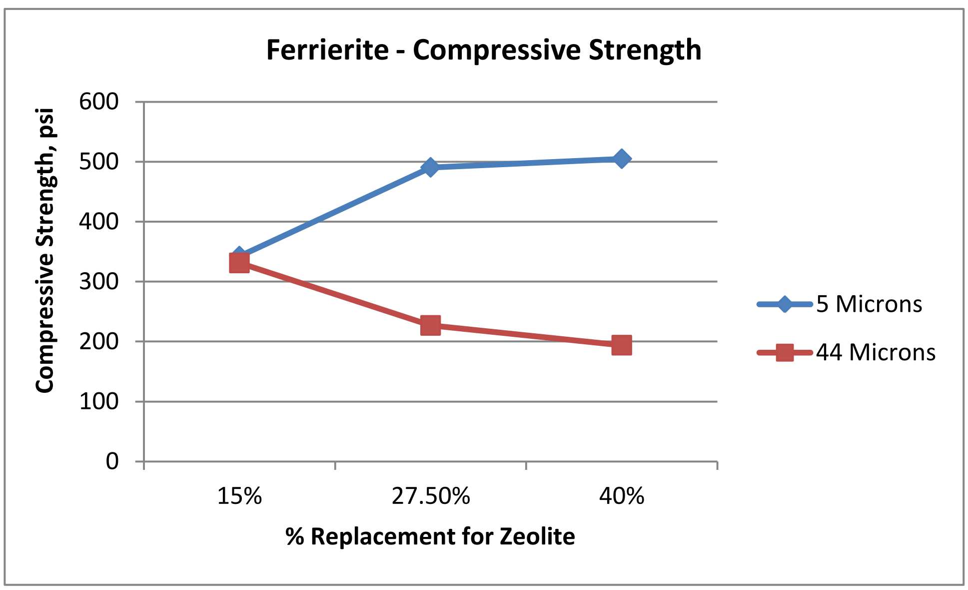

Figure 2 Compressive strength results for Ferrierite.

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Report Submitted by: Dr. Santanu Khataniar
University of Alaska Fairbanks

Reporting Period: April 2012

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Project: Development of novel geothermal well cement using zeolite

Progress:

Free water test was performed on Mud Hill Clinoptilolite of 44µm size for 15%, 27.5% and 40% replacement of Class H cement. Compressive strength test was also performed for 44µm Mud Hill Clinoptilolite.

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. The results are tabulated below.

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.

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.

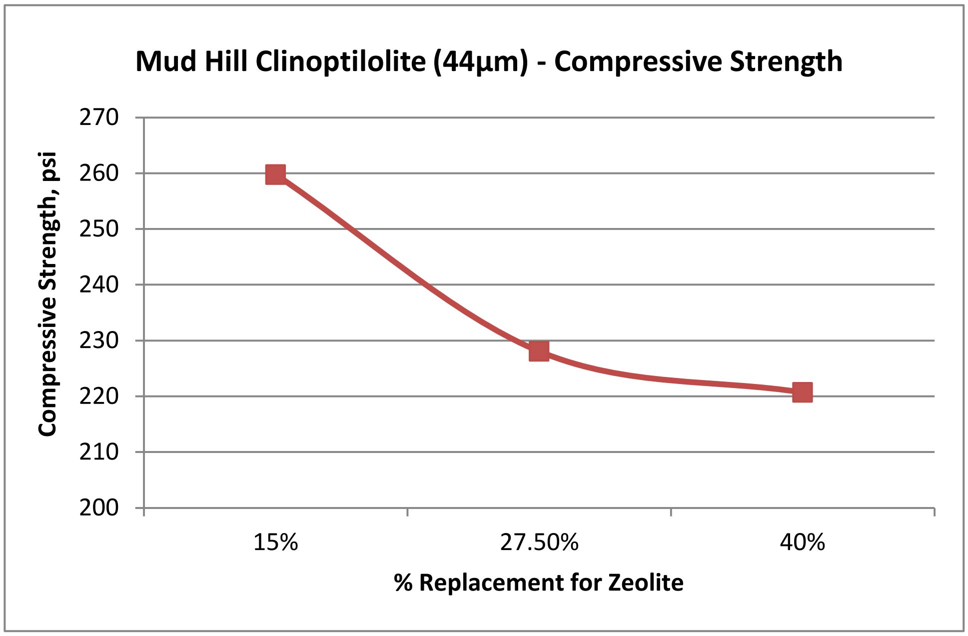

Figure 1: Compressive strength for 44µm Mud Hill Clinoptilolite using Class H cement

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Principal Investigator: George Trabits
Trabits Group, LLC

Report Submitted by: Dr. Santanu Khataniar
University of Alaska Fairbanks

Reporting Period: May 2012

Protected Data

This material is based upon work supported by the Department of Energy under Award Number DE-EE0002785

Project: Development of novel geothermal well cement using zeolite

Progress:

Free water tests were performed on Mud Hill Clinoptilolite of 5µm size and New Mexico Mine#1 Clinoptilolite of 44 µm size for 15%, 27.5% and 40% replacement of Class H cement. Also, compressive strength test was performed for 5µm Mud Hill Clinoptilolite.

Mud Hill Clinoptilolite and New Mexico Mine #1 Clinoptilolite were spread on trays 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. The slurries with Mud Hill Clinoptilolite of 5µm size were also poured into the cube molds for compressive strength measurement. The cylinder was placed at an angle of 45° for measuring the free water. For compressive strength measurement, the cement molds were cured in an oven at controlled temperature of 100°F for 24 hours.

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

Table 1: 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.

The results for New Mexico Mine #1 (44µm) free water test are shown in table 2.

Table 2: 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

The increase in the amount of zeolite resulted in a slight increase of the 24 hour compressive strength of the cement. Figure 1 shows the result for compressive strength of 5µm Mud Hill Clinoptilolite for different replacements.

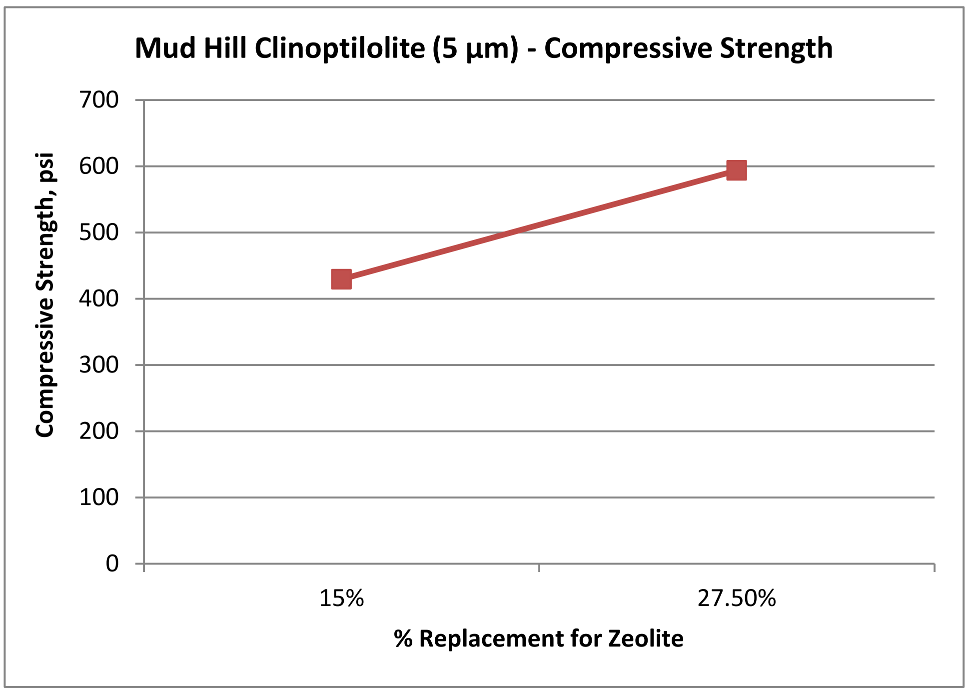

Figure 1: Compressive strength for 5µm Mud Hill Clinoptilolite using Class H cement

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

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Principal Investigator: George Trabits
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Report Submitted by: Dr. Santanu Khataniar
University of Alaska Fairbanks

Reporting Period: June 2012

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Free water tests for the remaining samples of the initial screening test matrix have been completed. 24 hour compressive strength tests for all 5 micron and 44 micron size samples in the test matrix have also been completed. All of these tests were done using 13.5 ppg API Class H cement-zeolite blends. The results are summarized in the two comprehensive tables below.

Table 1: 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.

Table 2: 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.

Compressive strength testing of 10 micron samples is in progress.

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UAF report for August 2012

The initial tests are progressing rapidly and have yielded interesting data. 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 1 and 2. (***** 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 1.

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	5% Chab	5% clay
		15%	27.5%	40%	27.5%	27.5%	27.5%
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 disentegration issues, run 2nd verfication

Denisty avg. of comp. samp. [g/cc]

Cement H		15%	27.5%	40%
Chabazite	5 µm			
	10 µm			
	44 µm			1.640
Mudhill	5 µm			
	10 µm			
	44 µm			
1/2 Mudhill 1/2 Ferrierite	5 µm	1.641	1.575	1.595
	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
	10 µm	1.578	1.573	1.584
	44 µm	1.598	1.532	1.477
Ferrierite Treated	Out Spec	1.654	1.626	1.623
	5 µm	1.650	1.640	1.631
	10 µm	1.670	1.641	1.644
	44 µm	1.716	1.653	1.634
Mordenite	5 µm	0.000	0.000	0.000
	10 µm	0.000	0.000	0.000
	44 µm	0.000	0.000	0.000

Permeability (using Tiny Perm) [mD]

(before crushing | after Crushing | Dried not crushed)

Cement H		15%			27.5%			40%		
Chabazite	5 µm									
	10 µm									
	44 µm								0.0	
Mudhill	5 µm									
	10 µm									
	44 µm									
1/2 Mudhill 1/2 Ferrierite	5 µm	2.8	4.1		2.2	2.5		2.7	7.5	
	10 µm	4.5	5.9		3.2	2.8		17.3	3.9	
	44 µm	11.6	11.6		4.5	5.6		6.2	5.8	
Ferrierite	5 µm									
	10 µm									
	44 µm									
NM #1	5 µm									
	10 µm								0.0	
	44 µm									
NM #2	5 µm									
	10 µm									
	44 µm									
Mudhill Treated	5 µm					0.0			0.0	
	10 µm	3.7	4.4		5.0	6.8			0.0	
	44 µm		0.0			0.0			0.0	
Ferrierite Treated	Out Spec	7.0	2.2	11.6	2.7	2.1	11.6	1.9	3.7	11.6
	5 µm								0.0	
	10 µm	0.0	0.0			0.0			0.0	
	44 µm		0.0			0.0			0.0	
Mordenite	5 µm	0.0	0.0		0.0	0.0		0.0	0.0	
	10 µm	0.0	0.0		0.0	0.0		0.0	0.0	
	44 µm	0.0	0.0		0.0	0.0		0.0	0.0	

Table 2.

Consistency (5 h Atmo 80°F) [Bc]

		15%	27.5%	40%
Chabazite	5 µm	12	45	*
	10 µm	8	34	*
	44 µm	4	13	31
Mudhill	5 µm	10	25	*
	10 µm	8	20	47
	44 µm	5	7	14

Ferrierite	5 µm	6	11	30
	10 µm	5	10	28
	44 µm	3	6	7
NM #1	5 µm	8	19	*
	10 µm	8	14	31
	44 µm	5	6	11
NM #2	5 µm	7	20	*
	10 µm	8	10	27
	44 µm	3	7	10

Viscosity (avg reading at 300 rpm)

		15%	27.5%	40%
Chabazite	5 µm		237.5	
	10 µm			
	44 µm		106	
Mudhill	5 µm			
	10 µm			
	44 µm		48.5	

Ferrierite	5 µm	28.5	67	
	10 µm			
	44 µm	16	33.5	
NM #1	5 µm		120	
	10 µm			
	44 µm		49.5	
NM #2	5 µm		90	
	10 µm			
	44 µm		64.5	

Summary of Zeolite Response

Chabazite:
Passes free water and compressive strength criteria for nearly all particle sizes and replacement levels. It yields high compressive strengths at 24 hrs (45˚F) for 5µm and 10µm and 27.5% and 40% replacement levels. Mixing for fine particle size and high replacement levels may be challenging.
Verdict: High quality zeolite replacement. Very expensive to produce.

Mudhill Clinoptilolite:
Mudhill passes the free water criteria except for 15% replacement with 44µm particle size. The compressive strength criteria met for 5µm at 27.5% and 40% replacements and 10µm at 40% replacements. Significant strength is gained at the 40% replacement as compared to the 27.5% replacement. Mixing for high replacements may be challenging. A hypothesis has been proposed that the high gains in strength at the 40% replacement levels may be due to the presence of montmorillonite clay
Verdict: Good zeolite replacement at 5µm and 10µm at 40% replacement levels.

Ferrierite:
Free water issues at 44µm and 15% replacements. Higher free water contents at comparable particle sizes and replacement levels as compared to the other zeolites. The 24 hr compressive strength (45˚F) does not meet the 500 psi criteria except for 5µm and 40% replacement level. Mixability is good as the mix is quite fluid for all conditions. At low replacement levels, the mix tends to settle and experiences some shrinkage upon curing due to the higher free water contents.
Verdict: Generally does not meet the compressive strength criteria for 24 hrs at 45˚F. Marginal zeolite replacement.

NM#1 Clinoptilolite:
Free water is not significant. Compressive strength data at 24 hrs and 45˚F yield values below the 500 psi criteria. The 5µm and 40% replacement was not tested due to mixing difficulties. The data set is limited, however, the NM#1 set cement tend to yields densities that are slightly lower than 1.50 g/cm^3. This is lower than either the mudhill or ferrierite mixes. The lower densities may affect the resulting compressive strength
Verdict: Based on 45˚F curing conditions, compressive strength conditions are not met. Poor to fair zeolite replacement

NM#2 Clinoptilolite:
Results are consistent with the observations for NM#1. The 24 hr compressive strengths at 45˚F did not meet the 500 psi criteria.
Verdict: Poor to fair zeolite replacement

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.** However, strength retrogression at those increased curing temperatures will also need to be tested. Will the zeolite mixes behave similarly to added silica for strength retrogression mitigation?

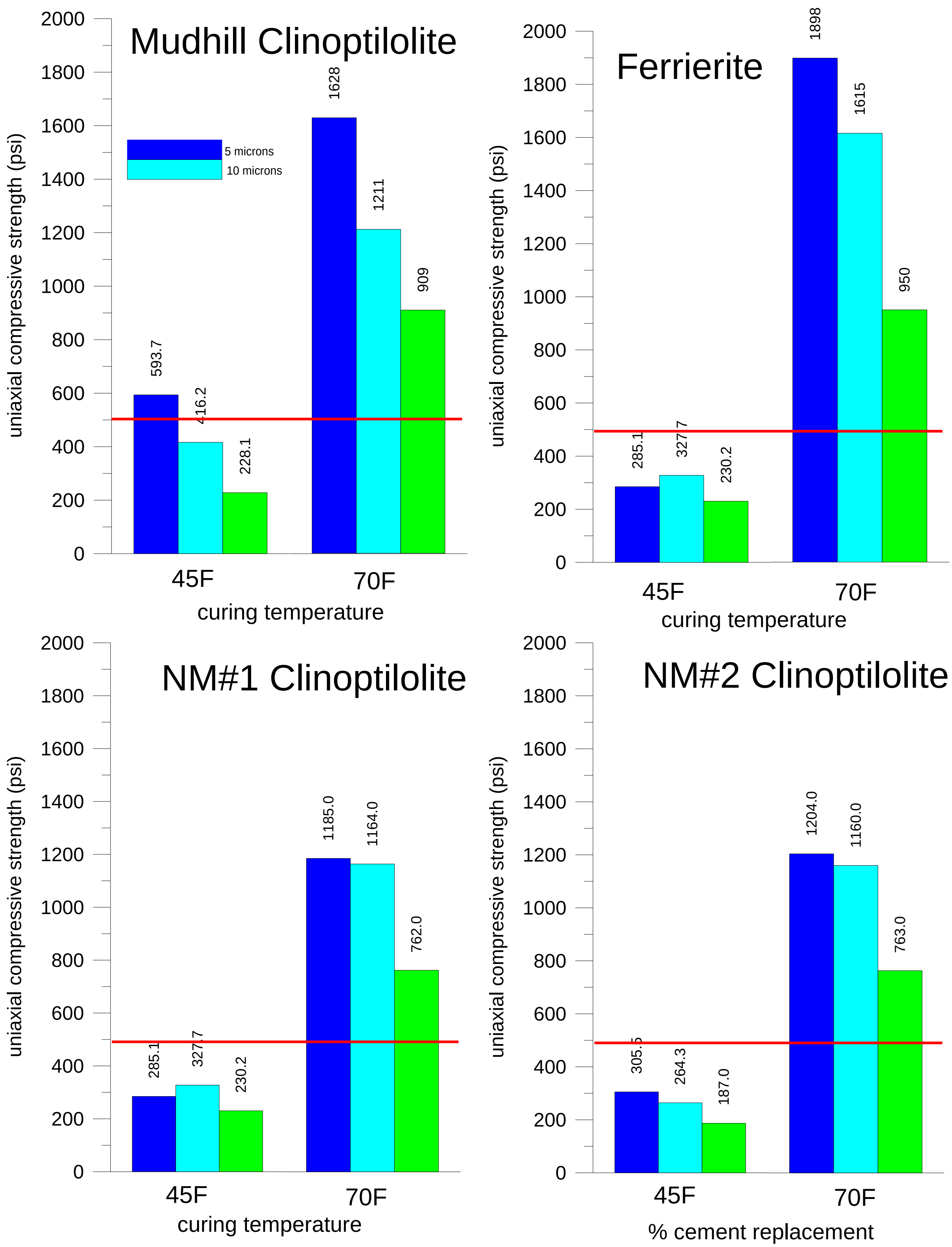

Figure 1. The 24 hour compressive strength is provided by mudhill, ferrierite, NM#1, and NM#2 as a function of curing temperature.

Mixed Zeolites

In response to the higher performance of chabazite and mudhill clinoptilolite as compared to ferrierite, NM#1, and NM#2, is 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.

Additional mixes (planned)

Trabits group identified that the mudhill clinoptilolite is composed of 10% to 20% montmorillonite clay. It is possible that the large increase in the compressive strength of mudhill at the 40% replacement levels for 5µm and 10 µm, is the result of the montmorillonite. In response, 5% replacement (% of total solids) of montmorillonite will be conducted for the 27.5% replacement levels. For example; the 27.5% replacement level for ferrierite will be modified to 5% montmorillonite and 22.5% ferrierite, which equates to approximately 18% montmorillonite content of the zeolite portion of the mix. Montmorillonite at both the 5 µm and 44 µm particle sizes will be tested. Dependent on the results for the replacements of ferrierite, the montmorillonite replacement may be extended to NM#1 and NM#2 clinoptilolite. The montmorillonite replacement may be applied to the 40% replacement levels with the addition of 7% to 8% montmorillonite replacing a portion of the zeolite.

In addition to the montmorillonite replacement, 5% chabazite replacements will also take place for the mudhill and ferrierite zeolites at the 27.5% replacement levels. Dependent on the results, the tests may be extended to NM#1 and NM#2. The test may also be extended to higher curing temperatures.

Thermally Activated Zeolites

Two zeolites underwent heat treating which is designed to attach nitrogen gas to the zeolite particles/structure, which upon mixing and curing, the nitrogen is released thus forming a light weight and easily pumpable cement mix. Ferrierite and mudhill clinoptilolite represent the heat treated zeolites. In July, spurious results were noted for 10µm Mudhill at 15% and 27.5% replacements for both the compressive strength and densities. Using our modified mold preparation procedure, verification tests yield results that are in the same approximate range as non heat treated samples. As a general observation, the free water and compressive strength between the heat treated and non heat treated zeolites are comparable.

Permeability

Permeability measurements have been adopted as part of the compressive strength testing program. Using an air permeameter field device trademarked at Tiny Perm II, the permeability in milliDarcies (mD) is measured at three stages. When the set cement is removed from the compressive strength molds at 24 hours, an initial permeability reading is obtained. Following the compressive strength test, an additional measurement is taken. Finally, the sample is allowed to either air dry or is oven dried with a third permeability reading taken. Typically the lowest permeability is measured from the first reading right after the sample is removed from the molds. This is expected due to surface tension and pressure differences between the air and fluid which is likely present in the voids of the sample. The permeability readings following the compression test generally provide equivalent or higher permeability readings which may be the result of micro-fractures in the sample or additional drying. The final readings taken from the dried samples yield much higher permeabilities. This value will be considered the most accurate representation of the actual permeability of the sample (gas permeability).

Outlier Observations

Occasionally, interesting scenarios develop which may or may not have relevance depending on the repeatability of the deviant behavior. The 5µm and 10µm mudhill samples at 70˚F curing showed edges or faces that disintegrated upon removal from the molds. We are adjusting the curing conditions by increasing the base humidity in the oven, adding additional plastic to the top portions of the molds, and preparing an alternative mix at a target slurry density of 12.5 ppg (more water) based on the hypothesis that drying of the sample was occurring. One additional mix of ferrierite_5µm_40% replacement was observed to disintegrate into block upon removal from the molds. A 2nd mix was attempted at 12.5 ppg with similar results. However, a third mix at the original 13.5 ppg slurry density resulted in competent samples. These observations are not typical patterns seen for the mixes, yet if they prove true, the results are significant.

Monthly Research Performance Progress Report
Protected Data

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Recipient Organization: Trabits Group, LLC
DUNS Number: 829739395

Recipient Address: PO Box 870404
Wasilla, AK 99687-0404

Award Number: DE-EE0002785
Project Title: Development Of An Improved Cement For Geothermal Wells
Project Period: 1/29/2010 through 9/30/2013

Principal Investigator: George Trabits
Trabits Group, LLC

Report Submitted by: Dr. Santanu Khataniar
University of Alaska Fairbanks

Reporting Period: July 2012

Protected Data

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UAF report for July 2012

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 Clinopt. gave very high compressive strength, and the result appeared anomalous. So, this compressive strength measurement was repeated, however, the result remained unchanged.

Free water tests and 24 hour compressive strength measurements were then performed using the Thermally Activated Nitrogen Bonded (ThermoActive or ThermaGen) Ferrierite and Mudhill Clinopt. zeolites. These are referred as the treated zeolites. Tables 2 and 3 show the free water and compressive strength results. The treated Mudhill zeolite, at 40% replacement and 5 and 10 micron sizes, showed very high compressive strengths.

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 Clinopts as well, to see how these differ from Mudhill Clinopt.

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

Table 2: Free Water [volume %] with Treated Zeolites

	Replacements:	15%	27.5%	40%
Mudhill Treated	5 µm	2.04%	0.20%	0
	10 µm	1.68%	0.28%	0
	44 µm	6.88%	0.76%	0.48%
Ferrierite Treated	5 µm	5.04%	0.32%	0%
	10 µm	8.64%	1.36%	0.12%
	44 µm	14.40%	5.72%	2.72%

Table 3: 24 Hour Compressive Strength [psi] with Treated Zeolites

	Replacements:	15%	27.5%	40%
Mudhill Treated	5 µm	329	635	1393
	10 µm	129	119	1266
	44 µm	285	227	198
Ferrierite Treated	5 µm	367	446	615
	10 µm	372	357	383
	44 µm	408	286	215

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Report Submitted by: Dr. Santanu Khataniar
University of Alaska Fairbanks

Reporting Period: September 2012

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Abstract

The effects of combining the zeolites with montmorillonite or chabazite have been studied. The addition of 5µm montmorillonite provides an increase in the 24 hour compressive strength at 45ºC 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.

Results and Discussion

Efforts have 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 1. 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 45ºC 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 1. Compressive strength summary

Compressive Strength [psi]

Cement H	847.0	15%	27.5%	40%	70°C 27.5%	5% Chab 27.5%	5% clay 27.5%	7.2% clay 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 44µm level, the total replacement was 30% zeolite and 10% clay. A 15% montmorillonite replacement at the 44µm level will be conducted thus spanning the range of 5% to 15%. A 5% 5µm chabazite replacement was conducted on the NM#1 10µm at the 27.5% total replacement level. The compressive strength between the 5µm 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, 5µm NM1 34.5% replacement mixed with 5µm 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 44µm NM1 30% replacement and 5µm 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 5µm ferrierite and NM1 at the 40% replacement levels. The post peak strength reduction rate is higher than lower replacement values or the 44µm 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.

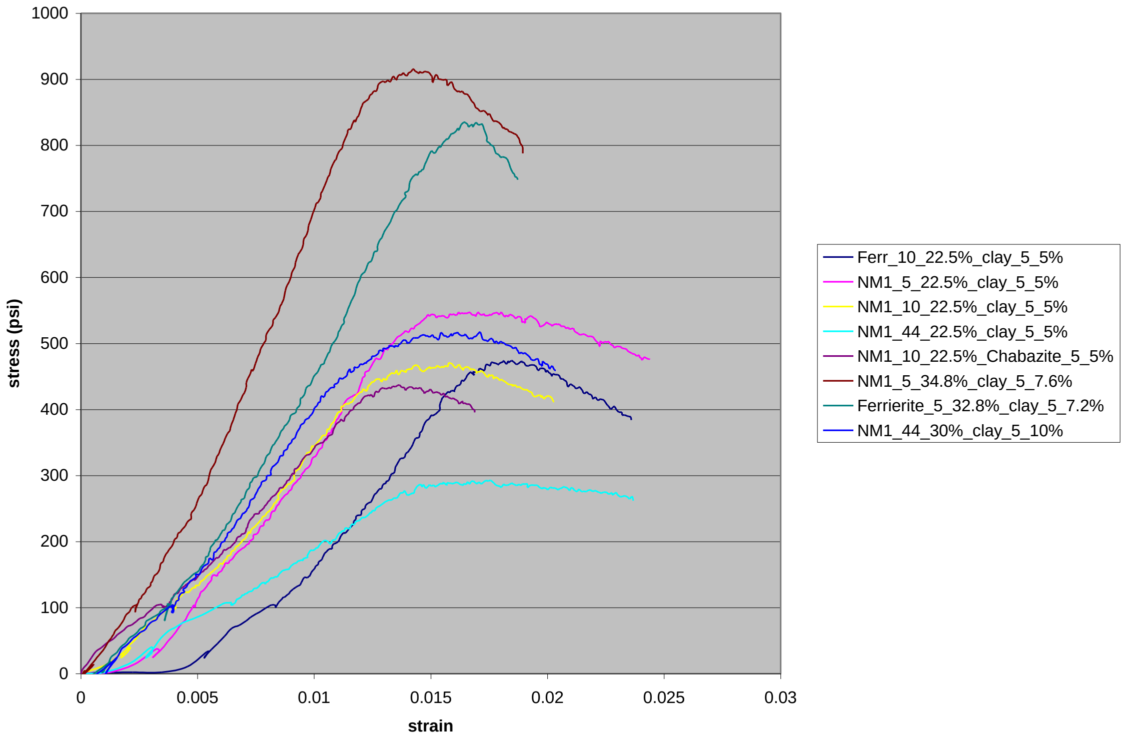

Figure 1. Stress-strain patterns for ferrierite and NM1 montmorillonite mixtures.

HPHT Ultrasonic Tests:

One trial test is be run on the Chandler HPHT Ultrasonic Cement Analyzer (UCA) for a 10µm 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.

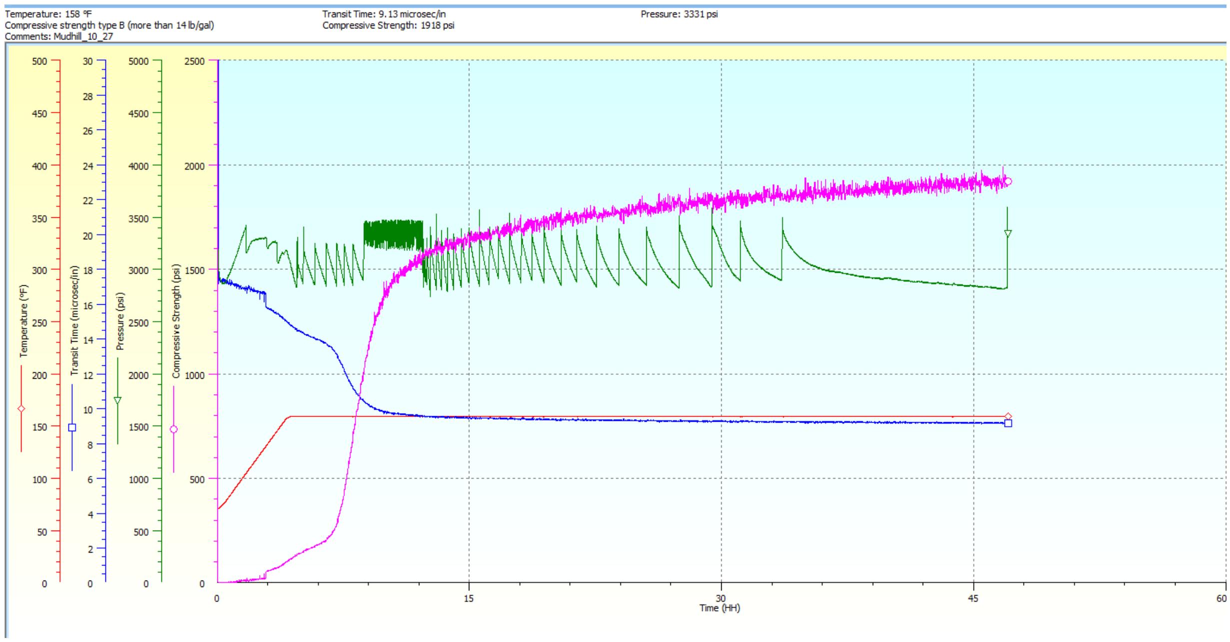

Figure 2. UCA analysis of 10µm mudhill at 27.5% replacement level at 70ºC. The pink/purple curve is the compressive strength and correlates to the first y-axis (far right).

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Report Submitted by: Dr. Santanu Khataniar
University of Alaska Fairbanks

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Abstract

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.

High temperature/High Pressure Testing

Chandler Engineering is providing training on the high pressure high temperature test apparatus starting October 22nd. HPHT testing of selected zeolites will commence following the training.

Based on initial screening, HPHT will be conducted on mudhill clinoptilolite and ferrierite at the 5μm and 10μm particle sizes. Based on positive results of montmorillonite, it will be included as a partial or total replacement. Diatomaceous earth will be tested at temperate above 300°F as a potential means to mitigate strength retrogression.

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

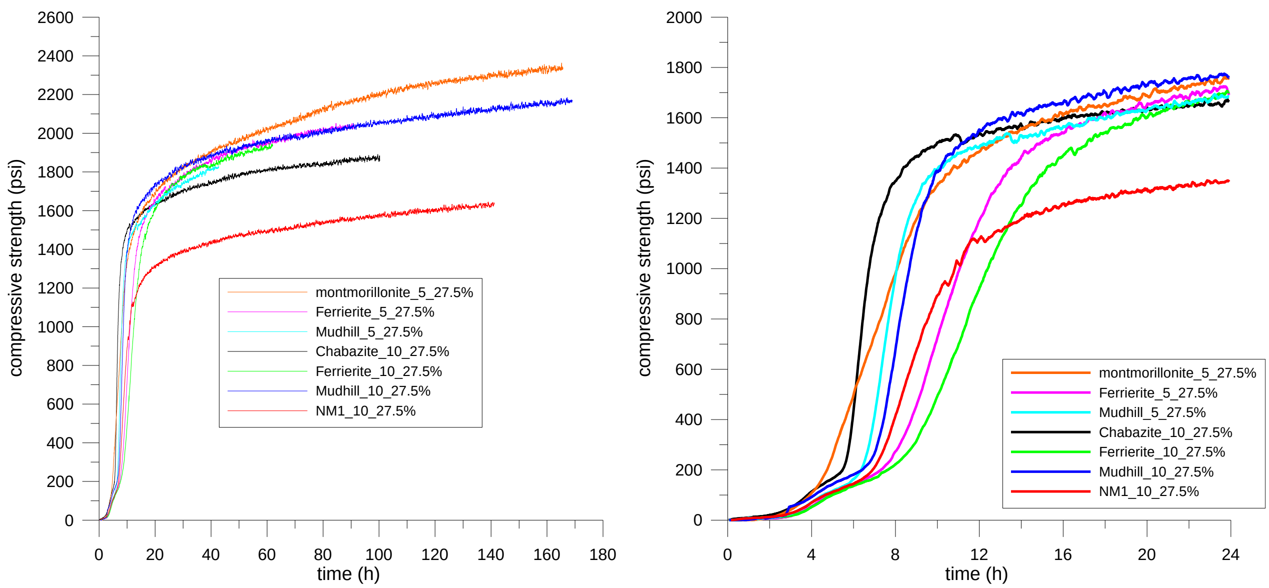

Figure 1. Real time compressive strength test at 27.5% replacement levels. Test conditions: 70°C, pressure ~3000 psi.

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/cm^3)

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_{init} = 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 montmorillonte 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 than 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/cm^3)

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, to 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]

Cement H	847.0	45°C			70°C	45°C 5%_Chabazite	45°C 5%_MM_5µm	45°C 5%_MM_44µm	45°C 7.2%_MM_5µm	45°C 7.2%_MM_44µm	45°C 10%_MM_5µm	45°C 15%_MM_5µm	45°C 5%_ DE	45°C 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/cm^3
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									
	44 µm				12.50									
Mordenite	5 µm													
	10 µm													
	44 µm													
Montmorillonite (MM)	5 µm		3.03											
	44 µm		7.90											
Diatamaceous Earth (DE)														
	60 µm		8.08											

Monthly Research Performance Progress Report
Protected Data

Federal Agency and Organization: DOE EERE – Geothermal Technologies Program

Recipient Organization: Trabits Group, LLC
DUNS Number: 829739395

Recipient Address: PO Box 870404
Wasilla, AK 99687-0404

Award Number: DE-EE0002785
Project Title: Development Of An Improved Cement For Geothermal Wells
Project Period: 1/29/2010 through 9/30/2013

Principal Investigator: George Trabits
Trabits Group, LLC

Report Submitted by: Dr. Santanu Khataniar
University of Alaska Fairbanks

Reporting Period: November 2012

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Abstract

This update presents preliminary observations from the early stages of the HPHT testing of selected zeolite samples. Ultrasonic compressive strength measurement tests were extended to 300°F. Early results indicate a significant strength decrease as compared to UCA results at 158°F. All tests show a strength decrease at 1 to 2 days. Tests were not extended to show if this is a short term effect as hydration phases stabilize or a long term trend. At the 40% replacement levels, ferrierite provides the best strength trends up to 100 hours as compared to mudhill clinoptilolite and diatomaceous earth (Montmorillonite). HPHT consistency tests for selected samples are being planned to follow up on the UCA measurements. Preliminary permeability measurements on some samples have been conducted using a mini permeameter device (TinyPerm).

Results and Discussion

Note:
The deposit identified in earlier reports as montmorillonite (MM) clay has been shown to be primarily diatomaceous earth based on SEM analysis by Trican Well Services.
UCA Analysis

At 158°F and 27.5% replacement levels, the zeolite/cement H mixtures show progressively increasing compressive strengths up to the max testing period of 180 hours (~7.5 days). Subsequent tests at elevated temperatures up to 300°F were run for a period of approximately 4 days (90-100 hrs). The strength properties of cement mixes at elevated temperature are known to be highly variable and depend on the metastable and stable hydration products formed under a specific temperature condition and to a lesser extent, pressure. Figure 1 provides a comparison for 27.5% ferrierite replacements at temperatures of 158°F, 220°F, and 300°F. Common phase transitions of hydration products and strength impacts typically occur between 200°F and 250°F. A significant decrease in the compressive strength for ferrierite was observed at 300°F. The long term strength trend is unknown; however, a stabilized zone is seen for a period between 30 and 100 hours. Included in Figure 1 is the UCA data for a 40% replacement at 300°F. Short term strength gains are significantly higher than the 27.5% levels. The increased strength and location of the peak strength suggests that variations in the type and relative amount of hydration products are likely. A decrease in strength is observed over the test period. A stabilization of the strength properties may occur as the hydration products stabilize.

Real time compressive strength data is presented in Figure 2 at the 5 micron, 40% levels for ferrierite, mudhill clinoptilolite, and diatomaceous earth (MM). Tests were conducted at 300°F and 5000 psi. Initial strength gains for ferrierite and mudhill are similar. Post peak strength reductions over the test period are higher for mudhill. For mudhill, the post peak reduction in strength may be stabilizing at approximately 70 to 80 hours. The long term strength reduction trend is unknown. In response to the post peak declines, diatomaceous earth was tested as a source of reactive silica. Note that the sample originally identified as montmorillonite clay has been shown to be primarily composed of diatomaceous earth based on SEM analysis by Trican Well Services. Current designation for this test deposit is DE (MM). As evidenced in Figure 2, peak strength and residual strengths are significantly lower than the ferrierite or mudhill mixes. The DE (MM) mix required additional water for adequate consistency of the sample, thus lowering the slurry density to ~12.0 ppg and increasing the water content. This may contribute to the lower strength values observed. Samples exhibiting compressive strengths in the range of 200 psi are generally poorly bonded and friable in nature. The 27.5% DE(MM) mix at 158°F performed very well.

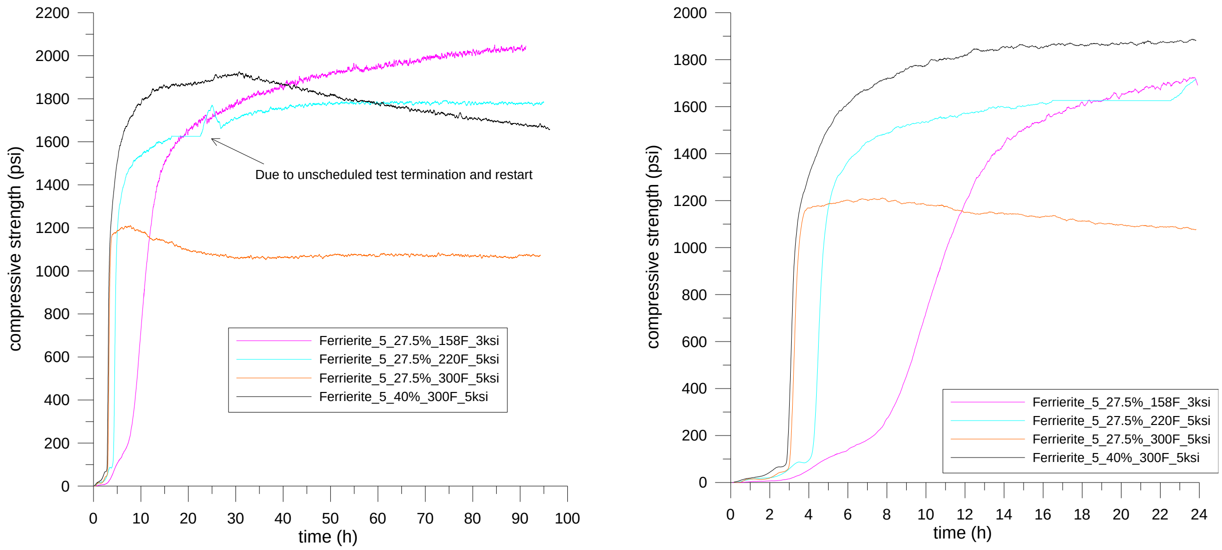

Figure 1. Real time compressive strength development for ferrierite (5 micron) based cement mixes at temperatures ranging from 158°F to 300°F. Target density 13.5 ppg.

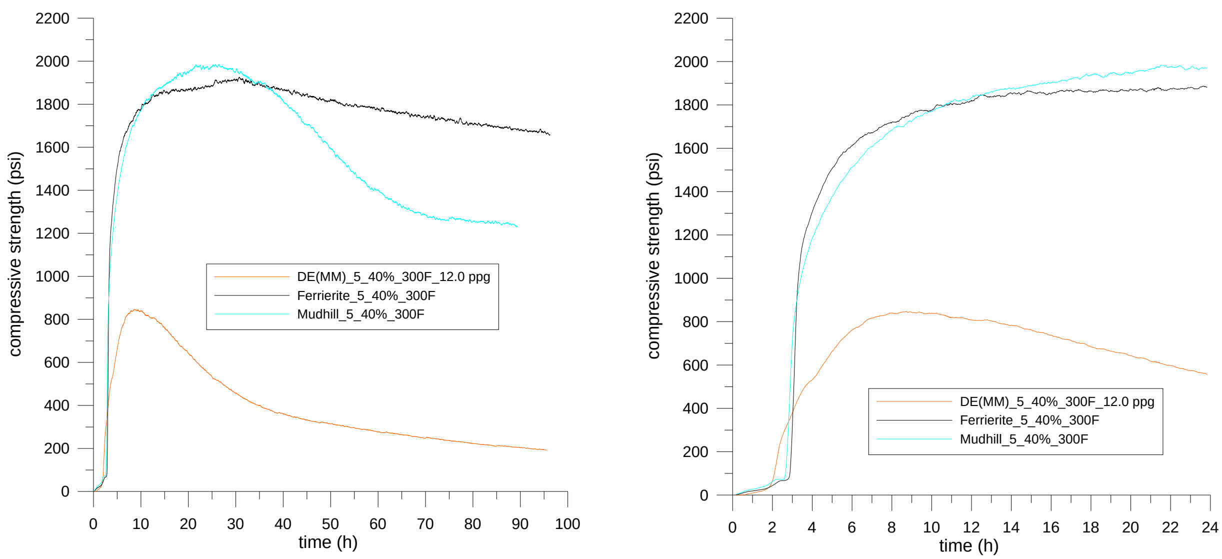

Figure 2. Real time compressive strength development for the 40% replacement level using 5 micron ferrierite, mudhill clinoptilolite, and diatomaceous earth (MM) at 300°F and 5000 psi.

Permeability

Several samples were cured under variable pressure and temperature during the period of 4 to 7 days with pressures up to 6000 psi and temperatures up to 200F. The bulk of the curing time was under 100 psi and 80°F. Permeability measurements were conducted on cored samples using distilled water at 70°F with a 250 psi pressure differential. Early measurements suggest very low permeabilities in the range of 1-10 μD. Measurements on the same saturated samples using the TinyPerm device provide permeability values in the range of 2.5 mD. Sample porosities range around 45%. These measurements are not intended to be definitive. They do suggest the permeabilities of these samples are low, however, it is not clear at this point if these permeabilities are sufficiently low. Attempts to measure permeability using a liquid (water) in a standard core holder have so far been unsuccessful because of very high pressure drops resulting from the low permeabilities.

Monthly Research Performance Progress Report
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Report Submitted by: Dr. Santanu Khataniar
University of Alaska Fairbanks

Reporting Period: December 2012

Protected Data

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Abstract

This report briefly summarizes the initial HPHT consistency data. Results indicate that thickening times are a concern, even with R8 (Baker Hughes) retarder. Thickening times decrease with increasing replacements and decreasing particle sizes. The retarder acts as a dispersant, resulting in free water and settling issues of the curing slurries. Negatively, the retarders greatly extend the development of compressive strength without meeting necessary working times. Retarders have only been tested at replacement levels of 40% or greater.

Results and Discussion

Consistency

Initial results from HPHT consistency tests are shown in Table 1 and Figures 1 and 2. Base mixes incorporating ferrierite, mudhill clinoptilolite, NM2 clinoptilolite, diatomaceous earth and montmorillonite/DE were tested. Tests were conducted at 300°F and 8500 psi. As expected the thickening time (70 Bc) and consistency increase with increasing temperatures. All thickening times for base mixes (i.e., no retarder) are below 90 minutes and do not allow sufficient working time for cement placement. A retarder identified as R8 from Baker Hughes was applied to several of the mixes in proportions from 0.8%BWOC to 1.6%BWOC. The retarder influences the thickening time significantly compared to the base levels, but thickening times are still significantly less than a target value of approximately 4 to 5 hours.
Retarders typically act as dispersants resulting in thinner mixes. This effect is observed on the test samples. A negative effect is an increase in free water and settling issues. This is pronounced in the ferrierite samples, but also noticeable in the mudhill and NM2 clinoptilolite. This effect is beneficial for high replacement levels (40% or greater) as it reduces the viscosity of the mixes. However, as a result of decreasing viscosity and increasing free water, settling affects are occurring. The influence of settling can be seen in Figure 2 as evidenced by the erratic consistency plots.

It was recommended that a generic hydroxycarboxylic acid/borax may be a potential retarder. Based on the R8 results, the generic retarder will be tested and most likely will consist of tartaric acid and borax.

Table 1. Summary of HPHT consistency data for zeolite based cement mixtures.

	Particle size (µm)	Consistency (Bc)	Time (minutes)				
			27.5%		40%	45%	60%
			158F	300F	300F	300F	300F
Ferrierite	5	30	51	43	12		37
		70	72	61	42		49
Ferrierite	10	30	67	57	21		
		70	82	63	57		
Ferrierite (R8_1.3%BWOC)	10	30			91		
		70			104		
Ferrierite	44	30			64		
		70			69		
Ferrierite_35%_ Moltan DE_10% (R8_0.8%BWOC)	10	30				44	
		70				47	
Ferrierite_35%_ Moltan DE_10% (R8_1.6%BWOC)	10	30				68	
		70				70	
Mudhill	5	30	23	15	* (0)		
		70	60	40	20		
Mudhill (R8_1.3%BWOC)	5	30		73			
		70		78			
Moltan DE	20	30			22		
		70			43		
Montmorillonite (DE)_12.0 ppg	5	30			** (0)		
		70			20		
NM2	5	30	26				
		70	65				
NM2 (R8 1.3%BWOC)	5	30			79		
		70			86		

* Base consistency of 69 Bc, slurry density target 13.0 ppg

** Base consistency of 38 Bc

	30 Bc	70 Bc	100 Bc
Ferrierite_5_27.5%_300F_8.5ksi	43	61	63
Ferrierite_5_27.5%_300F_14ksi	51	58	61

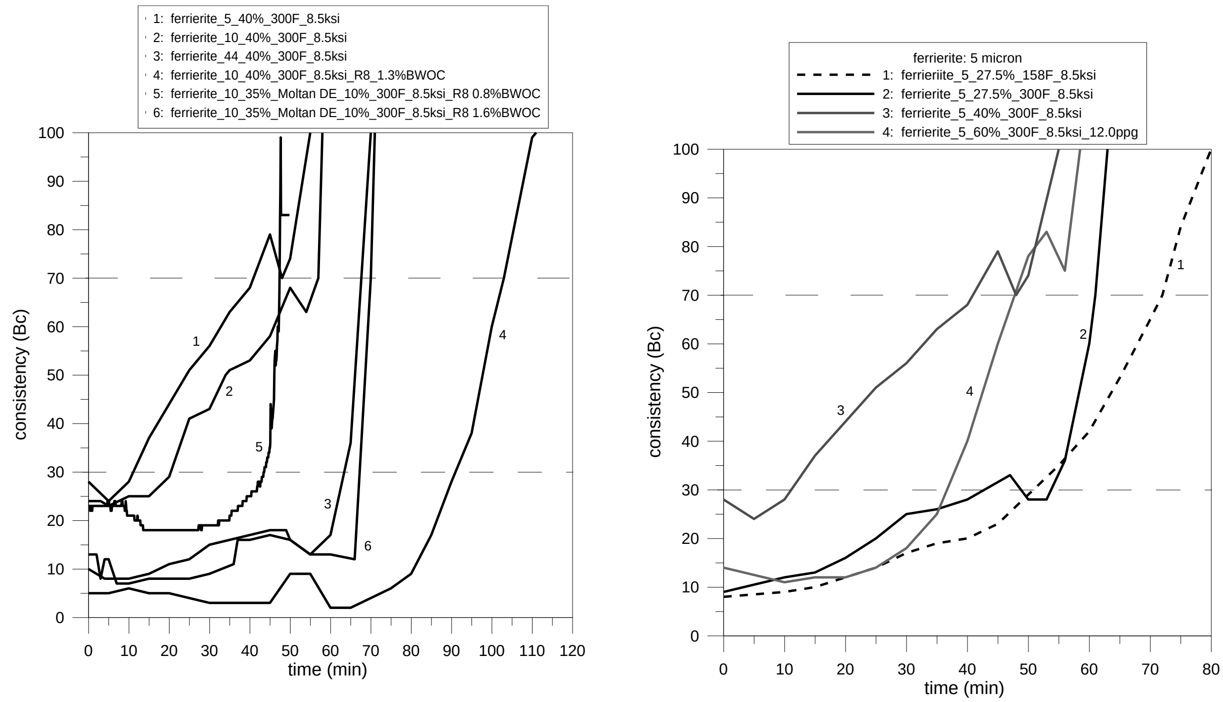
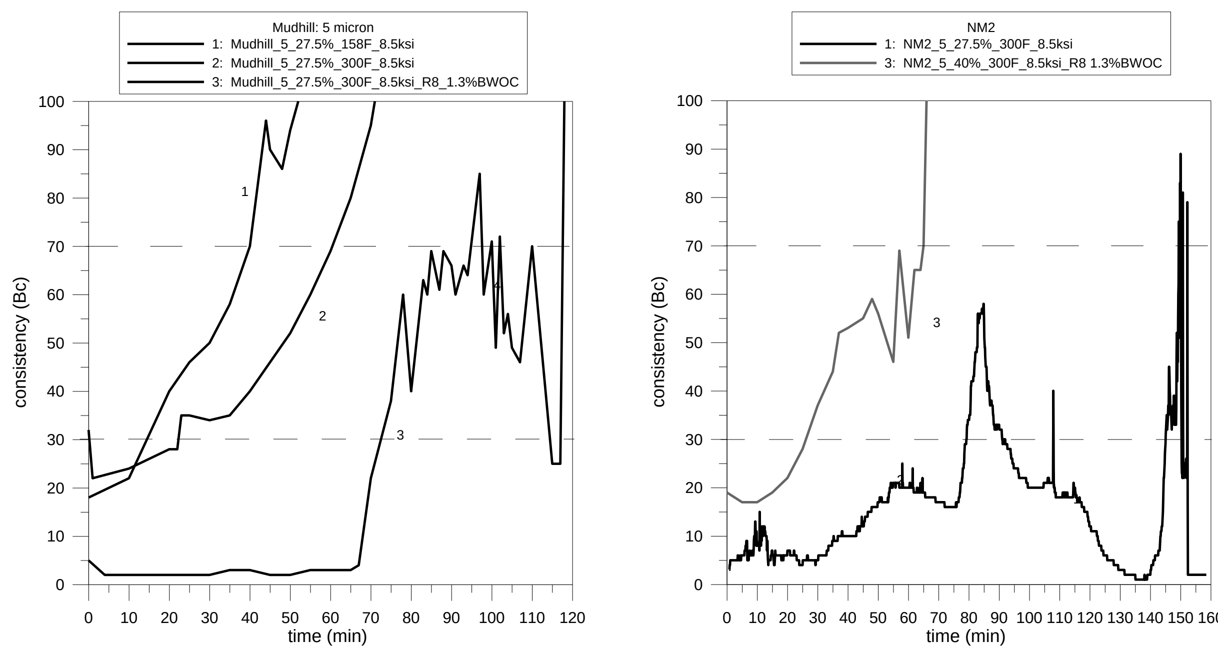


Figure 1. Consistency plots for ferrierite based mixtures. Temperature ramping schedules: 300°F (60 min).



(A) (B)

Figure 2. Consistency plots for mudhill clinoptilolite (A) and NM2 clinoptilolite (B) based mixtures. Temperature ramping schedules: 300°F (60 min).

UCA results

Test results from UCA tests are shown in Figure 3. In general, ferrierite provides better strength development and less post peak reduction than mudhill clinoptilolite. Increasing replacement levels result in improved strength characteristics. Decreasing slurry density as evidenced by curves 6 (montmorillonite (DE)) and 7 (Moltan DE) show significant post peak strength reduction which is likely the result of increasing water contents. Curve 8 provides strength development for a NM2 clinoptilolite/Moltan DE mix. The compressive strength is significantly lower than ferrierite based samples. However, NM2 clinoptilolite provides better free water characteristics than ferrierite and may be a viable mix, especially if added to the ferrierite. Initial observations of the ferrierite and NM2 slurries at 35% replacements with an additional 10% Moltan DE added suggest that post peak reductions may be less than the singular replacement of each zeolite (40%)

Not shown in Figure 3 is the strength development data for ferrierite_10μm_35%_Moltan DE_10%_300F_5ksi_R8 1.6%BWOC. The peak strength for this sample was approximately 1700 psi with a 200 psi drop. However, the strength appeared to stabilize. This represents a retarded sample providing a thickening time of 70 min. However, no appreciable strength development occurred until 30 hours. In this case the retarder had an unacceptable impact on strength development.

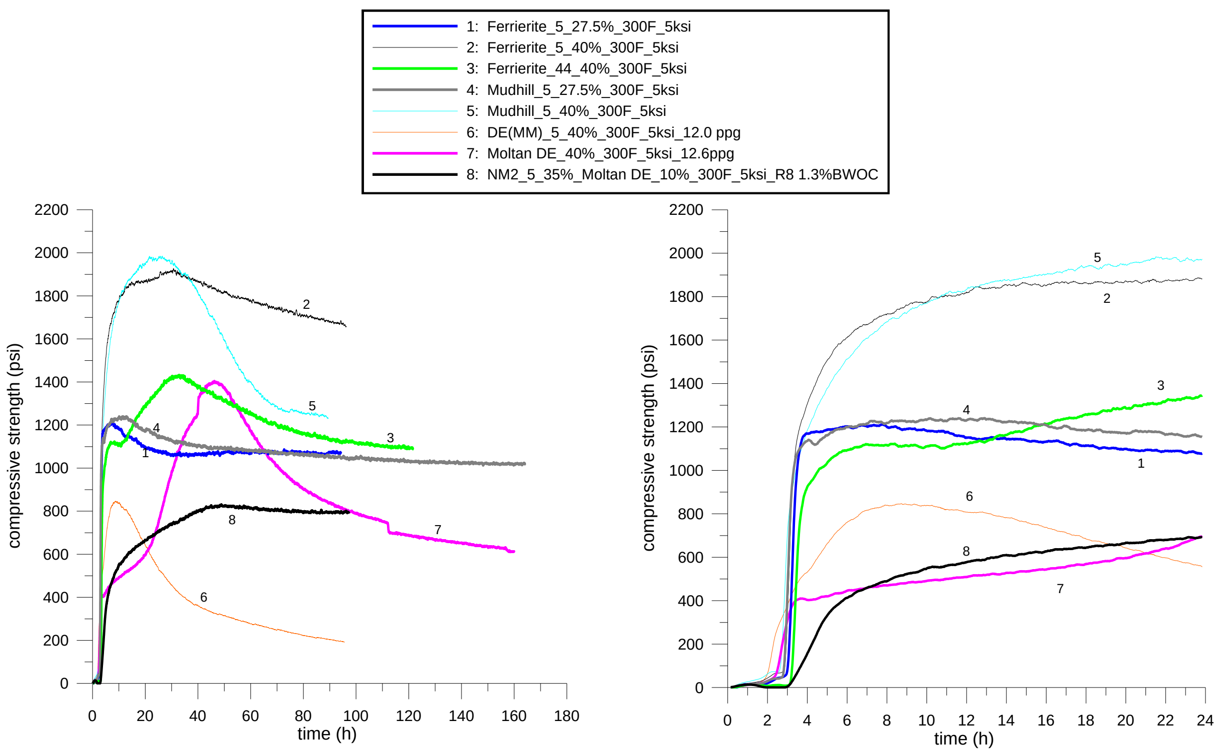


Figure 3. HPHT UCA test results for tests conducted at 300°F and 5000 psi.