



University of
Stavanger

Faculty of Science and Technology

MASTER'S THESIS

Study program/ Specialization: Master of Science in Petroleum Engineering Drilling and Well Technology	Spring semester, 2012 Open
Writer: Safa Gasimov (Writer's signature)
Faculty supervisor: Helge Hodne External supervisor(s): Helge Hodne	
Title of thesis: Influence of different factors to the strength development of the cement slurry with aplite as a pozzolanic material.	
Credits (ECTS): 30	
Key words: Cement Compressive strength Additives Pozzolan Cementing in HTHP Silica Sea water	Pages: 31 + enclosure: 9 Stavanger, 08.06.2012 Date/year

Table of Contents

1 Introduction 1

2 Materials and Experimental Procedures	2
2.1 Portland Cement Class “G”	2
2.1.1 Manufacturing of Portland Cement	2
2.1.2 Effect of Temperature to the Curing.....	4
2.2 Synthetic seawater.	4
2.2.1 Sodium chloride.....	5
2.3 Pozzolan	5
2.3.1 Pozzolanic reaction.....	6
2.3.2 Aplite	6
2.4 Calcium Carbonate	7
2.5 Description of the Test	8
3 Results and discussion.....	10
3.1 Test number 1	10
3.2 Test number 2	10
3.3 Test number 3	11
3.4 Test number 4.....	12
3.5 Test number 5	13
3.6 Overview of tests 1, 2, 5. Effect of seawater on the strength development	14
3.7 Test number 6.....	14

3.8 Test number 7	15
3.9 Test number 8	16
3.10 Test number 9	17
3.11 Overview of tests number 3, 7, 8, 9.....	18
3.12 Test number 10	19
3.13 Test number 11	19
3.14 Test number 12	21
3.15 Overview of the test number 4, 10, 11, 12	21
3.16 Test number 13	22
3.17 Test number 14	23
3.18 Test number 15	24
3.19 Test number 16	24
3.20 Test number 17 and 18	25
5 Conclusion.....	29
6 Nomenclature.....	30
7 References	31
8 Appendix	32

Abstract

This study has 18 experiments which were performed in order to see the influence of different factors to the strength development of cement slurry containing Aplite. Aplite is a pozzolanic material consisting mainly from silica. It provides beneficial strength development for cement slurries curing above 110°C, more environmental friendly than cement and more cost effective.

Experiments showed that Aplite has a pozzolanic effect and prevent cement slurry from strength retrogression at the temperatures higher than 110°C. Also it was discovered that proportional replacement of Aplite by cement has a positive effect to the strength development. Experiments showed that curing under high pressures has positive effect to the strength development. Temperature has also positive effect to the strength development, but in a different way for the slurries curing above and under 110°C.

Acknowledgements

This report presents my final thesis work as part of MSc study of Petroleum Engineering faculty at University of Stavanger.

First of all, I am very grateful to my professor and supervisor, Helge Hodne deeply for his guidance during this project and for willingness to share his expertise in cementing technology that contributed a lot on strengthening my ideas towards this project. Special thanks for spending his precious time in order to help me and provide the guidance when I was facing the challenges. I would not hesitate to say that because of his continuous encouragement and belief in me that initially looking impossible task turned into very interesting project.

Special thanks to Jostein Djuve who provided me with safety guidance

I am thankful to University of Stavanger and to all my professors for gained knowledge, most of which I used for implementation of this project.

This thesis dedicated to my grandmother Firanqiz Qulieva who untimely passed away last year waiting for me to come back for holidays.

Finally, I would like to deeply thank my family and friends for their support and understanding. Thank you!

Safa Gasimov

Stavanger, June 2012

1 Introduction

Problems such as stuck pipe, mud losses, failure of equipment, poor cement job and other unwanted situations still occur while drilling and completion, however the drilling is the most progressive part of the oil industry. When deeper reservoirs which specifications and properties are not the same as in shallower reservoirs are reached; it should be considered that specificity of technology for deeper reservoirs is also changing due to different geological, physical and chemical parameters. Each field or even well usually is a special case and require particular solution. However, sometimes it takes a lot of time, hence money to develop a particular design or solution for a well. Companies use mathematical methods like simulation and correlation for design which do not take into account small but very important details, such as integration of cement slurry for physicochemical and lithological properties of structure. Poor cement job results in annular gas migration in the wells with high temperatures and pressure. Also permeability of set cement changes after the well start to produce. As a result companies pays a lot of money for remedial cementing, however, it is better to spend more time on analyzing, testing and appropriate designing of slurry for a given condition in order to avoid such cases and decrease expenses and accidents. Recent accident in Mexican Gulf, which was the biggest ecological catastrophe in US history, killed 11 people and caused enormous expenses after the accident. This is a clear example of what can happen as a result of a poor cement job.

Cement plays the main role in well abandonment. It is very important to design the isolation as it was before drilling. But, it should be considered that set cement can be exposed to influence of strength destroying elements, compounds which can affect together with pressure and temperature conditions. Pressure and temperature specificity of HPHT wells must be considered even if reservoir conditions are different from initial. Designs of correspondent cement slurry for safely and qualitative abandonment is an actual challenge under mentioned conditions.

Nowadays it is not common to have only water and cement in the slurry. Numerous factors can change properties of the slurry in a different ways. Some of them are not controlled by engineers (Pressure, Temperature) while cementing. But on other hand cement engineers has a big amount of additives in their arsenal. Using that additives engineers design slurry that fit in best for a given conditions and cost effective. These additives are retarders, accelerators, extenders and others that makes slurry physically, chemically and economically more suitable for particular cases. One of such additives is pozzolan. Slurry containing pozzolan able to withstand under high temperatures however without pozzolan slurry loses its strength. In other hand it is more cost effective to replace the cement with pozzolan in a slurries. At this study numbers of experiments were performed in order to see the effect of Aplite as a Pozzolanic material. Slurries with different ratio of aplite and cement were tested under different pressures and temperatures.

2 Materials and Experimental Procedures

It is almost impossible to imagine petroleum technology without cement. Cement is used in a variety of applications and operations. Main application of cement slurry is isolation and support of casing on wellbore or annulus between casings. Key part of cement is quality of injection and strength development in order to do it strong, impermeable barrier. Other important aspect is providing enough strength to support the casing and spend less time to get that strength. It is important to design slurry that will be exposed to high pressure, temperature and different chemicals in order to get better integration for a given case.

2.1 Portland Cement Class “G”

Portland cement is a finely ground gray powder chemically formed by combining raw materials containing calcium oxide(CaO), silica (SiO₂), alumina (Al₂O₃), and iron oxide (Fe₂O₃), heating this mixture at high temperature, and then grinding the resulting material, called clinker, with a small quantity of calcium sulfate (CaSO₄).[1, 3]

2.1.1 Manufacturing of Portland Cement

Cement is manufactured by sequential procedures. First material called *Clinker* have to be prepared. The Clinker is prepared by burning oxides of calcium with silicates, aluminates and aluminoferrites. After mixing that materials is pulverizes to a fine, homogeneous powder. Raw materials for clinker can be limestones, coral, calcium carbonate, clays, shale, volcanic ashes and others. Mineralogical composition of cement clinker is shown in Table 1.

Table 1 Mineralogical composition of cement clinker

Oxide composition	Cement notation	Common name	Concentration(wt%)
3CaO*SiO ₂	C ₃ S	Alite	55-65
2CaO*SiO ₂	C ₂ S	Belite	15-25
3CaO*Al ₂ O ₃	C ₃ A	Aluminate	8-14
4CaO*Al ₂ O ₃ *SiO ₂	C ₃ AF	Ferrite phase	8-12

Before cement preparation clinker goes through wet and dry processes respectively. In a dry process materials are mixed, grinded, dried and classified by size. Wet process contains some of procedures of dry process but water is added after putting raw materials together. Size classifica-

tion is performed by vibrating screen which allows penetrating appropriate sizes and sends back to a grinding mill coarser material. In order to keep slurry homogenous it is stored in specially equipped tanks with mixing arms. After that the slurry goes through burning procedures in a rotating kiln in order to bring it back to dry condition. There are 6 temperature regimes as shown in Figure 1; each of them performs different operation [1].

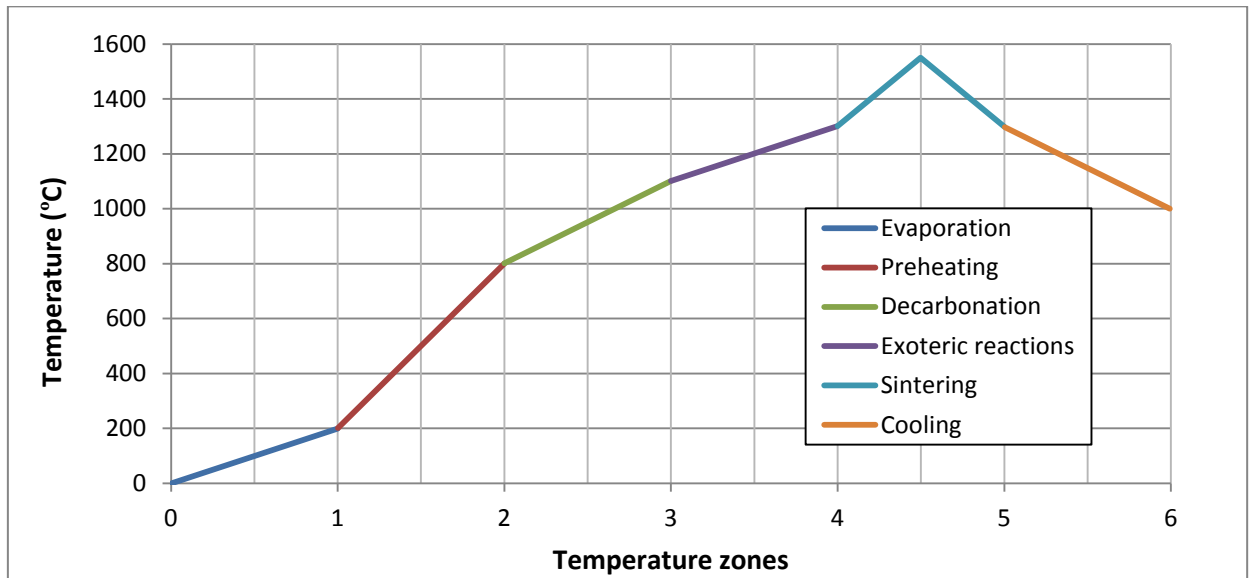


Figure 1 Temperature zones in rotating kiln

- 1) Evaporation of free water
- 2) Dehydroxylation of clay
- 3) Dehydroxylation completed and beginning of crystallization, formation of free lime
 $\text{CaCO}_3 + \text{heat} \rightarrow \text{CaO} + \text{CO}_2$
- 4) Clinkering temperature, most of cement produces
- 5) Formation of C_3A and C_4AF fractions

After heat treatment the clinker is cooling. Quality of clinker and cement is very dependent of cooling rate. If cooling rate is small 4-5 °C /min the cement becomes less hydraulically active, hydration at ambient temperatures of such kind of cement gives good development of strength in early periods but total strength becomes small. Fast cooling rate gives opposite effect thereby giving small buildup of strength in early periods but high long-term strength [1, 3].

Cooled clinker goes through grinding procedures using CaSO_4 being milled by hard steel balls. As clinker reacts with CaSO_4 Portland cement start to exist. Particles of cement vary from 1-100µm [1, 3].

As cement needs a water to react it is very important to keep it as dry as possible. There are big storage tanks in factory which reduces humidity in order to keep cement unhydrated [1, 3].

2.1.2 Effect of Temperature to the Curing

One of the major parameters which affect the hydration of Portland cement is temperature. Temperature also affects the rate of strength buildup as it increases the rate of hydration. High temperature conditions shortens the period of induction and setting in other words a certain amount of strength develops faster under high temperature. Among the individual clinker material only hydration of C_2S found to be accelerated significantly even months after mixing with water. However, at some temperatures hydration and strength buildup is going intensive at the beginning but after that it is not increasing and start to decrease; in a result there is small strength development and lose of permeability(Fig. 2). But such scenario happens with conventional cement slurry system. Slurry in tests described in study consisted aplite (pozzolan).Using pozzolan at high temperatures strength development of tested slurry hasn't decreased after intensive buildup moreover it continued to build up the strength but with smaller rate [1, 2, 7].

Up to $50^{\circ}C$ the composition of C-H-S phase differs a little from those hydrated at ambient temperature. At temperatures higher than $110^{\circ}C$ products of hydration are not the same as those under smaller temperatures .At that temperature C-S-H phases transforms to higher crystalline $\alpha-C_2SH$ phase. Also at that temperatures C_3S and C_2S in lack of SiO_2 forms other products than C-H-S, C_3A and $C_3(AF)$ yields. For the reactions at high temperatures it is recommended to have a source of high reactive SiO_2 in order to not lose the strength. Addition of pozzolan will decrease CaO/SiO_2 ration slurry from 3 to 1 making it silica stabilized cement. Having that ratio hydration forms tobertomite which is thermally stable thereby stopping formation of maleficent crystalline $\alpha-C_2SH$ [1 ,2, 6].

2.2 Synthetic seawater.

It is proven that cement slurry has much better strength development hardening in sea water than in distilled one. This happens because of salts which is dissolved in sea water (see Table 2).Silje Harestad (2012)[10] has tested the same sample but with distilled water. Table 2 shows the composition of synthetic sea water used in experiments

Table 2 Composition of Synthetic Seawater

Salt	NaCl	Na_2SO_4	$NAHCO_3$	KCl	$MgCl_2$	$CaCl_2$	$MgCl_2 \times 6H_2O$	$CaCl_2 \times 2H_2O$
gr/lt	23,38	3,41	0,17	0,075	4,24	1,44	9,05	1,91

2.2.1 Sodium chloride

Sodium chloride takes major part from salts in the seawater. And effect of seawater to the curing is mainly because of NaCl. Sodium chloride affects to the strength development of the cement. However that influence in not a positive all the time. Up to 10-15% in water it acts as an accelerator. However bigger concentrations of NaCl can act as a retarder. As fraction of NaCl is less than 10 of total weight slurries based on seawater has a better strength development. See Fig. 8 which shows curing of slurries based on distilled and seawater [1].

2.3 Pozzolan

Pozzolan is a type of material used as an additive (extender) to cement slurries in order to maintain some operations. It is used when Portland cement is placed in thermal well in order to prevent strength retrogression (see Fig.2). Name pozzolan came from the name “pozzolana” which was the name of volcanic ash. Pozzolan is mainly siliceous or alumina-siliceous material. Fly ash is most commonly used type of pozzolan, however, now days aplite, silica fume, metakaolin and others are also used as it. Pozzolan has few or no cementitious properties. As pozzolan is mainly siliceous material being reacted with $\text{Ca}(\text{OH})_2$ it gives in a result CS(calcium silicates) and starts to behave as a cement resulting strength buildup and forming minerals .The name of that reaction is Pozzolanic reaction, chapter 2.2.3 shows detail of that reaction. Pozzolan is more environmental friendly than other cement additives .To use pozzolan in a cement slurry is also useful in economical point of view. Pozzolan is more cost effective that Portland class “G” cement.

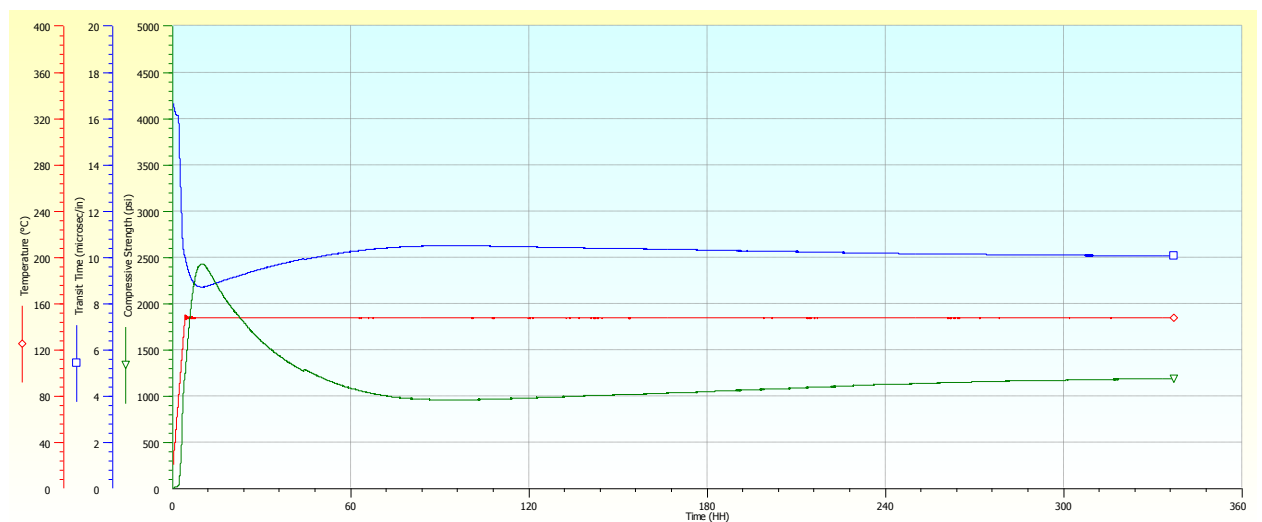


Figure 2. Strength retrogression of Portland cement at 150°C without pozzolan.

When cement hydrates at temperatures higher than 110°C, Ca(OH)₂ liberates from reaction and has a the negative effect to the strength development.

IADC/SPE 136276 [6] says: “*Portlantide, in other hand, exists as huge hexagonal crystals among the C-S-H phases. It contributes no strength to the set cement, disrupts the interlocking mechanism of the C-S-H phases, and is susceptible to corrosive fluids (e.g. can be easily leached out in the presence of acids). Therefore portlantide is a truly weak point in set cement and its formation must be minimized to improve durability*”.

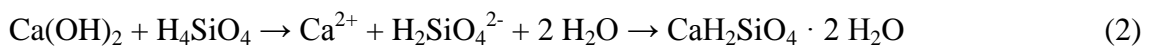
But as portlantide reacts with pozzolan it becomes cementitious compound (secondary C-S-H) which is very durable. See Fig. 8 where slurry is under the same conditions as in Fig.2 but presence of pozzolan together with cement [1].

Pozzolan is effective for cements under high temperatures of curing. At high temperatures cement loses strength after intensive, early buildup because temperature conditions is not appropriate for strength buildup[4].Probably big amounts of Ca(OH)₂ forms at that moment. Experiments performed on current study showed that by adding aplite (pozzolan) to the cement slurry case with strength retrogression under high temperature can be avoided. However aplite affects to early, most intensive, strength buildup rate making it more slower than in slurries with bigger concentration of cement.

However there are types of pozzolanes (silica fume, metakaolin) which lets to pozzolan react faster hereby it takes less time to gain a desired strength [1, 3, 11].

2.3.1 Pozzolanic reaction

The Pozzolanic reaction is the chemical reaction that occurs in calcium hydroxide (portlantide) with silicic acid (H₄SiO₄) (1), (2)



or summarized in abbreviated notation of cement chemists(3):



The product of general formula (CaH₂SiO₄ · 2 H₂O) formed is a calcium silicate hydrate, also abbreviated as CSH in cement chemist notation. The ratio Ca/Si, or C/S, and the number of water molecules can vary [1, 3, 12].

2.3.2 Aplite

Aplite in petrology, the name given to intrusive rock in which quartz and feldspar are the dominant minerals. Aplite has a Pozzolanic properties and used as a pozzolan in this work. Aplite is usually very fine-grained, white, grey or pinkish, and their constituents are visible only with the help of a magnifying lens. Quartz is the main consistent of the aplite used in experiments. See Table 3 which represents the composition of Aplite. Aplite used in experiments was collected from a quarry in Finnvollidalen, Nord-Trøndelag, Norway [16].

Table 3. Chemical composition of aplite [17]

SiO ₂ %	83,4	MgO%	0,06	TiO ₂ %	0,03	BaO%	0,02
Al ₂ O ₃ %	8,29	Na ₂ O%	2,16	MnO%	0,02	LOI%	0,8
Fe ₂ O ₃ %	0,9	K ₂ O%	2,86	P ₂ O ₅ %	<0.01		
CaO%	0,92	Cr ₂ O ₃ %	<0.01	SrO%	0,01	Total%	99,5

2.3.2.1 Quartz

Quartz one of the most spread minerals in earth's crust and variety of geological environments. It can be found in igneous and metamorphic rocks. It is major constituent of sedimentary rocks. Chemical notation is SiO₂. Quartz is widely used in glass and silicone production, electronics and jewelry industry [5].

2.3.2.2 Feldspars

The feldspars are most rife minerals in the earth's crust. They are found in nearly all igneous rocks, most metamorphic rocks and are major part of many sedimentary rocks and sediments. The feldspars include three principal compositional end members: K- feldspar (KAl₂Si₂O₈), Albite (Na₂AlSi₃O₈), and Anorthite (CaAl₂Si₂O₈) whose abbreviations are Ks, Ab, and An, respectively [5].

2.4 Calcium Carbonate

CaCO₃ had not so big effect on strength development of the composition used in study. Based on test number 6 there are minor differences on strength development between slurries with and without Portlantide. First reason to add it to the slurry is because CaCO₃ is activator for Pozzolanic reaction, however cement has the same properties. The second reason is fact that compressive strength increases proportional to the amount of lime which can react with excessive pozzolan.. Probably it was added to the slurry in order to have more reactive Calcium which will form portlantide(5),(6) which will react with pozzolan (2),(3) to form a material with cementitious properties



However test number 6 showed that $\text{Ca}(\text{OH})_2$ which is product of cement hydration is enough or almost enough for pozzolan to react. However there is possibility what some portion of aplite haven't reacted because of lack of Ca that is why specimen in absence of CaCO_3 showed bit less strength [2].

2.5 Description of the Test

Specific gravity of slurry is 1.92 s.g. In order to not overfill mixing container it was chosen that total weight should be 1150 g which comes from equation (7):

$$1,92(s.g) * 600(ml) = 1152(gr) \quad (7)$$

The main idea of experiments was to investigate the strength development of the slurry under different temperature and pressure conditions. Strength of cement is amount of uniaxial stress under which cement fails completely. Also it was desired to explore the influence of concentration of particular materials in a slurry. Portland cement Norcem® class “G”, Aplite (pozzolan), CaCO_3 and synthetic sea-water were materials which were used in the tests. Samples were tested under different temperatures and pressures. Majority of the tests were performed at 3000 psi pressure with different temperatures and compositions. However in order to check the influence of pressure to the strength development of samples experiments were performed at 6000 and 10000 psi.

Each experiment started with 4 test glasses which contained basic materials for a slurry. Initial composition of slurry in experiment was:

- 1) 333,33 g – Portland cement, Norcem® class “G”
- 2) 450 g of Aplite
- 3) 50 g of CaCO_3
- 4) 318,67 g of synthetic seawater.

However, at some experiments had different compositions:

- 100g more aplite, 100 g less cement, under 80°C and 150°C, 3000psi
- 100g less aplite, 100 g more cement, under 80°C and 150°C, 3000psi
- 200g more cement and 200 g less aplite under 80°C and 150°C, 3000psi
- Absence of CaCO_3 under 80°C, 3000psi

After having prepared each component in separate glass; cement, aplite and CaCO_3 were mixed in one big glass. It was done in order to have better dispersion of particles when add them to the constant speed blender (CSB)

On the next step mix of dry components is added to constant speed blender in order to disperse liquid phase in a dry phase. Actually from that time hydration starts and gel forms. CSB has a cup and blades in bottom which rotates thereby mixing liquid phase with dry. Cup with rotating blades on the bottom was filled with organic sea-water after that blades started to turn with 4000 rpm for 15 seconds. During those 15 seconds dry components should be added there. After all components were added in CSB it should be turned to 12000 rpm for 35 seconds. [9]

It is very important to consider that hydration starts just after cement contacts with water. In order to keep it liquid all the mixture procedures should not take long time. If the slurry after 50 second mixing is still in the glass for relatively short time it hardens and becomes more and more viscous than it just after mixing. After 50 seconds of total mixing in a constant speed blender slurry should be placed in atmospheric consistometer for secondary and more effective 20 minutes long mixing. Atmospheric consistometer provides dispersion of the particles, constant density for the slurry and simulates cement mixing conditions in offshore. Bottle for secondary mixing should be already prepared to be filled. [14]

After 20 minutes mixing in consistometer slurry should be placed in UCA (Ultrasonic Cement Analyzer) cell. Before place there slurry all the parts (Bottom , cylindrical part and cover) of the cell should be cleaned, rubber rings should be removed and everything (threads and smooth parts) should be greased. Otherwise bad isolation can cause leakage because of high pressure used in experiment .In other hand if there are no grease inside it is very problematical to remove the sample from chamber after experiment. When placing slurry inside the chamber the bottom should already be screwed to the cylindrical part . After placing slurry to the chamber it have to be closed by cover part and placed to the UCA. Being in UCA sample should be connected with data cable and have temperature measured device screwed in. Each 30 seconds all the data transmits to the computer. Special Software from “Chandler” reports results and shows it both numerically and graphically. This is compressive strength, velocity of ultra-sonic waves and temperature. The main feature of UCA is that it is non-destructive method of measuring the strength of sample. That means that while specimen is in UCA every 30 seconds it reports about different data and there are no need to break the sample [15].

Chapter 4 in bachelor thesis of Mirkamil Turkel (2011) describes in detail procedures mentioned above.

All the experiment were performed accordingly to API standards and following university HSE regulations [8].

3 Results and discussion

3.1 Test number 1

First test was performed at ambient temperature. Main idea behind that was to see the strength development at relatively low (for well cementing) temperature. In other hand it was important in order to get some reference data. As the literature about cement mainly describes behavior under normal temperatures for civil engineering, it was a good point to correlate and compare. The test was performed at a pressure of 3000 psia. Compressive strength of 50 psia was reached after 6:49*, 500 psia was reached after 17:30 after test has started. In cement engineering 50 psi compressive strength is minimum gel strength (initial setting) and 500 psi is a minimum strength which needed to support the casing. In the following tests time of reaching those strengths will be reported.

*here and in following tests the hardening time will be given as hh:mm.

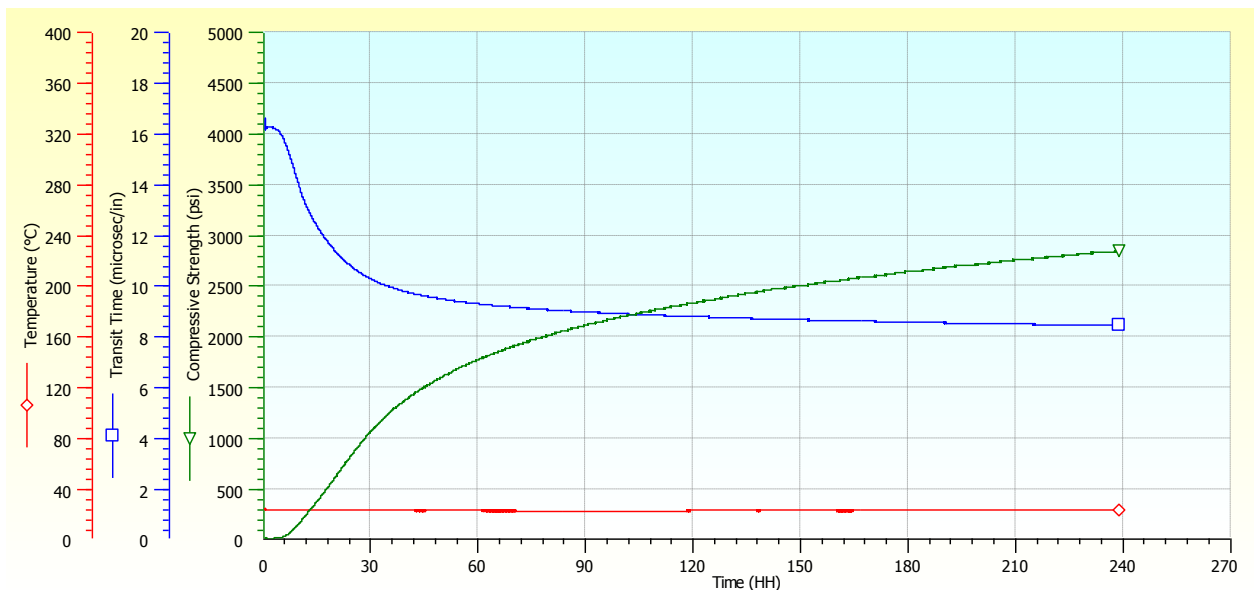


Figure 3. Test 1. Strength development of initial slurry at 20°C and 3000 psi.

3.2 Test number 2

At the test number 2 temperature was increased up to 55°C. Other parameters remained the same as in Test number 1. After this test it became observable how temperature influences to the initial slurry. It also became easier to observe that there are two periods of strength buildup. First is in-

tensive and continues approx. For 9 hours, during that time more than 1500 psi strength buildup is observed. Second period has a slower rate of strength buildup. In comparison with the first test this time 50 and 500 psi were reached faster. 50 psi was reached after 2:00 and 500 psi after 4:45 respectively. Graph 1 in Appendix shows comparison between strength development in test 1 and 2.

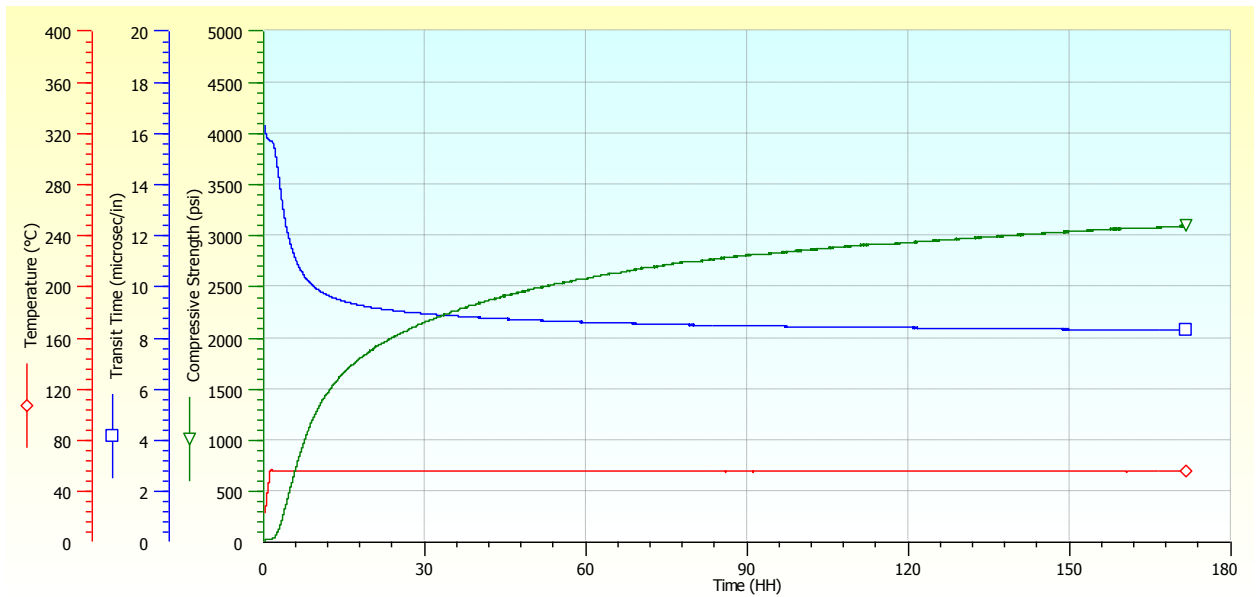


Figure 4. Test 2. Strength development of initial slurry at 55°C and 3000 psi

3.3 Test number 3

Test number 3 was performed at 80°C. That temperature was chosen because majority of conventional oil wells have a temperature in that temperature range. However, temperature was higher than in test number 2. The time to reach 50 and 500 psi was very close to those in test number 2. It was 2:05 and 4:35s respectively. Though at some time intervals sample at 55° had better strength development than one at 80°C; overall sample at 80°C had better strength development. At 24-th hour 55°C sample was about to move to second phase, however 80°C was still on intensive and early strength buildup period. After 24 hour rate of strength buildup was much

higher than that at 55°C in previous test. Graph 2 in Appendix shows the difference between strength development of initial slurry at 55°C and 80°C.

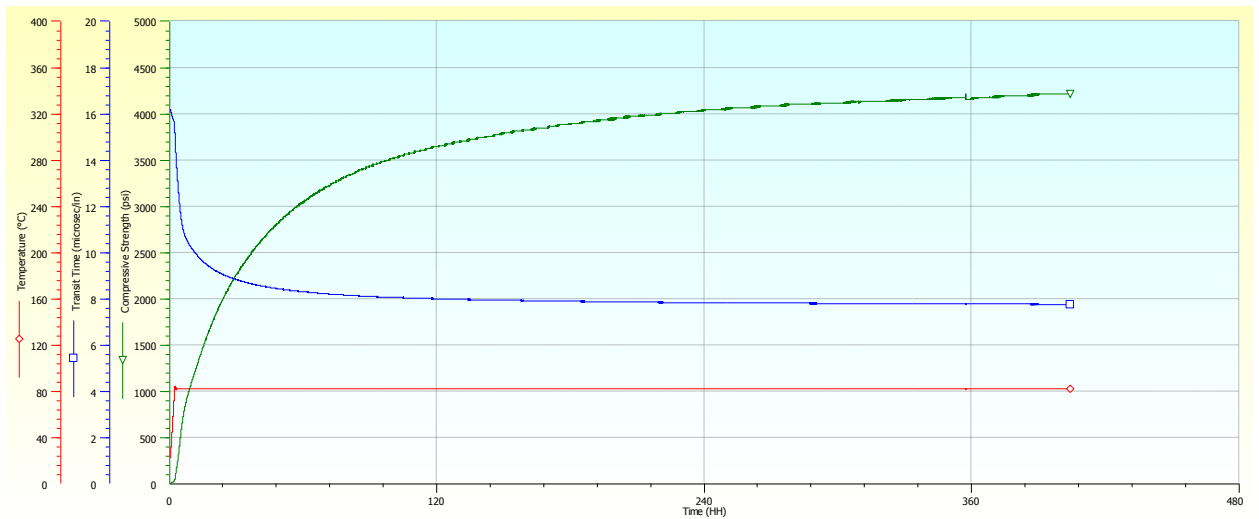


Figure 5. Test 3. Strength development of initial slurry at 80°C and 3000 psi

3.4 Test number 4.

Test number 4 was performed at 150°C. First reason to test a sample at that temperature was the fact that cement changes its properties at 110°C, C-S-H phase does not exist and slurries with neat cement lose strength after some time. Also 150°C is the maximum temperature for gas to occur [17]. So there is possibility to use that slurry in such kind of wells. After performing that test it was obvious that apilite has pozzolanic properties and provides strength development. The manner of strength development was different than at 80 °C. It was very intensive strength development in the first 6 hours, after it became much less intensive than it was. Compressive strength of 50 psi and 500 psi were reached at 1:47 and 3:11 respectively. In compare with 80°C, at the first phase compressive strength increased up to 2200 psi, second phase of strength buildup probably was due to Pozzolanic reaction and wasn't so intensive, however, it was still strength buildup. Graph 3 in Appendix shows comparison between curing at 150°C and 80°C. From that graph it is clearly observable that high temperature responsible only for early buildup in the beginning, however, after some time the difference between compressive strengths decreases to zero and strength development of sample under 80°C becomes higher.

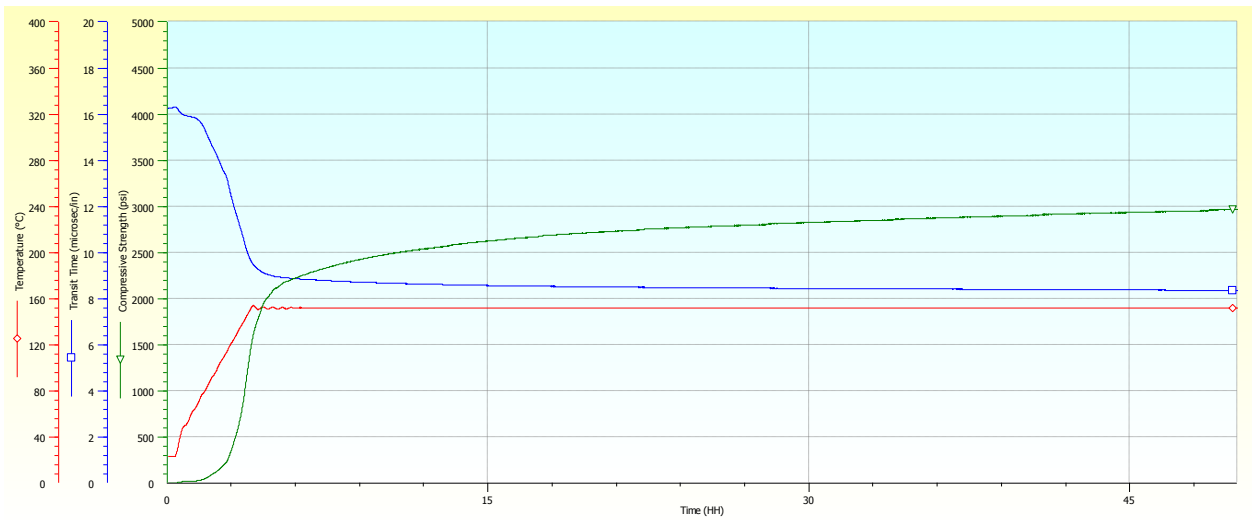


Figure 6. Test 4. Strength development of initial slurry at 150°C and 3000 psi

3.5 Test number 5

In test number 5 maximum temperature of 170°C was reached. It was done in order to see what happens at higher temperatures, and to be sure that strength development in early phase is directly proportional to the temperature. The maximum compressive strength in the first phase was even longer than in sample at 150°C. Compressive strength of 50 and 500 psi were reached at 1:55 and 3:20 respectively. Rate of strength buildup at the second period was almost the same for 150°C and 170°C sample. Consequently the dominance of 170 °C sample was because it gained more strength in first phase. See Graph 4 and 5 in Appendix to compare 150°C and 170° strength development.

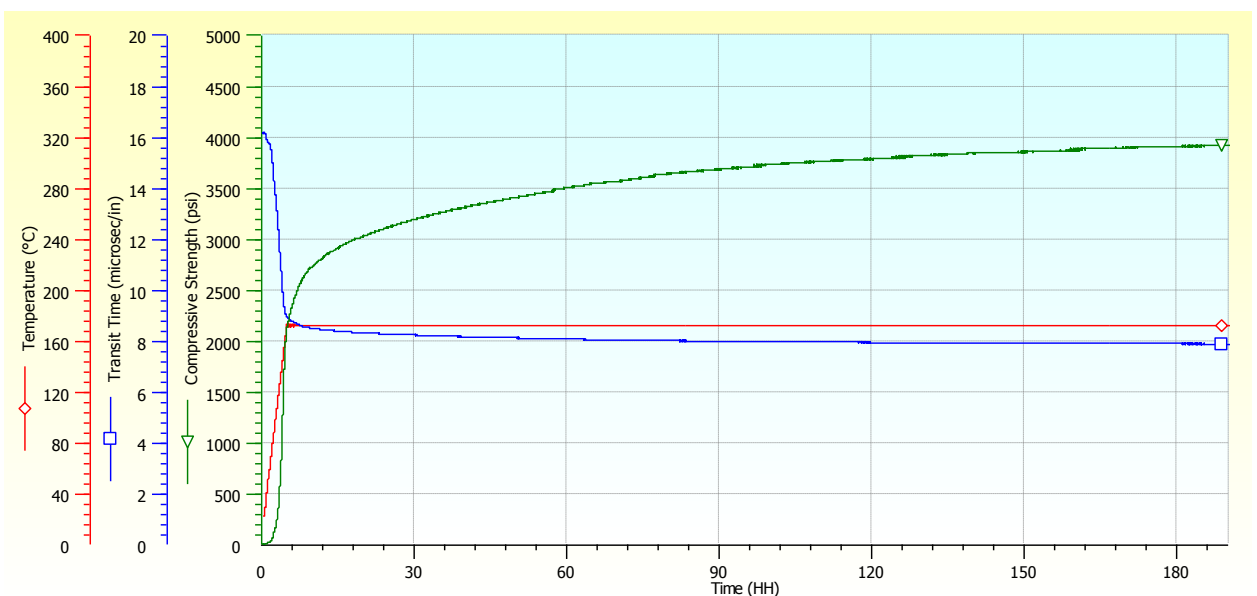


Figure 7. Test 5. Strength development of initial slurry at 170°C and 3000 psi

3.6 Overview of tests 1, 2, 5. Effect of seawater on the strength development

In order to see the effect of seawater on strength development Figure 8 shows 6 different tests. 3 of them were done in this study, however, the others have the same composition but with distilled water instead of synthetic sea water [10]. It is clearly observable that the samples with seawater have a better strength development than ones with distilled water.

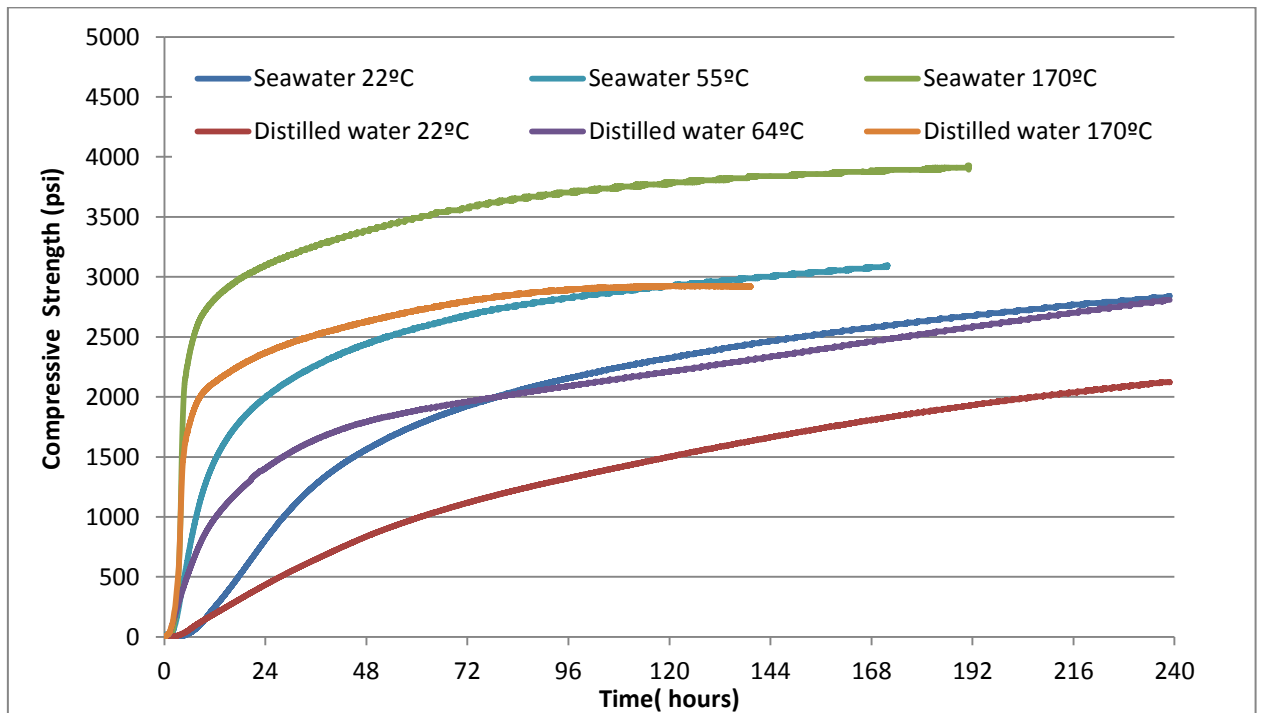


Figure 8. Comparison of the strength development of slurries with distilled or seawater under different temperatures.

3.7 Test number 6

Test 6 was performed in absence of CaCO_3 . Slurry was designed in order to see the effect of CaCO_3 to the strength development. Components replaced 50 grams of CaCO_3 according to their weight in the slurry (see Table 4).

Table 4 Replacement of CaCO₃

	Aplitt	Seawater	Cement	CaCO ₃	Total
Mass	450	318,67	333,33	0	1102
weight in slurry,%	0,4090686	0,28792066	0,303011	0	1
How they replace 50 grams	20,4534298	14,3960329	15,15054	0	50
New mass	470,45343	331,126033	348,4805	0	1152

Graph 6 in Appendix shows that sample with CaCO₃ shows little bit better strength development and dominates over sample without CaCO₃ on 10-75 psi. Tests were performed at 80°C and 3000 psi pressure. 50 psi strength was reached after 2:20 and 500 psi at 4:54 after test began. In contrast the sample with CaCO₃ reached that strength at 2:05 and 4:35 respectively. Which proves again that sample with CaCO₃ has better strength development.

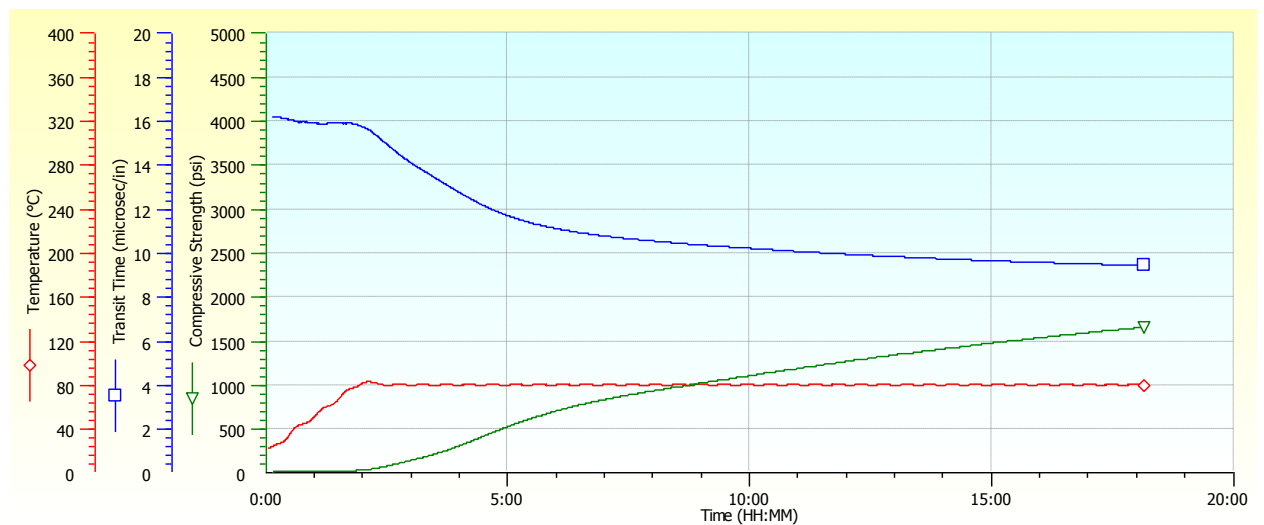


Figure 9. Test 6. Strength development of a slurry without CaCO₃

3.8 Test number 7

Test number 7 was performed in order to see the influence of aplite to the strength development of the sample. By keeping constant amount of seawater and CaCO₃, the mass of cement was decreased by 100 grams less (233,33g) while mass of aplite increased by 100g more (550g). Temperature was 80°C, pressure 3000 psi. 50 and 500 psi were reached at 1:51 and 5:41 respectively. Though 50 psi were reached faster than in initial sample (2:05) at the same conditions, soon it was clearly observable that strength development in initial sample (80°C, 3000 psi)

was much better and dominates with 575 psi at last measurement. Moreover when looking to the difference function in Graph 7 in appendix it shows that by the time it will increase and possible that at following days strength in initial sample will dominate. See Graph 7 in Appendix for the difference between slurry in test number 7 and initial slurry.

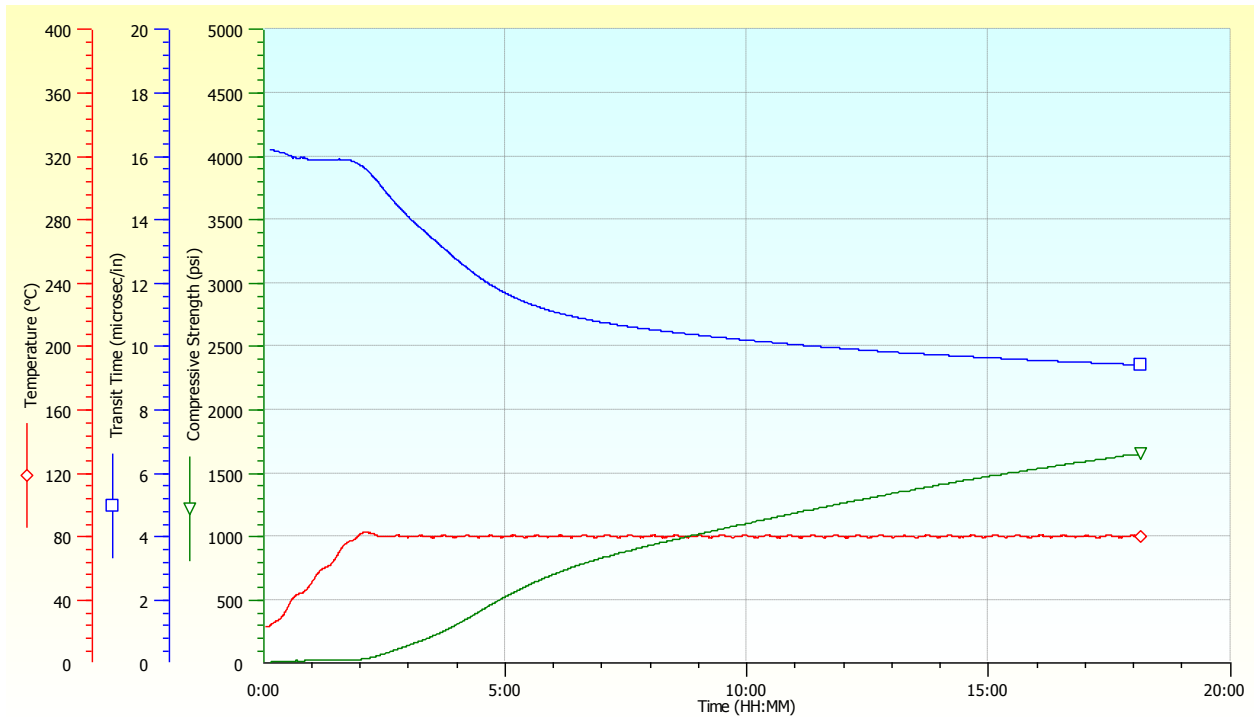


Figure 10. Test 7. Strength development of slurry containing 100g more aplite and 100g less cement than in initial slurry, 80°C and 3000 psi

3.9 Test number 8

Test number 8 was performed in order to see the influence of the cement to the slurry. It was 100g more cement (433.33) and 100g less aplite in that slurry. The amount of CaCO_3 and sea-water remained the same. Temperature was 80°C, pressure 3000psi. 50 and 500 psi compressive strength were reached faster than at initial sample and sample from the test number 7. For 50 and 500 psi time was 1:36 and 3:16 respectively. From the Graph 8 in Appendix it is observable that higher amount of cement helps to gain early strength buildup. However, difference in compressive strength shows that after 13 hours initial sample has better rate of strength buildup than sample with 100g more cement.

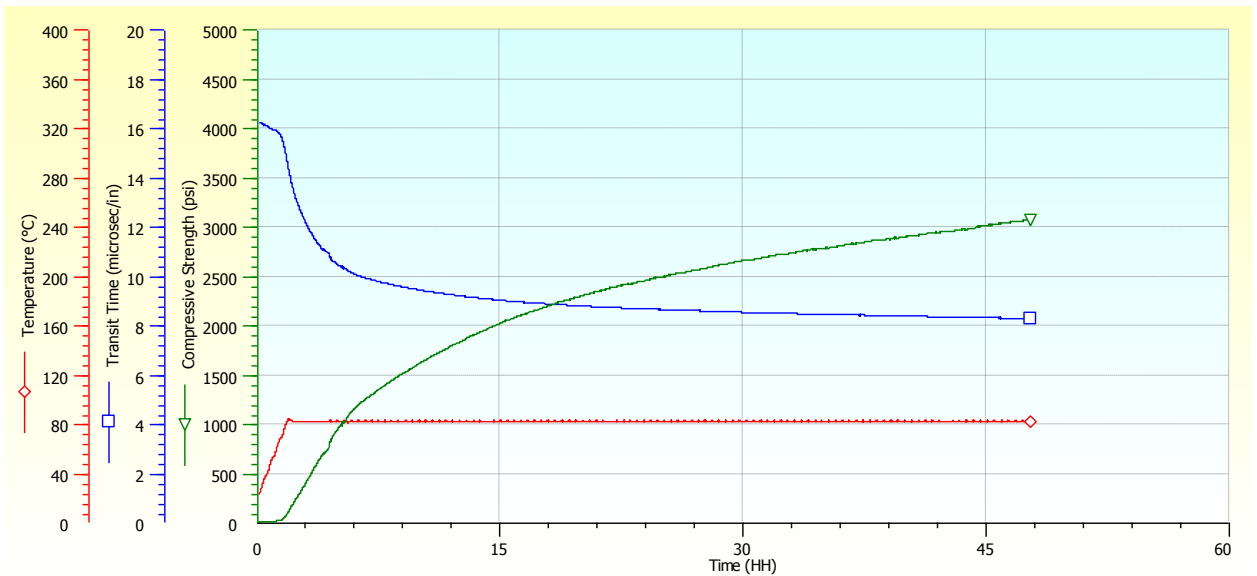


Figure 11. Test 8. Strength development of slurry containing 100g more cement and 100g less aplite than in initial slurry, 80°C and 3000 psi

3.10 Test number 9

Chart in test number 8 shows that bigger portion of cement provides better strength development. Test number nine was performed in order to see if the strength development was directly proportional to the mass of cement. Slurry at test number 9 has 200g more cement (533.33g) and 200 g less aplite(250 g). Test was performed at 80°C and 3000 psi pressure. 50 psi and 500 psi were reached at 1:38 and 2:46 respectively. This was even earlier than in test number 8. That test proved that cement in initial slurry is more “responsible” for the strength development than aplite. To crown it all from the difference Graph 9 in Appendix it is visible that development in test number 9 goes even faster than in test number 8 that’s why difference line steeps upwards which says that by time strength difference between samples 9 and 8 will be higher.

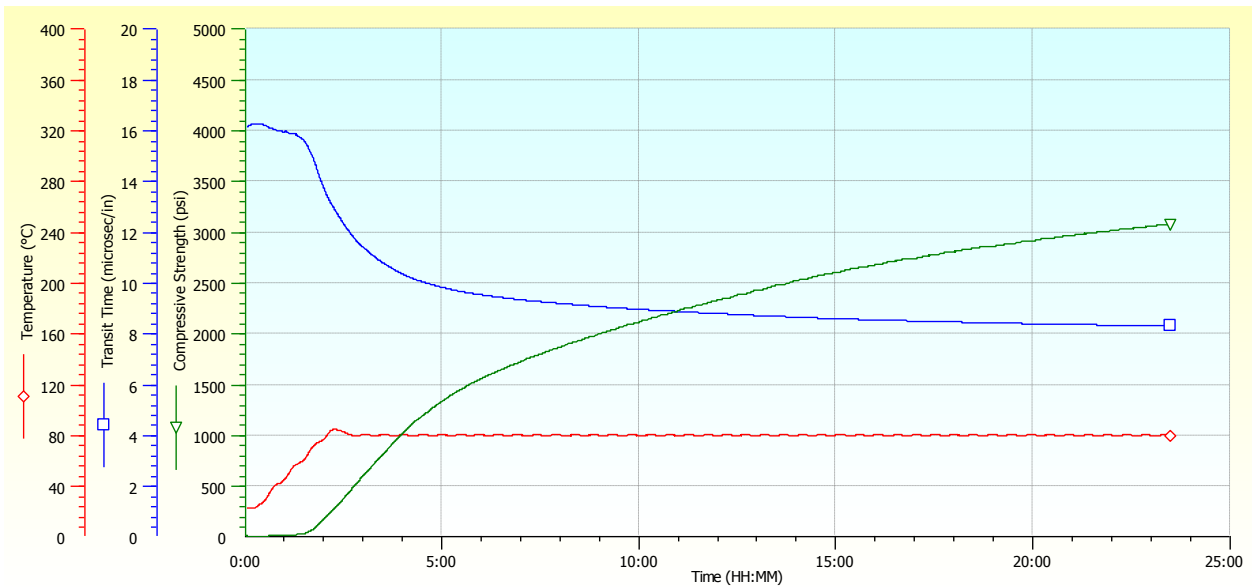


Figure 12. Test 9. Strength development of slurry containing 200g more cement and 200g less aplite than in initial slurry, 80°C and 3000 psi

3.11 Overview of tests number 3, 7, 8, 9

Tests number 7, 8, 9 proved that strength development of slurry is proportional to the weight of cement in slurry. But weight of cement and strength development is not constantly proportional. For example if we look to Fig. 13 it is clearly observable that 3000 psi was reached at different times. However, time interval at 3000 psi between initial sample and sample at test number 8 is 14 hours while between sample from test number 9 and sample from test number 8 is 24 hours. The same picture can be observed at other pressures, however, it is possible that they are very much the same at some pressures (for example 2300 psi).

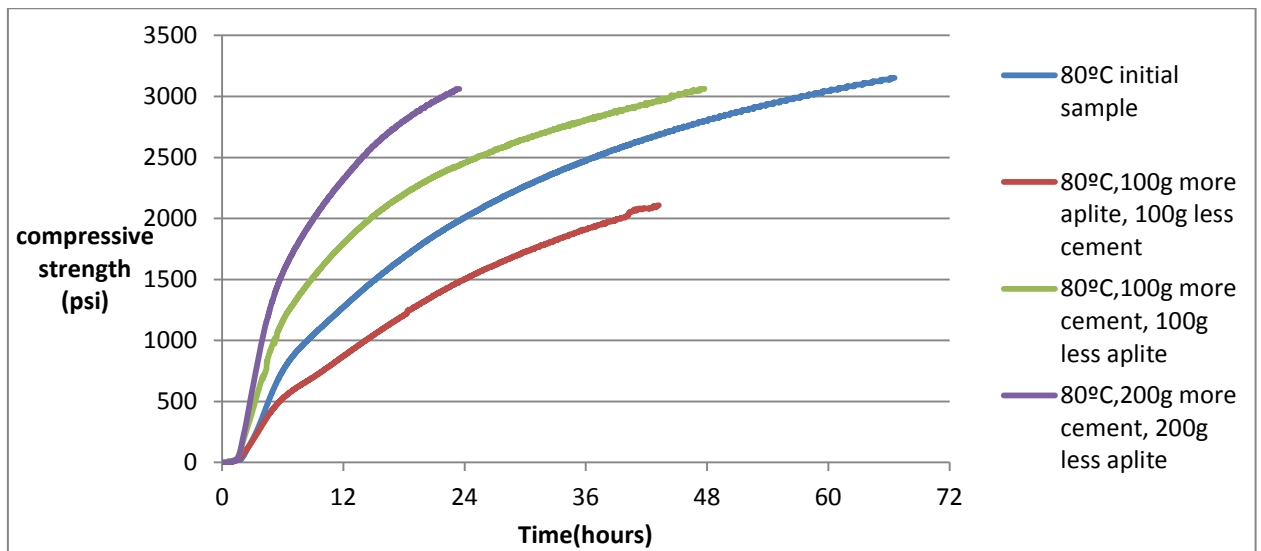


Figure 13. Overview of tests number 3, 7, 8, 9

3.12 Test number 10

As in test number 7 it was decided to test slurry with 100g more aplite (550g) and 100g less cement (233.33g). All conditions were the same as in test number 7 except of temperature. Test number 7 shown in Fig.14. Temperature was set to 150°C. Knowing that after 110°C cement produces other crystals than C-S-H, it was relevant to test slurry at that condition. 50 and 500 psi were reached at 1:54 and 3:12 respectively. As in the test with initial sample at that temperature and pressure intensive strength buildup was also observed from the graph. It was due to temperature which was more than 110°C. Initial sample reached 50 and 500 psi strength at 1:47 and 3:11 respectively. The reason why sample at initial conditions reached that strength faster is because it had more cement. Also after intensive and early strength buildup difference between initial sample and sample at test number 10 was almost constant which says that the graphs will develop parallel (or close to parallel) for a long time. For comparison see Graph 10 in Appendix.

3.13 Test number 11

Test number 11 was performed in order to see the influence of cement to the strength development of the slurry at temperatures higher than 110°C this is shown in Fig.15. It was also important to know if the aplite in smaller amounts is able to provide strength development by reacting with portlandite. As there was no retrogression of strength it was clear that even smaller portions of aplite is enough for Pozzolanic reaction and strength buildup. All conditions were the same as in test number 8 but temperature was 150°C. Compressive strength of 50 and 500 psi were reached at time 1:39 and 2:53 respectively. The fact that slurry at test number 11 had more

cement than slurry in test number 10 also proven by the time which was spent to reach 50 and 500 psi compressive strength. As for all the samples at temperature of 150°C Fig.15 shows two phases of the strength development one is very intensive and takes short time while second phase has less intensive strength buildup. From Graph 11 in Appendix it is visible that after some time difference between sample at initial conditions and sample in test number 11 becomes almost constant. It means that intersection of the curves is not expected for a long time and the strength in sample of test 11 will dominate strength of initial sample for a long time under mentioned conditions.

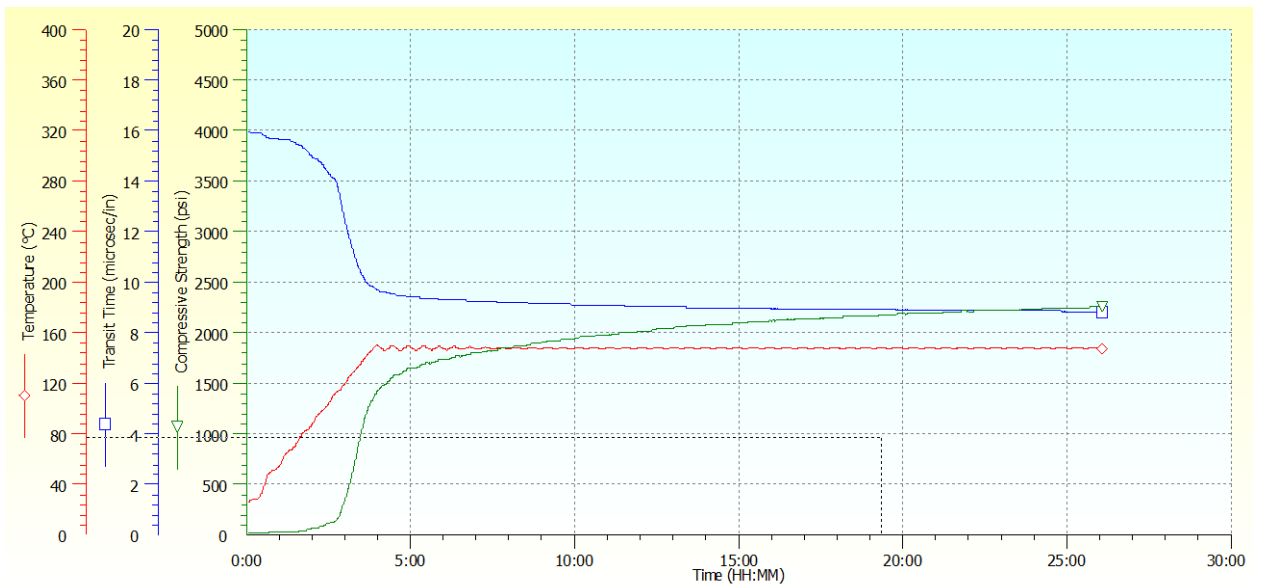


Figure 14. Test 10. Strength development of slurry containing 100g more aplite and 100g less cement than in initial slurry, 150°C and 3000 psi

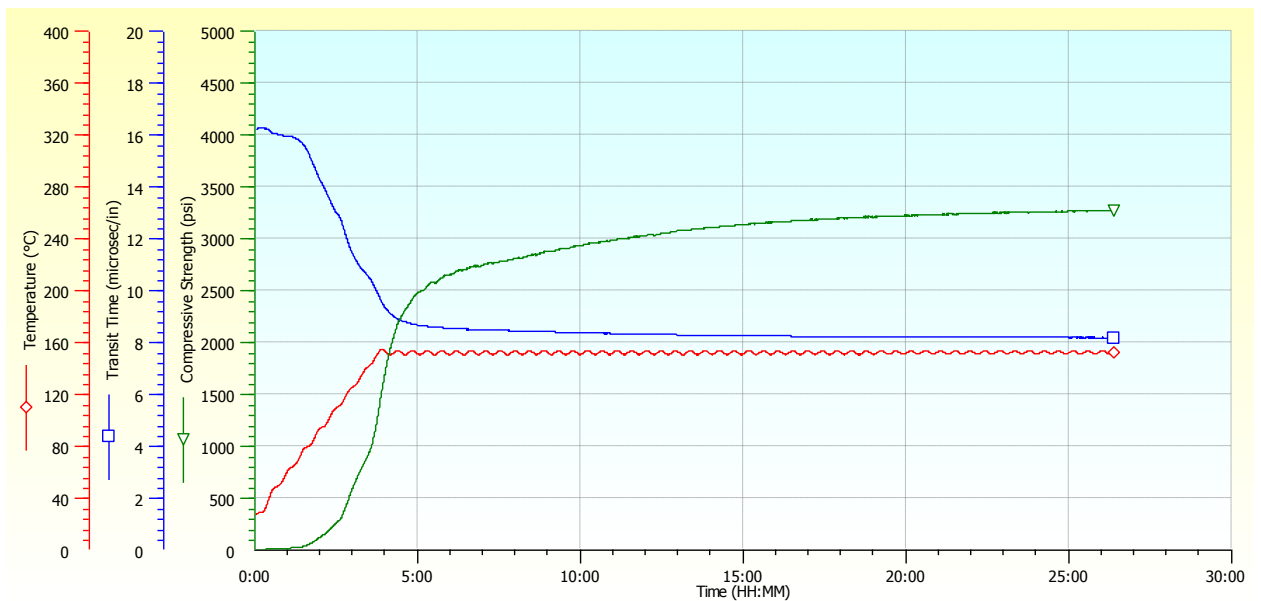


Figure 15. Test 11 Strength development of slurry containing 100g more cement and 100g less aplite than in initial slurry, 150°C and 3000 psi

3.14 Test number 12

Test number 12 was performed in order to see the strength development of new slurry at 150°C temperature. In other hand it was important to see if weight of cement is directly proportional to the strength development, the results are shown in Fig. 16. Slurry at that test had 200 g more cement (533.33g) and 200g less aplite (250g). Compressive strength of 50 and 500 psi were reached at 1:37 and 2:51 respectively. Behavior of strength development was specific as that at 150°C. There was a sudden increase at the beginning and after sometime sudden decrease of rate.

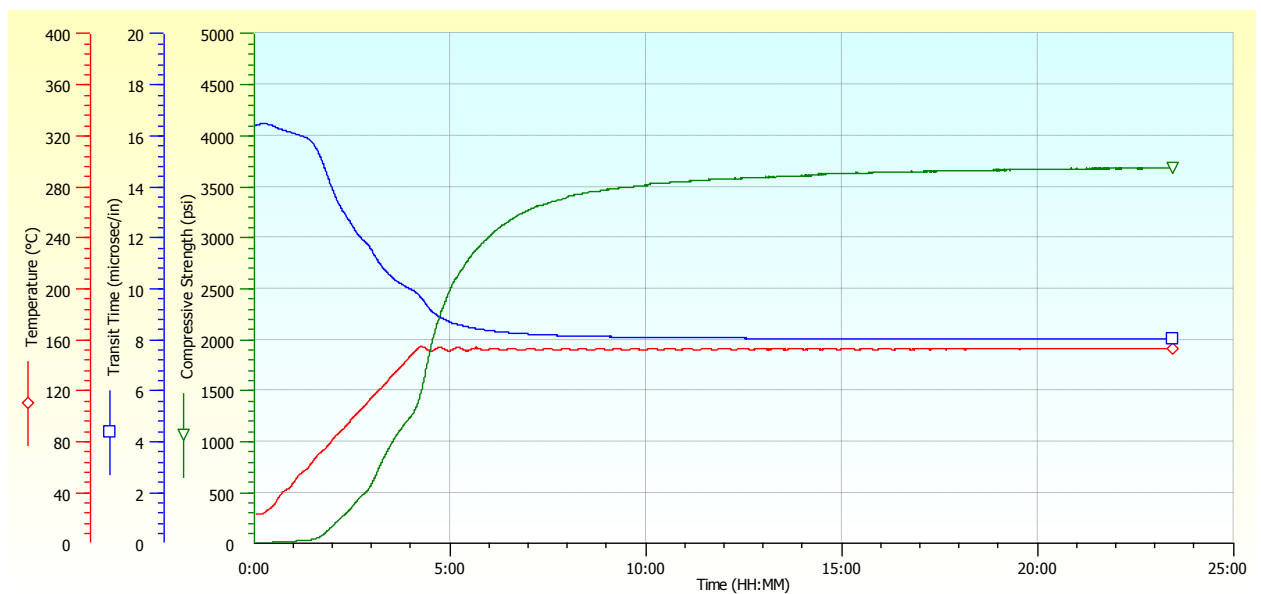


Figure 16. Test 12. Strength development of slurry containing 200g more cement and 200g less aplite than in initial slurry, 150°C and 3000 psi

3.15 Overview of the test number 4, 10, 11, 12

Tests 10, 11 and 12 prove that cement fraction in slurry is proportional to the compressive strength at early and intensive phase of strength buildup, this is shown in Fig. 17. In addition the rate of gaining the strength is almost the same for all the samples tested at 150°C at the first phase of strength buildup. It proves that composition is not influences on strength buildup as much as temperature does. However, composition plays a role when it comes to at which strength intensive buildup transfers to the more passive buildup of strength because of Pozzolanic reactions. Beginning of Pozzolanic reaction depends on composition. As it comes to the period of pressure buildup while Pozzolanic reactions, curves seem parallel but still has difference in strength due to the strength they had when Pozzolanic reaction begun. That difference seems constant or very slowly regressive or progressive. Early and intensive strength buildup at 150°C may be because C-S-H phase hydrates quickly under high temperature. But at some time

it becomes different material and high temperature has a negative influence in absence of pozzolanes. That is actually the reason why after some time sample under 80°C reached higher strength than sample at 150°C. High temperature play positive role in hydration at 80°C making compressive strength increasing by time and have a better overall buildup than at 150°C. However, at the beginning sample at 150°C had much better strength development.

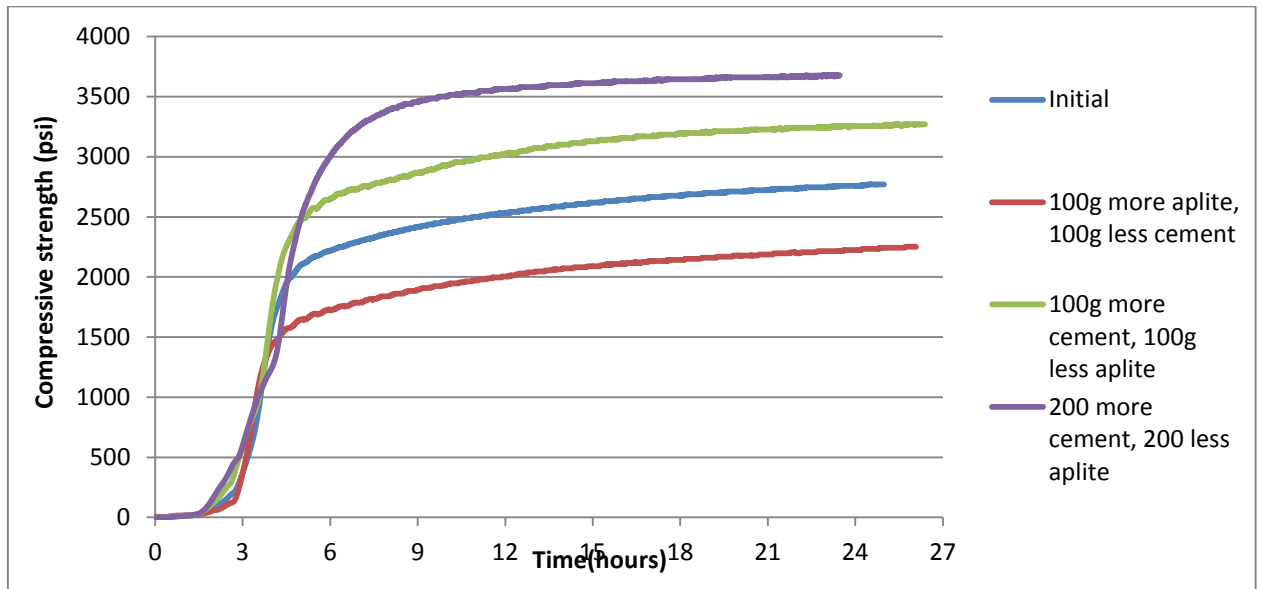


Figure 17. Overview of tests number 4, 10, 11, 12.

3.16 Test number 13

Test number 13, initial slurry was tested at 80°C and 6000 psi pressure, the results are shown in Fig. 18. The main idea behind that test was to check the effect of higher pressure. Because as higher is pressure as higher is energy in system and energy is proportional to hydration which is proportional to strength development. Compressive strength of 50 and 500 psi were reached at 1:30 and 3:27 respectively. See Graph 13 in Appendix to see the difference between initial sample at 3000 psi and 6000 psi pressure at 80°C. In the Graph 13 in Appendix chart of 3000 and 6000 psi looks going parallel to each other, however, their difference slowly decreasing by the time.

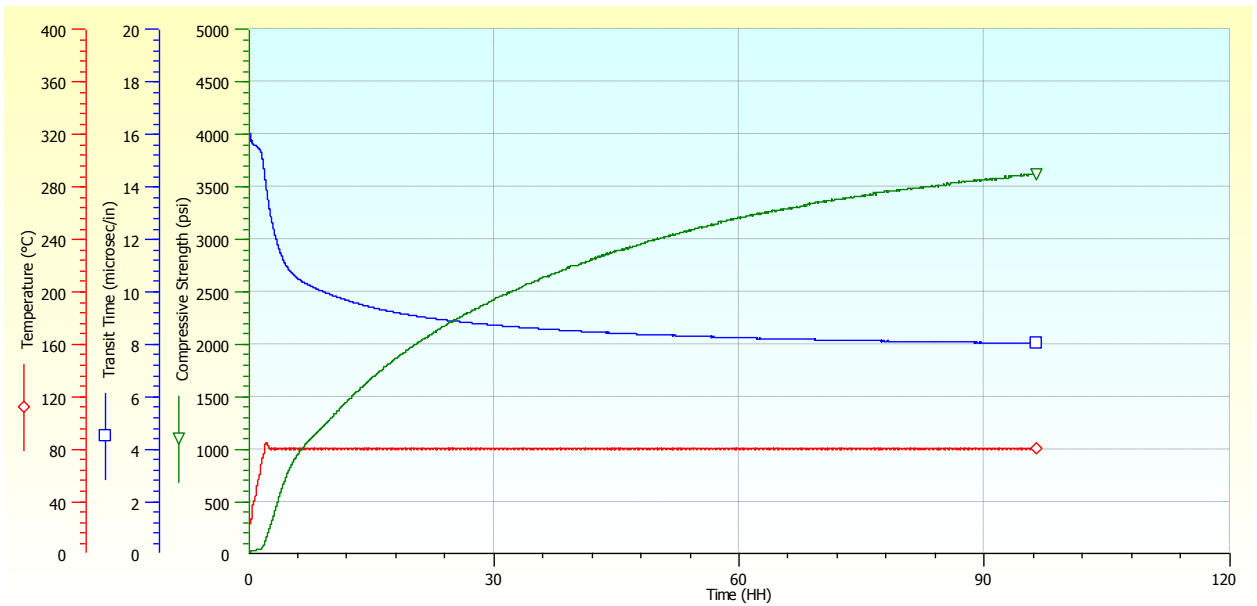


Figure 18. Test 13. Strength development of initial slurry at 80°C and 6000 psi

3.17 Test number 14

Test number 14 was performed also at 6000 psi as the test number 13 but temperature was set to 150°C, this is show in Fig. 18. Obtained graph was inherent to those tests done at temperature higher than 110°. Compressive strength of 50 and 500 psi were reached at 1:25 and 3:04 respectively. It was active buildup of the strength at the first hours which suddenly transfers to the passive buildup which its turn is a sign of beginning of Pozzolanic reaction. See Graph 14 in Appendix to see the difference between initial sample at 3000 psi and 6000 psi.

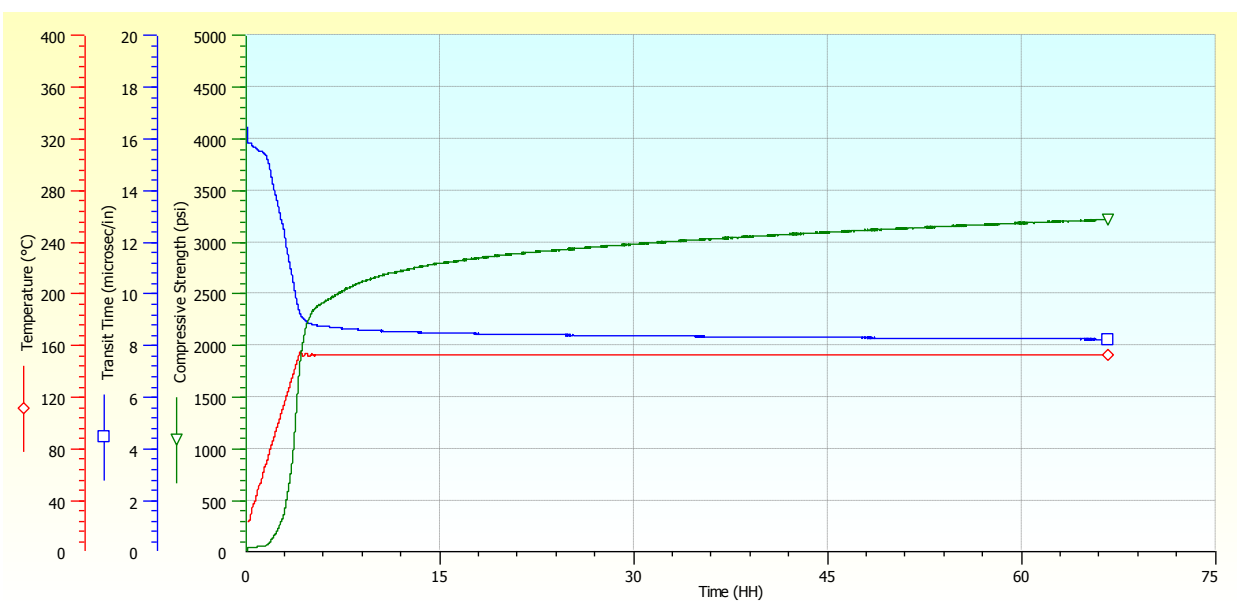


Figure 19. Test 14. Strength development of initial slurry at 150°C and 6000 psi

3.18 Test number 15

Test number 15 was performed in order to see the behavior of initial slurry at high pressure wells. In order to that equipment was set to 10000 psi pressure. Temperature was set at 80°C, the measurements are shown in Fig 20. Graph was looking like others at 80°C. Compressive strength of 50 and 500 psi were reached at 0:49 and 2:49 respectively. That time was even smaller than in test number 13 (1:30 and 3:27). That proved that higher pressure provides better strength development at 80 degrees. Graph 15 in Appendix shows difference in strength development under 6000 psi and 10000 psi at 80°C of initial slurry.

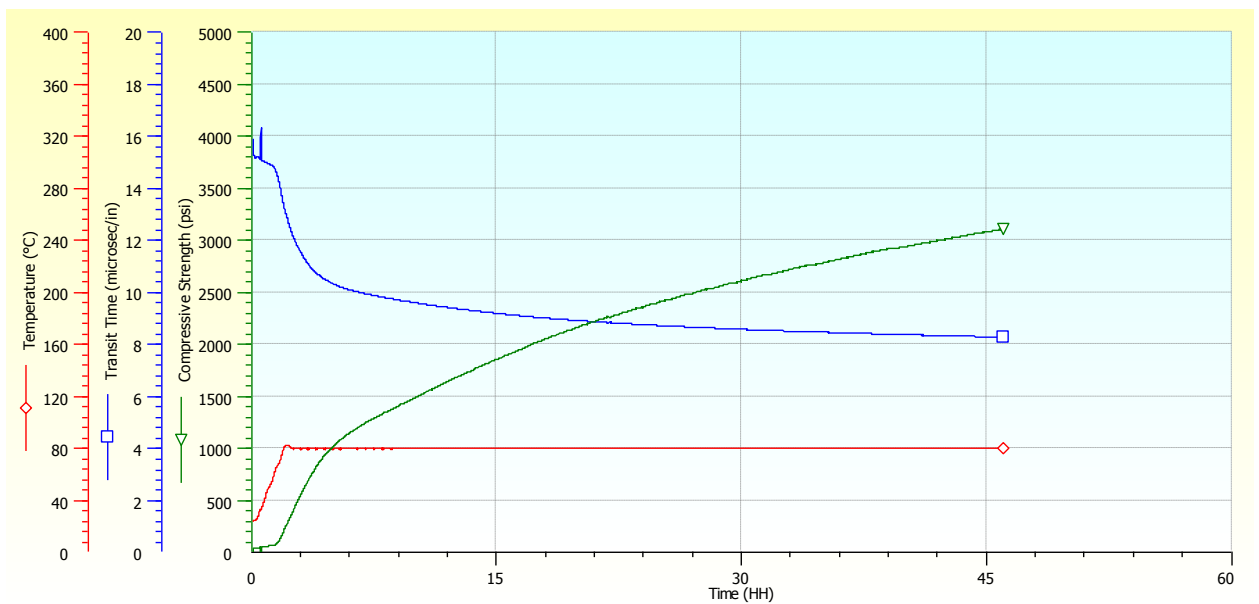


Figure 20. Test 15. Strength development of initial slurry at 80°C and 10000 psi

3.19 Test number 16

In order to see the behavior of slurry in HPHT wells temperature in that test was increased to 150°C and pressure set to 10000 psi, results are shown in Fig. 21. Graph had a form like others made at that temperature. Compressive strength of 50 and 500 psi were reached at 0:15 and 2:22 respectively. It was the shortest time of reaching 50 and 500 psi among all experiment done in that thesis. Look to Graph 16 in Appendix to see the difference in strength development at 150°C between initial slurry at 6000 psi and 10000 psi.

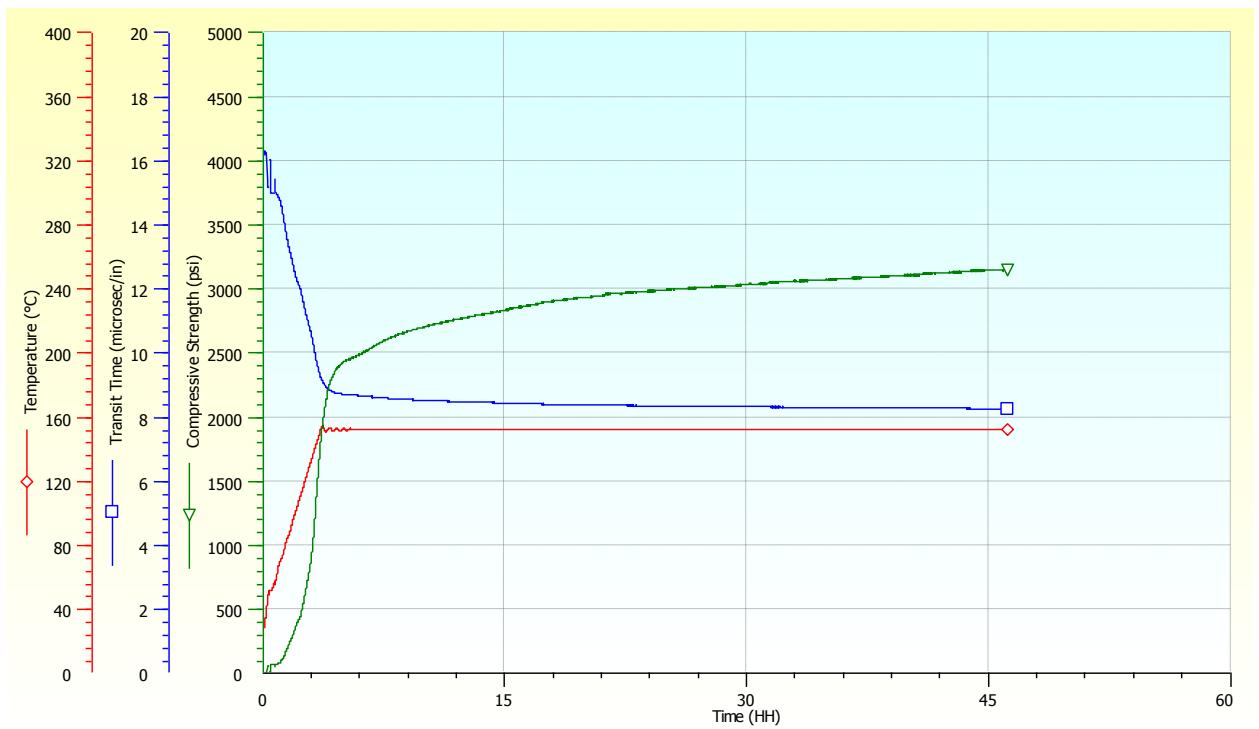


Figure 21. Test 16. Strength development of initial slurry at 150°C and 10000 psi

3.20 Test number 17 and 18

These tests were performed in order to prove that at 110°C cement changes its properties and hydrates in a different way. The results are shown in Fig. 22 and Fig. 23. Because of the shape of strength development curves at 80°C and 150°C were not the same. The idea was to be sure that 110°C is the point where strength develops in another way and the C-S-H phase fails at some time during the pozzolanic reaction. Initial samples were tested at temperatures of 100°C and 120°C in order to be closer to 110°C. Obtained results showed that there are some temperature between 120°C and 100°C at which the behavior of strength development changes. If we take a middle, it will be 110°C.

For the tests performed at the temperature of 100°C and less, the line of strength development is smooth and increasing with almost the same constant rate, meaning that the C-S-H phase is hydrating by time and there is not so much Ca(OH)_2 for pozzolan to react. Even when the strength buildup rate is changing, it becomes slowly and smoothly. Temperature differences can be observable in graphs after the first minutes. Comparison between tests at 80°C and 100°C can be observable at Graph 17 in Appendix. Strength decrease in the graph at 100°C at 18:30 was because of a temporary temperature decrease. The graph continued to develop in the previous slope after the temperature increased at 100°C again. See Graph 18 in Appendix.

In contrast, the tests which were performed at the temperature of 120°C and higher curve of strength development is different. Typical manner of strength development of such curves is early and intensive pressure buildup at first 3-4 hours. After that time the rate of strength development suddenly decreases (however, stays positive) and continues decreasing by the time. It happens because C-S-H phase is not hydrating anymore and loses its structure. Probably at that time big amount of Ca(OH)_2 produced and reacted with aplite. Because of Pozzolanic reaction strength is not decreases but even increases; however, the rate is not so big as the rate of hydration of C-S-H phase. The samples which were tested under 100°C have not so quick buildup of strength at the beginning, however after some time they are able to gain more strength than those cured at temperatures higher than 110°C. See Graph 18 in appendix to compare the strength development of the sample at 120°C and 150°C.

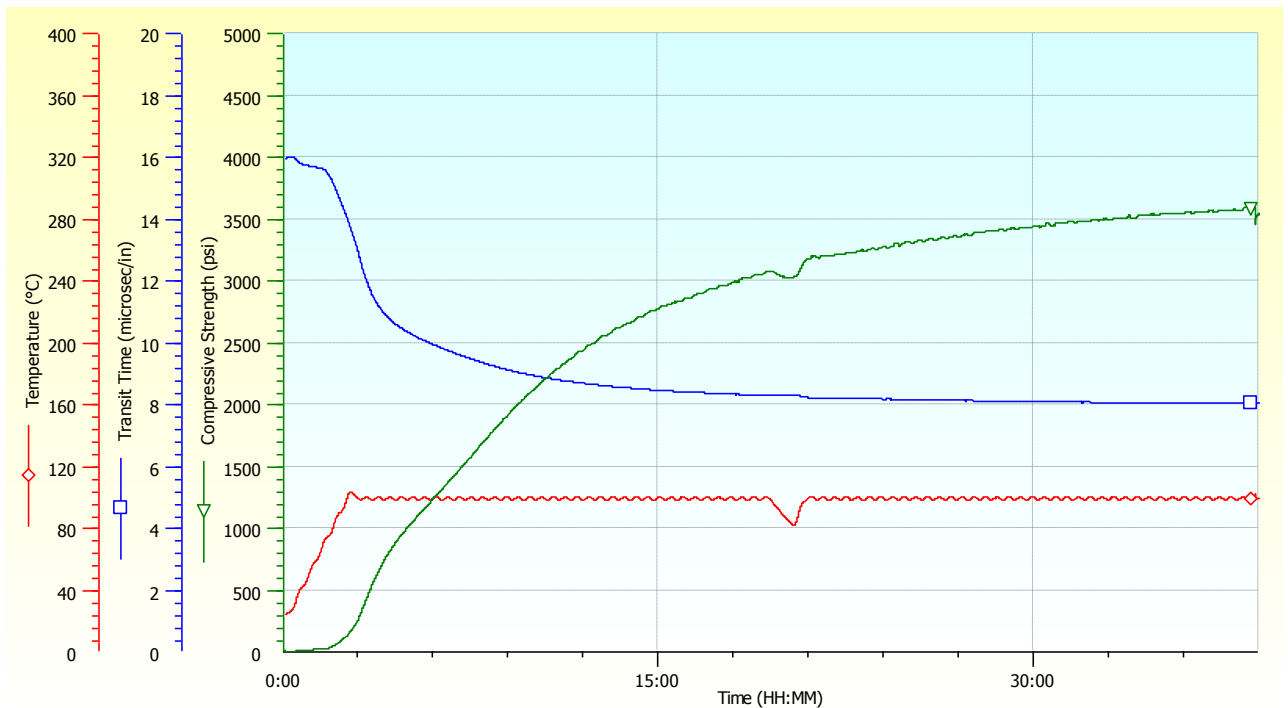


Figure 22. Test 17. Strength development of initial slurry at 100°C and 3000 psi

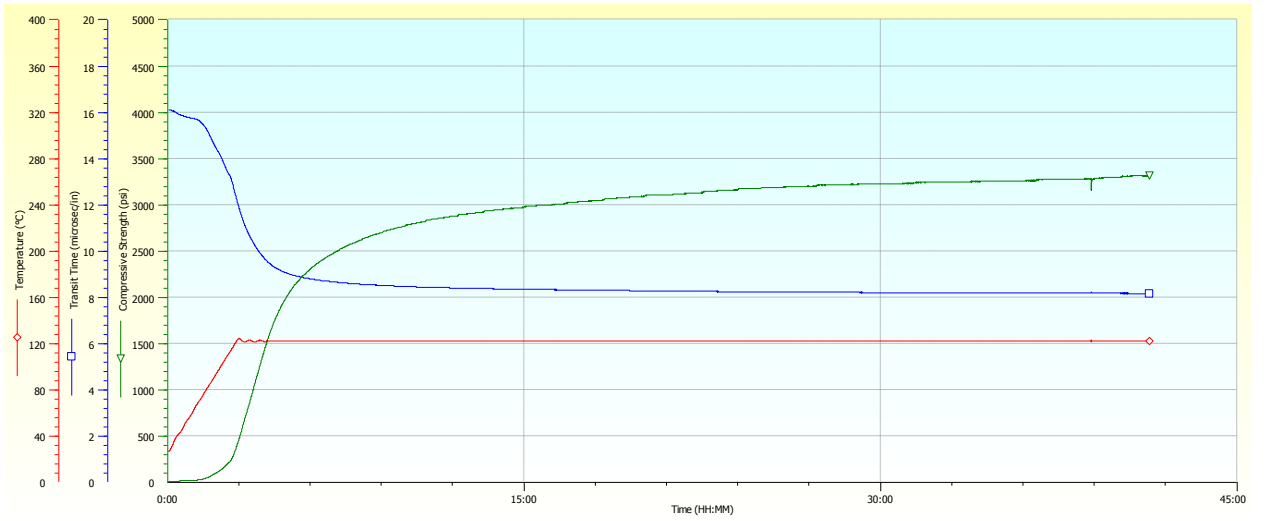


Figure 23. Test 18. Strength development of initial slurry at 120°C and 3000 psi

Table 4 shows summary descriptions of the tests done in this study. Nothing other than provided data was changed during the tests.

Table 5 Tests data review

Test№	Aplitt	Cement	Seawater	CaCO ₃	Temperature	Pressure
1	450	333,33	318,67	50	22	3000
2	450	333,33	318,67	50	55	3000
3	450	333,33	318,67	50	80	3000
4	450	333,33	318,67	50	150	3000
5	450	333,33	318,67	50	170	3000
6	470,4534	348,4805372	331,12603	0	80	3000
7	550	233,33	318,67	50	80	3000
8	350	433,33	318,67	50	80	3000
9	550	233,33	318,67	50	150	3000
10	350	433,33	318,67	50	150	3000
11	250	533,33	318,67	50	80	3000
12	250	533,33	318,67	50	150	3000
13	450	333,33	318,67	50	80	6000
14	450	333,33	318,67	50	150	6000
15	450	333,33	318,67	50	150	10000
16	450	333,33	318,67	50	80	10000
17	450	333,33	318,67	50	100	3000
18	450	333,33	318,67	50	120	3000

5 Conclusion

Temperature and pressure has a positive effect on the strength development. All the experiments showed that samples which hydrated at higher temperatures have a strength dominance on those which cured at lower temperatures and pressures. Though that dominance is only at the beginning when sample hydrates at a temperature above 110°C. It happens because at those temperatures product of hydration is not C-S-H but other material. At that moment Pozzolanic reaction starts providing slow strength development to the sample.

In contrast, the samples cured at temperatures lower than 110°C have not so quick strength buildup like those which cured at temperatures above 110°C. But later strength development of those which cured under 110°C start to prevail on those which cured at temperatures higher than 110°C. It happens because under 110°C hydration gives C-S-H phase which develops strength better than product coming from Pozzolanic reaction.

Also tests showed that addition of cement mass while decreasing proportionally mass of aplite gives better strength development than in initial sample under the same conditions. Consequently replacement of cement by aplite resulted in worsened strength development that in the initial sample, probably because Pozzolanic reaction has not so progressive buildup of strengths as C-S-H phase do.

Other set of experiments showed that additional pressure has a positive effect to the strength development regardless if temperature was higher or lower than 110°C

The findings confirm that aplite based cement slurries shows more favorable mechanical properties, better economics than a conventional cement system for the temperatures higher than 110°C. However, for the slurries curing at temperatures lower than 110°C aplite has a negative effect on the strength development, however, it still stays more economical and environmental friendly solution. Aplite based cement slurry increasing its strength development with increasing pressure and temperature conditions.

6 Nomenclature

API - American Petroleum Institute

ASTM - American Society for Testing Materials

CSB – Constant Speed Blender

C-S-H – Calcium silicate hydrates

HHP – High temperature high pressure

Psi – pounds per square inch

RPM – Rotation per minute

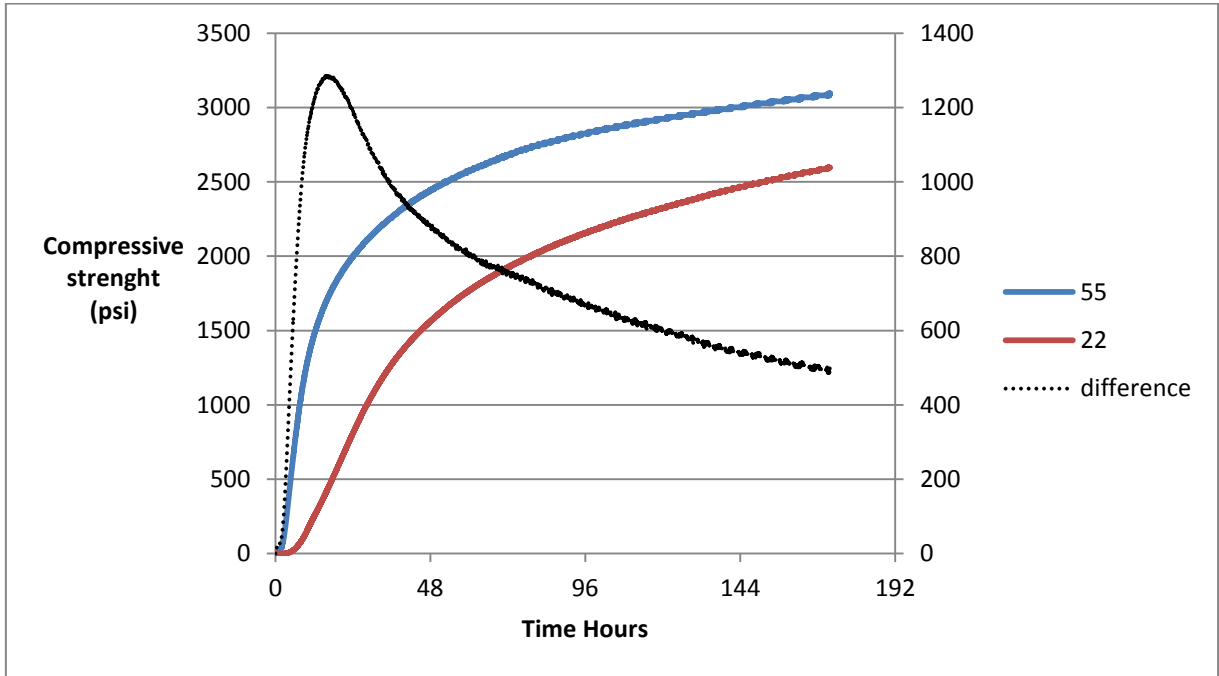
s.g. – Specific gravity

UCA – Ultrasonic Cement Analyzer

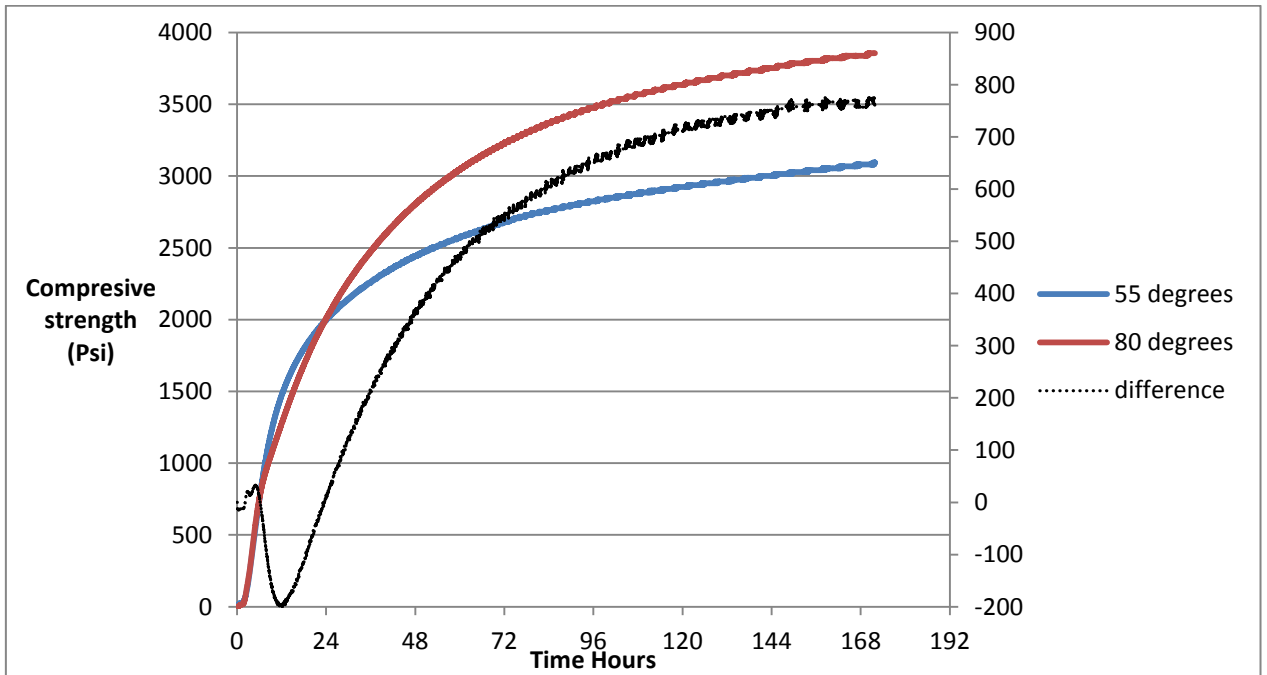
7 References

1. Erik B.Nelson, Dominique Guillot| Well cementing, second edition, Schlumberger 2006
2. Peter C.Hewlett | Lea's chemistry of Cement and Concrete, fourth edition, Elsevier 1998
3. H.F.W. Taylor| Cement chemistry, 1992 ISBN 0-12-683900-X
4. Mirkamil Ablikim Turkel| *Time and strength development of cement mixtures due to low temperature.2011*
5. William D.Nesse| Introduction to mineralogy, 2000
6. IADC/SPE 136276| *Technically and Economically improved cementing systems with Sustainable Components* A.Brandl, W.S. Bray, D.R. Doherty, BJ Services Company, 2010
7. SPE-5028| Long-term effects of high temperature on strength retrogression of cements, 1974
8. ANSI/API- American Petroleum Institute| *Recommended Practice for testing well cement, 10B-2 First edition, July 2005*
9. OFITE testing equipment, Inc.| Instruction manual Model 20 Constant Speed blender 2008
10. Silje Harestad| master thesis for UiS 2012
11. <http://en.wikipedia.org/wiki/Pozzolan>
12. http://en.wikipedia.org/wiki/Pozzolanic_reaction
13. <http://en.wikipedia.org/wiki/Aplite>
14. OFITE testing equipment, Inc.| Instruction manual Atmospheric Consistometer 2008
15. Halliburton services| Ultrasonic Cement Analyzer manual NO. 458.9728
16. Lasse Telstø email consultation
17. Alejandro Escalona| Lectures in "Petroleum Geology" 2010-2011

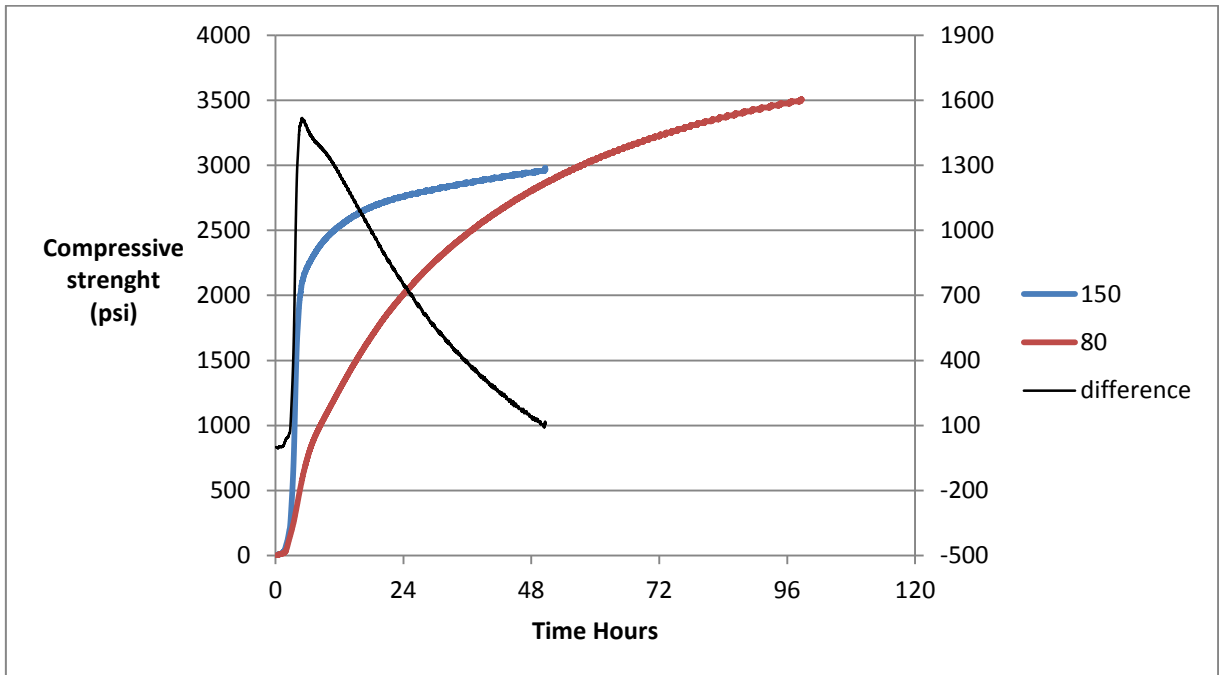
8 Appendix



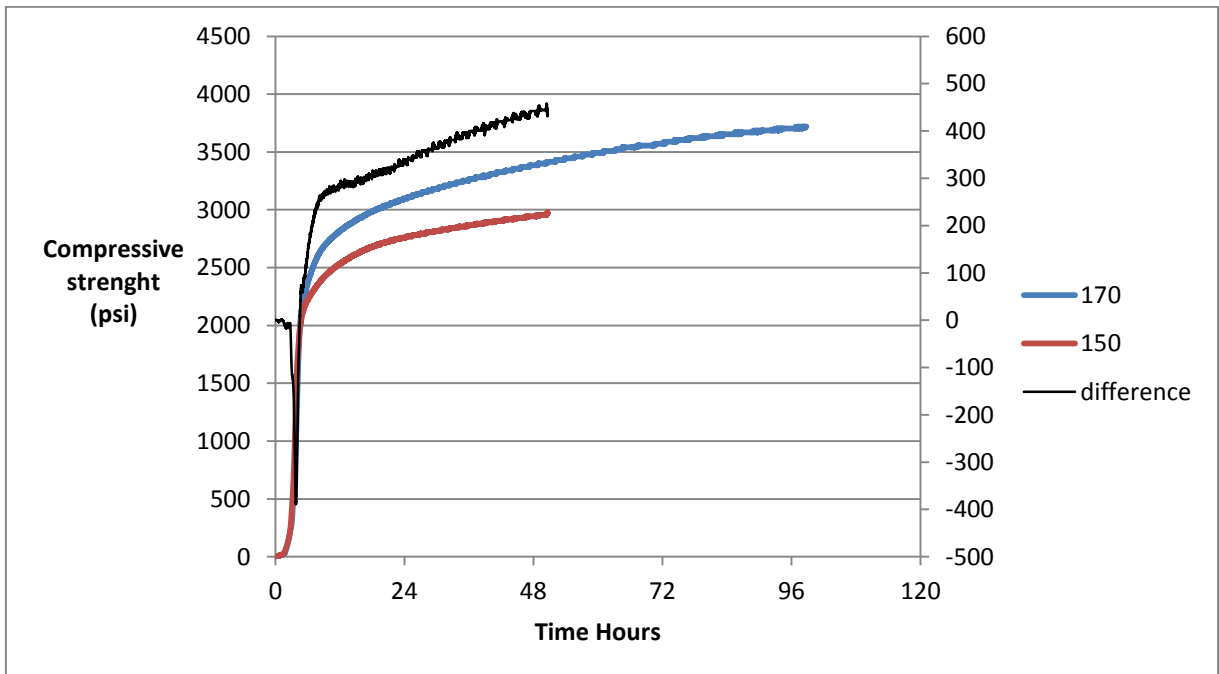
Graph 1. Comparison of 55°C and 20°C strength development of initial slurry at 3000 psi pressure



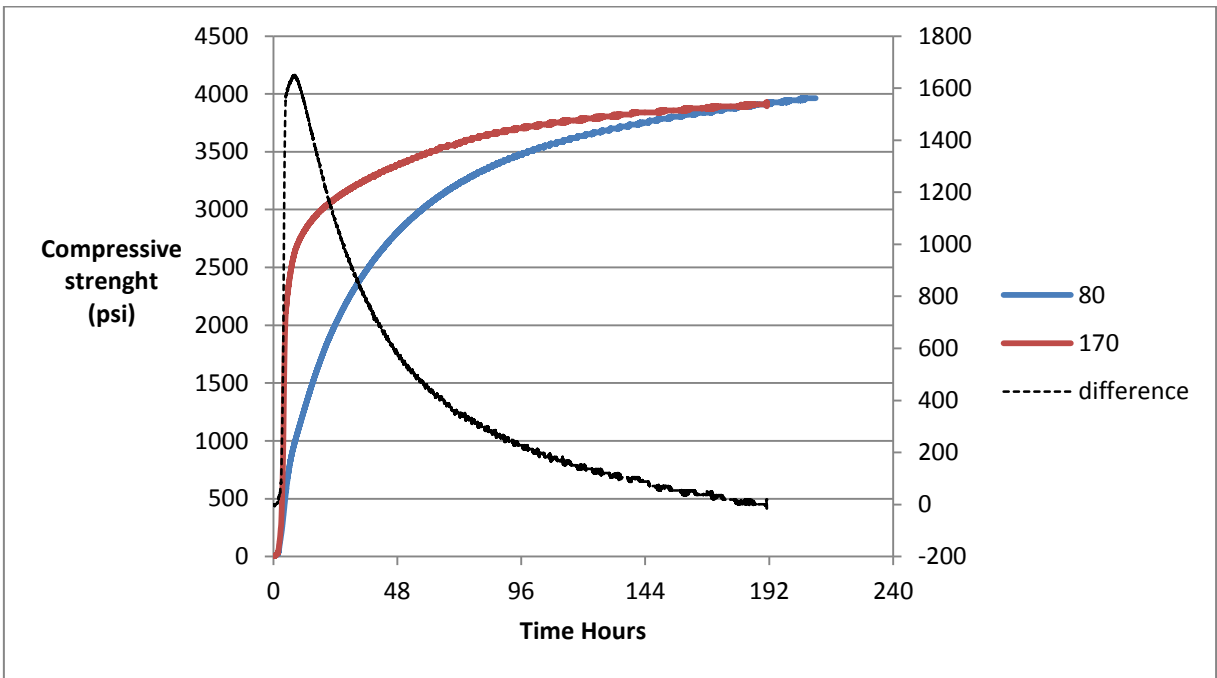
Graph 2. Comparison of 80°C and 55°C strength development of initial slurry at 3000 psi pressure



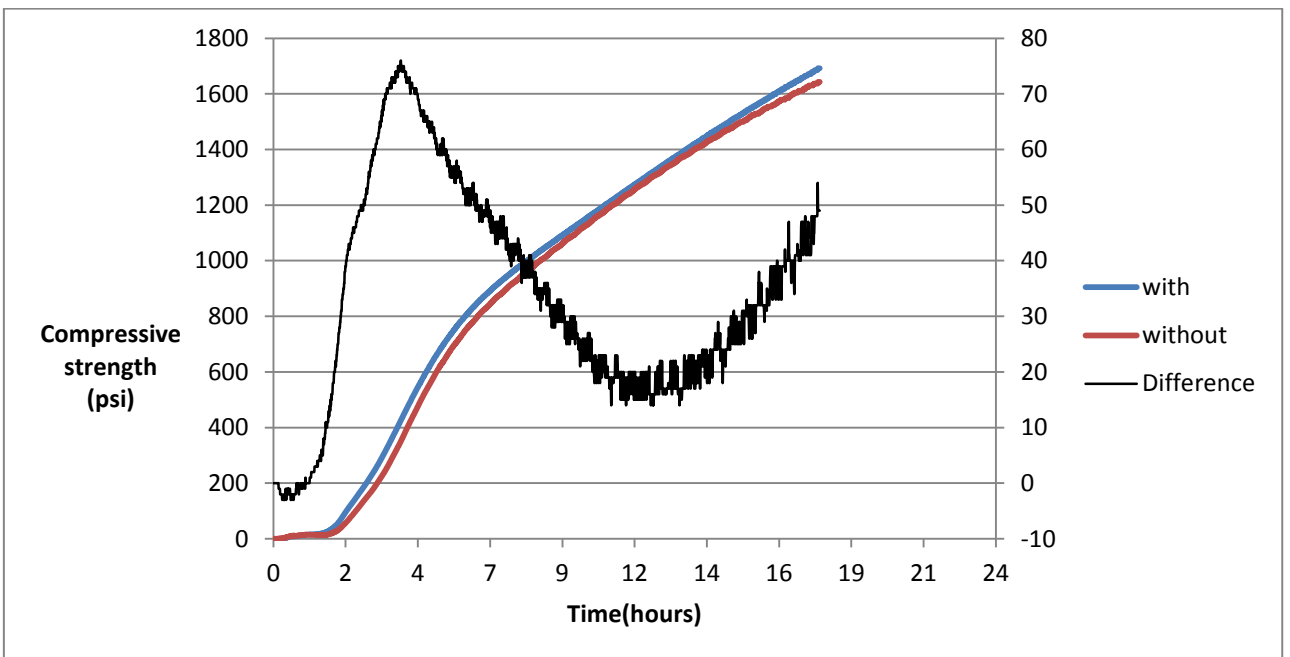
Graph 3. Comparison of 80°C and 150°C strength development of initial slurry at 3000 psi pressure



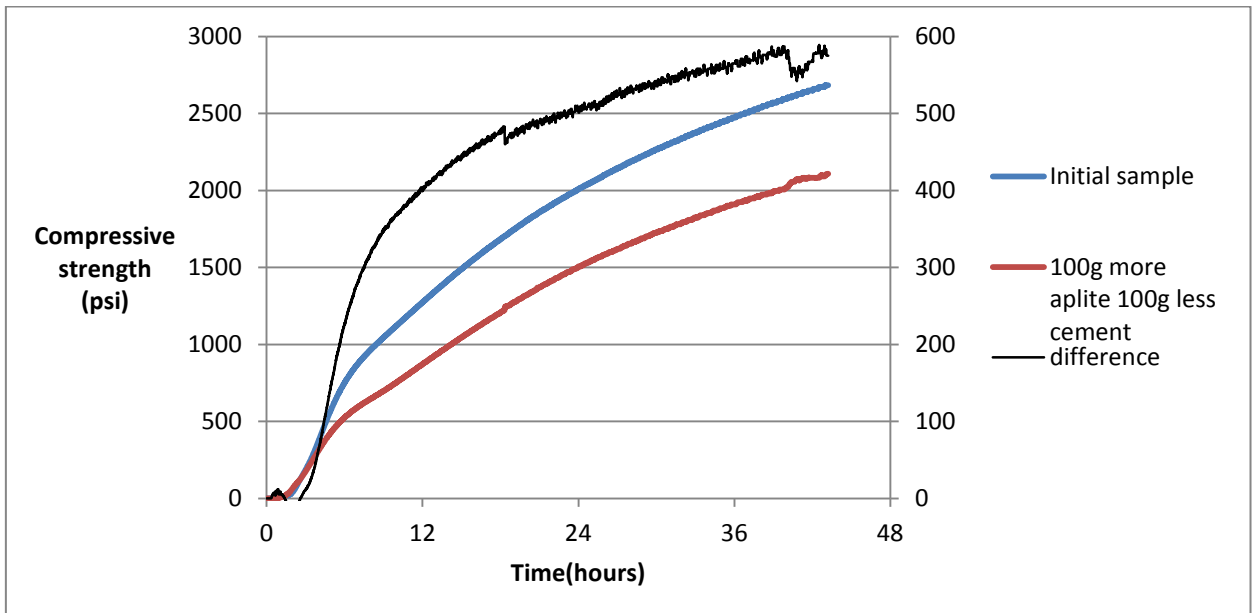
Graph 4. Comparison of 80°C and 55°C strength development of initial slurry at 3000 psi pressure



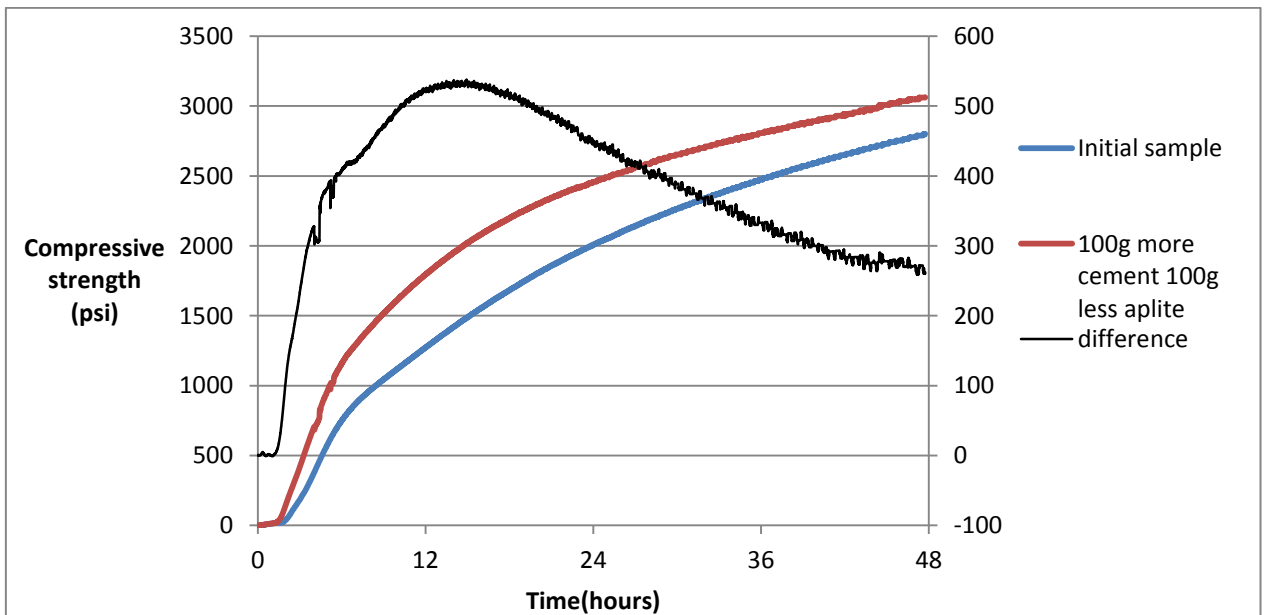
Graph 5. Comparison of 150°C and 170°C strength development of initial slurry at 3000 psi pressure



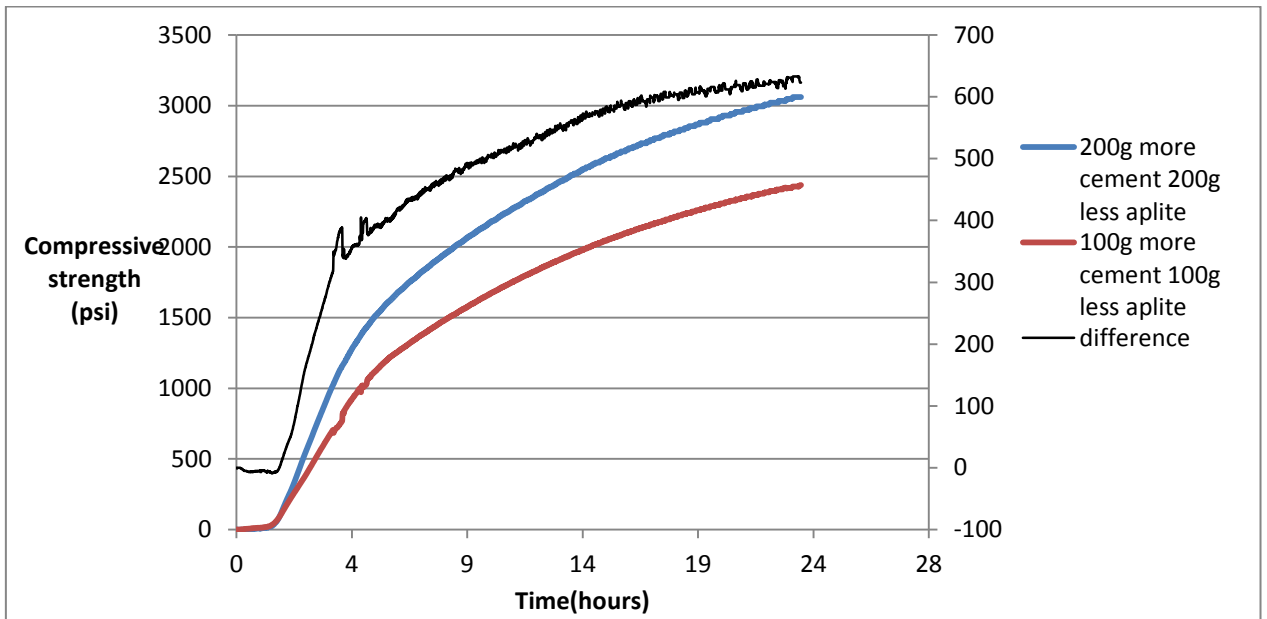
Graph 6. Comparison of slurry with and in absence of CaCO₃



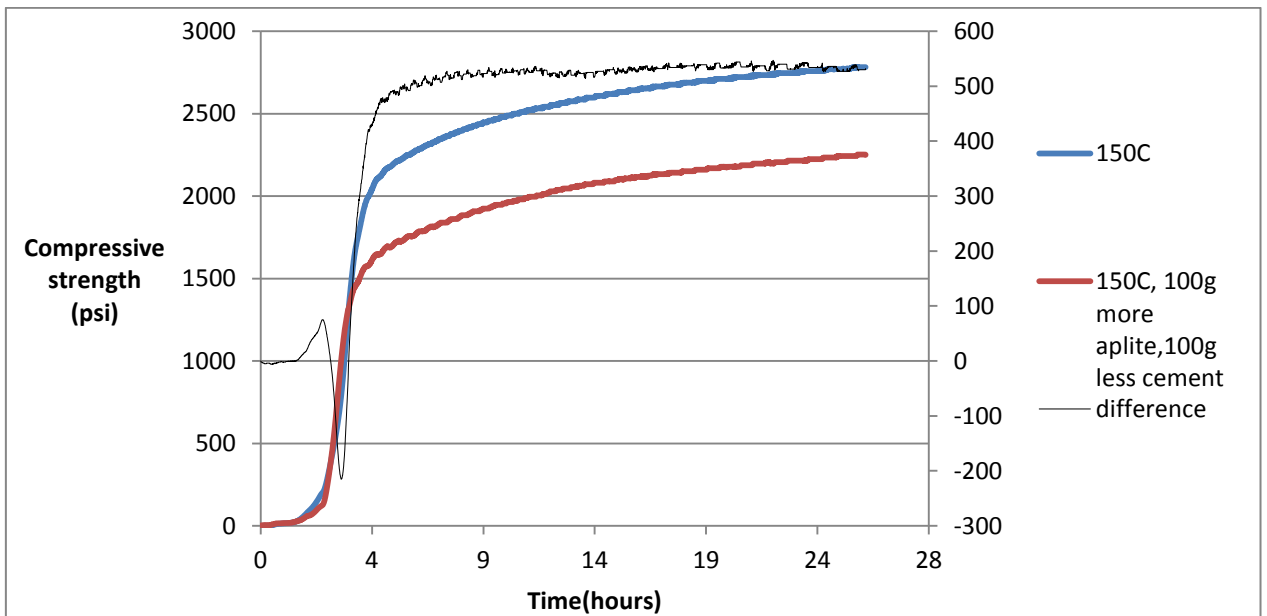
Graph 7. Comparison of initial slurry and slurry with 100g more aplite and 100 less cement at 80°C and 3000 psi



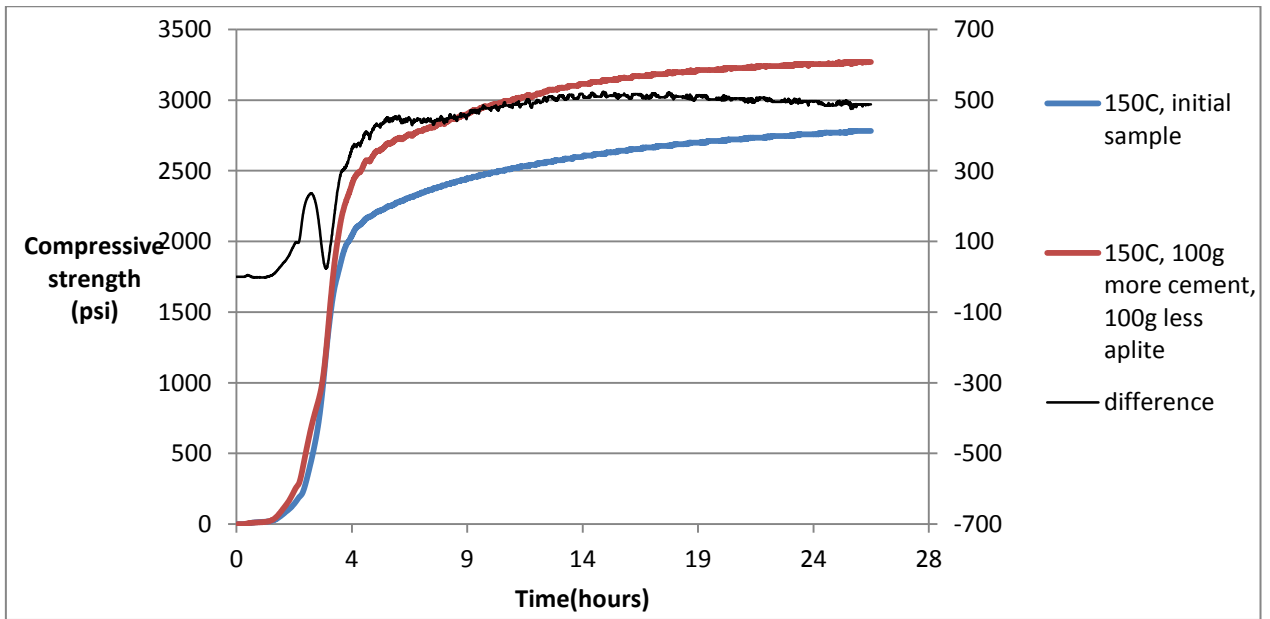
Graph 8. Comparison of initial slurry and slurry with 100g more cement and 100 less aplite, 80°C, 3000 psi



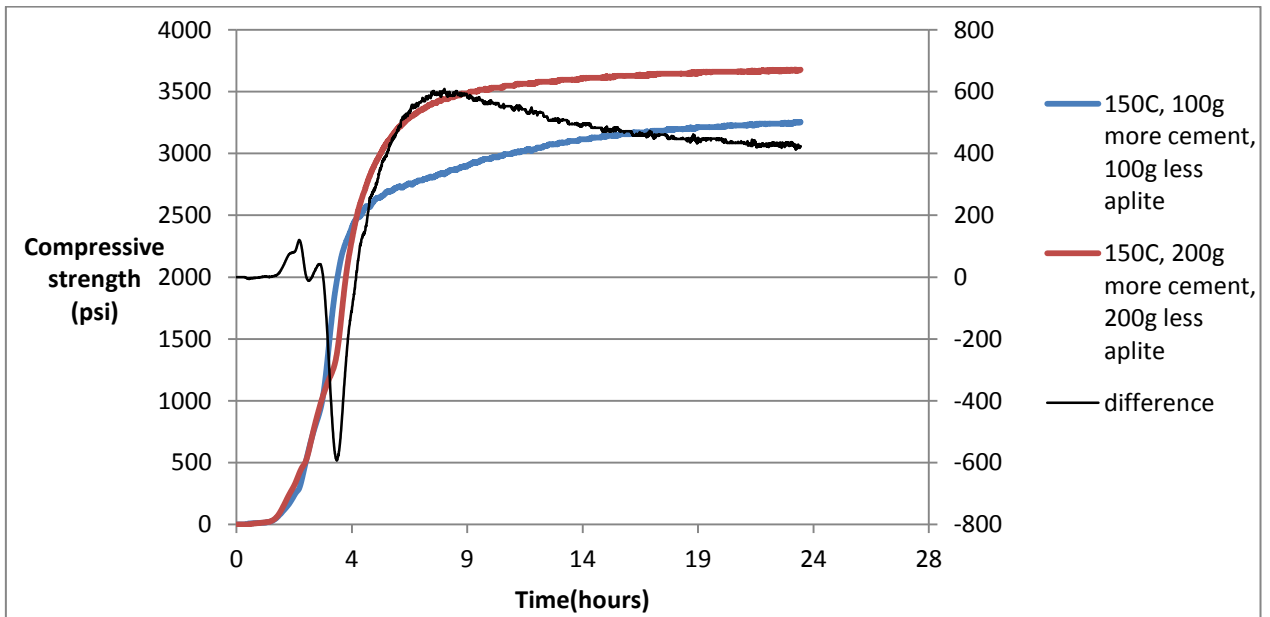
Graph 9. Comparison of initial slurry and slurry with 200g more cement and 200g less aplite, 80°C, 3000 psi



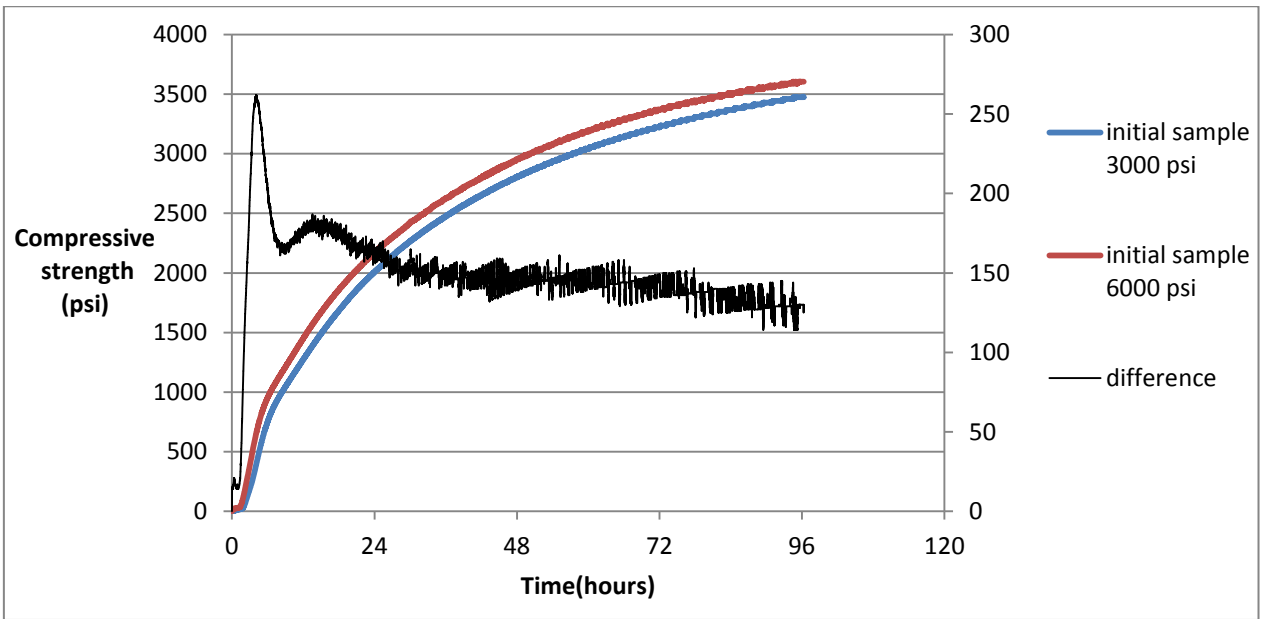
Graph 10. Comparison of initial slurry and slurry with 100g more aplite and 100g less cement, 150°C, 3000 psi



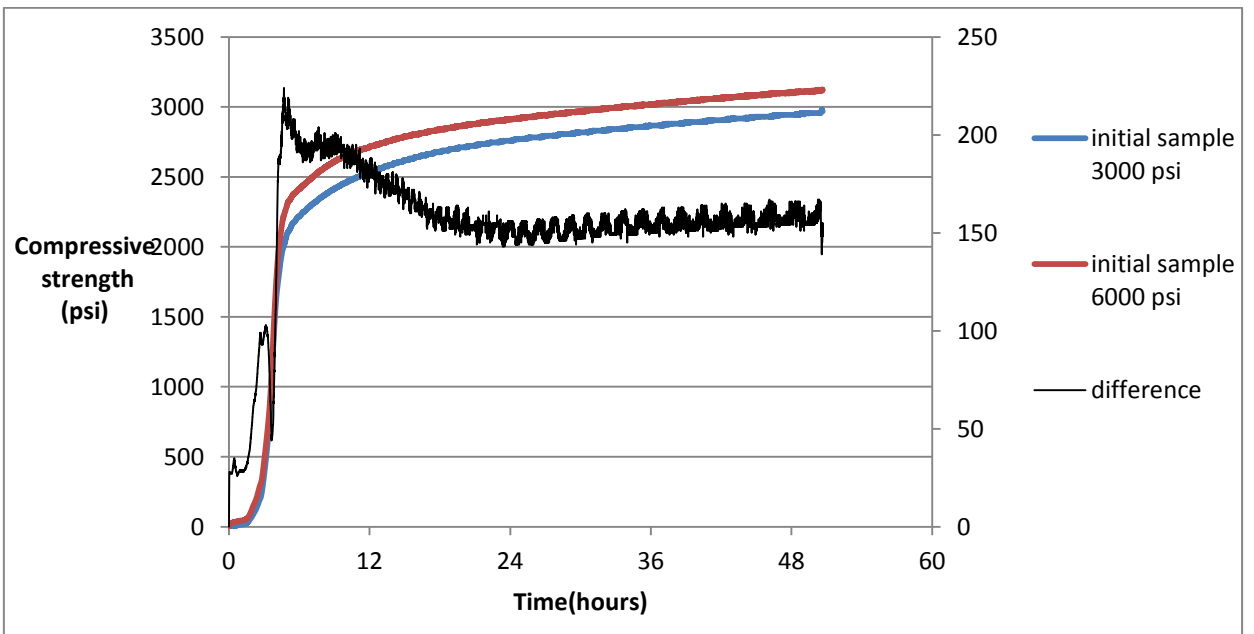
Graph 11. Comparison of initial slurry and slurry with 100g more cement and 100g less aplite, 150°C, 3000 psi



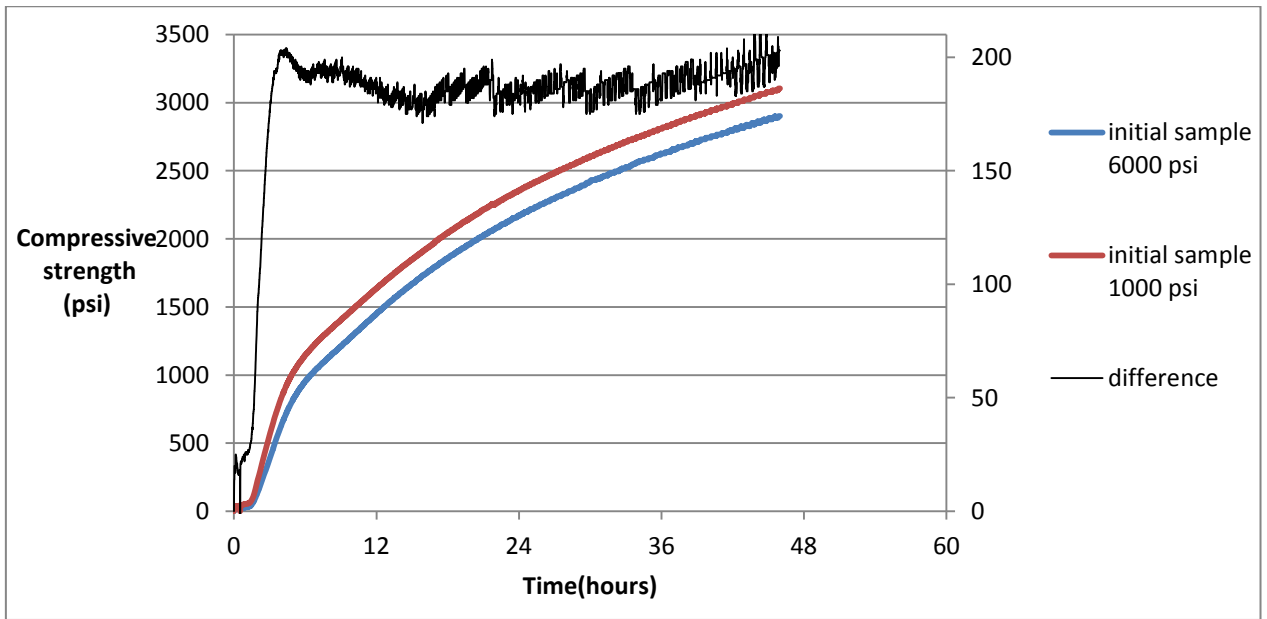
Graph 12. Comparison of initial slurry and slurry with 200g more cement and 200g less aplite, 150°C, 3000psi



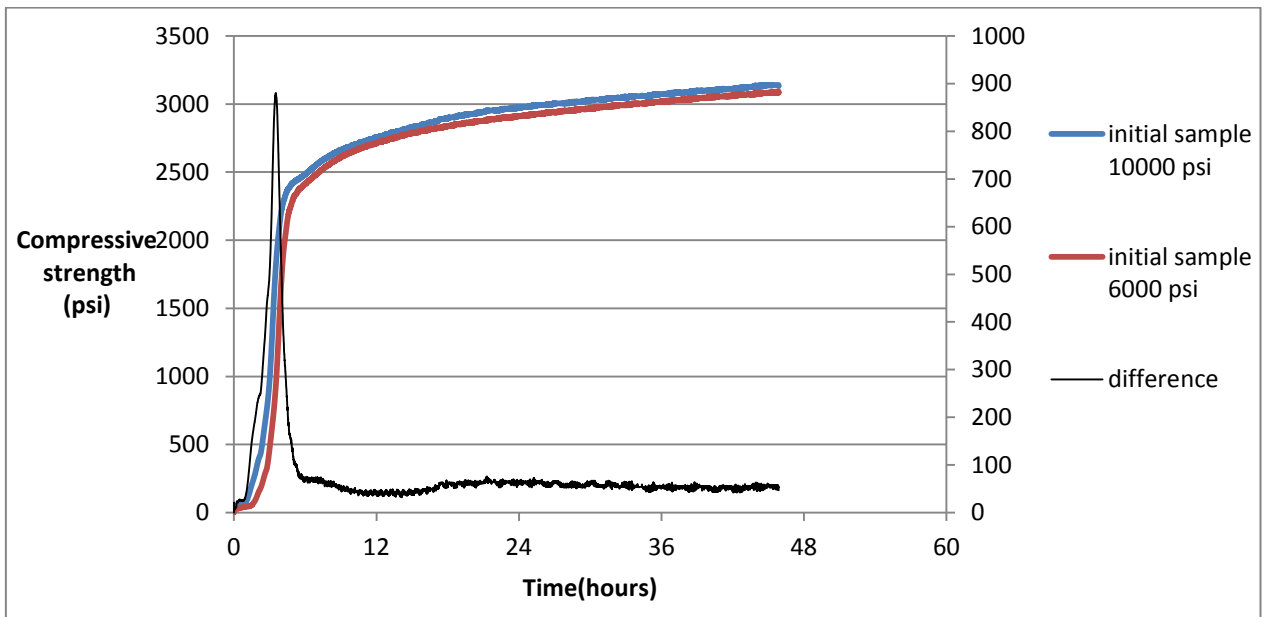
Graph 13. Comparison of initial slurry at 3000 psi and 6000 psi under 80°C temperature



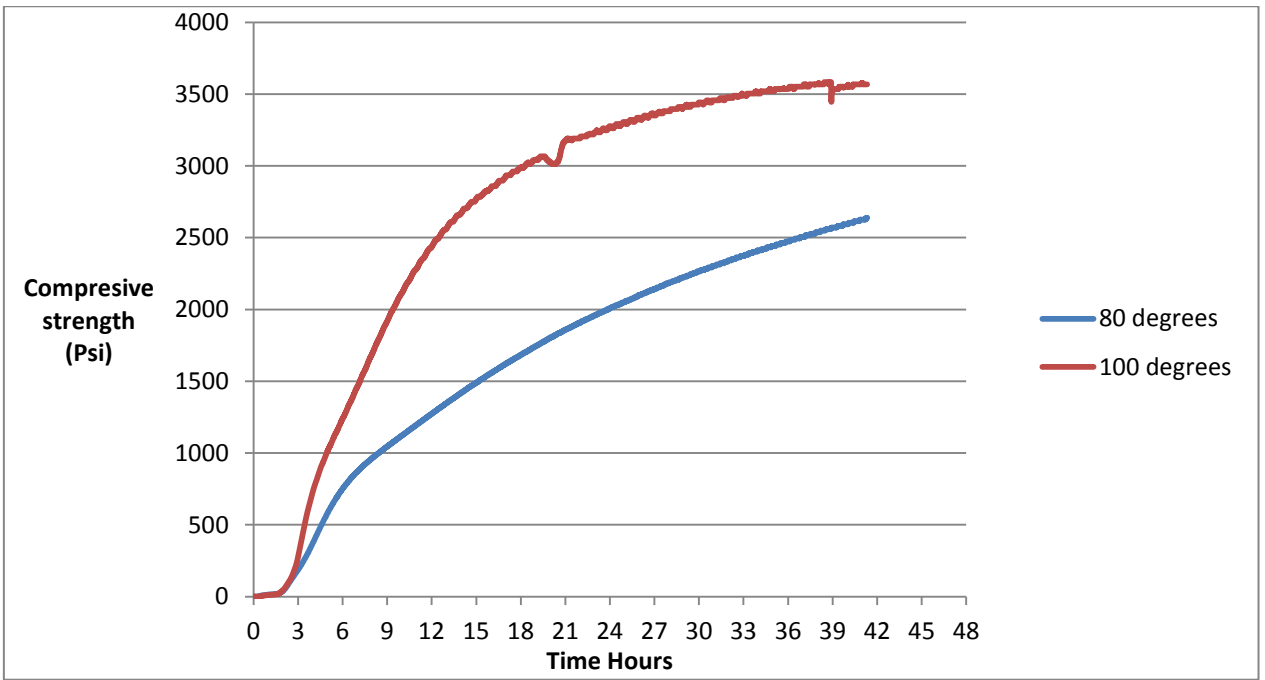
Graph 14. Comparison of initial slurry at 3000 psi and 6000 psi under 150°C temperature



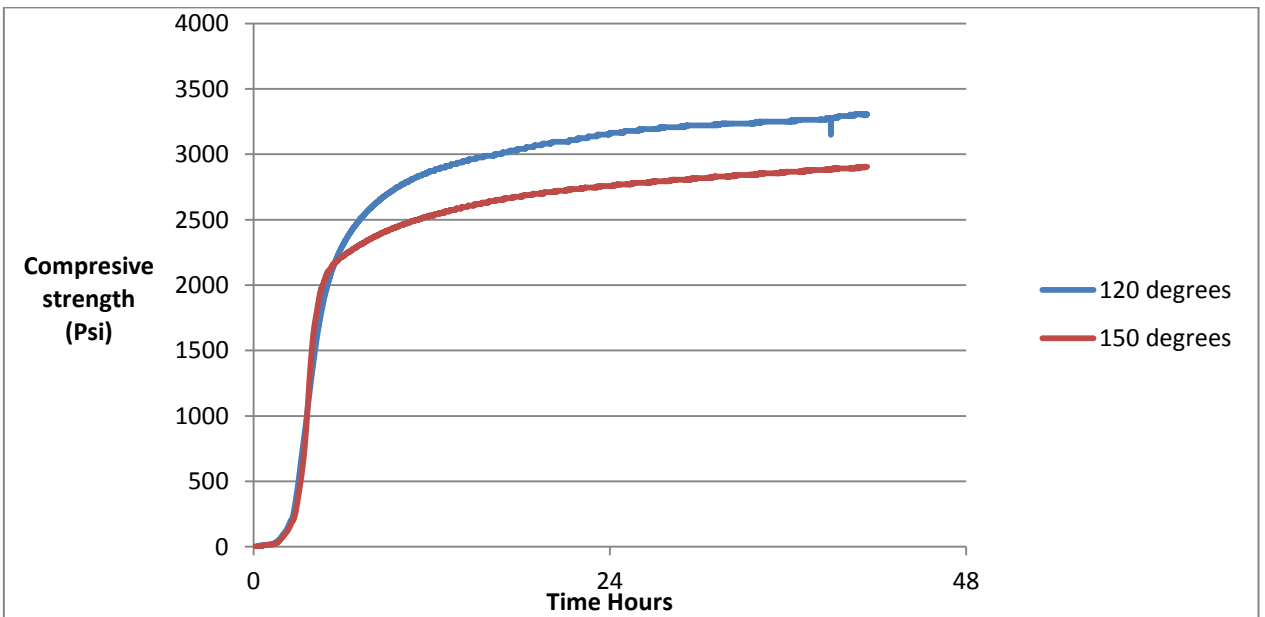
Graph 15. Comparison of initial slurry at 6000 psi and 10000 psi under 80°C temperature



Graph 16. Comparison of initial slurry at 6000 psi and 10000 psi under 150°C temperature



Graph 17. Comparison of initial slurry at 80°C and 100°C at 3000 psi



Graph 18. Comparison of initial slurry at 120°C psi and 150°C psi at 3000 psi