Universitetet
i Stavanger

FACULTY OF SCIENCE AND TECHNOLOGY

MASTER'S THESIS

Study program/specialization: Industrial Economics	Spring semester, 2012 Open
Author: Silje Harestad	…………………………………………. (signature author)

Instructor: Helge Hodne

Supervisors: Arild Saasen, UiS, Erik Berg, Baker Hughes

Title of Master's Thesis:

Effects of temperature on the strength development of cementitious materials

ECTS: 30

Subject headings: Aplite Quartz Liquid Stone Cement Compressive strength Plug and abandonment	Pages: 40 + attachments/other: 1 Stavanger, 14. 06. 2012

EFFECTS OF TEMPERATURE ON THE STRENGTH DEVELOPMENT OF CEMENTITIOUS MATERIALS

THESIS PERFORMED AT UNIVERSITY OF STAVANGER THE SPRING OF 2012

BY

SILJE HARESTAD

MASTER IN INDUSTRIAL ECONOMICS

Preface

This study is the finishing thesis for my master degree in Industrial Economics at the University of Stavanger, Norway.

The work of this thesis was performed at the cementing laboratory at the University of Stavanger and Baker Hughes' offices in Tananger. I want to thank Baker Hughes for giving me the opportunity to write this thesis.

I would like to thank my supervisor at Baker Hughes Erik Berg for good guidance and useful comments. In addition, I would like to thank Hans Buller, Per Skadsheim, Atle Døskeland and Ståle Håheim who also works at Baker Hughes for shearing your knowledge with me.

I will especially thank my instructor at the University of Stavanger, Helge Hodne for excellent guidance and inspiration during the work of this thesis.

Also, I want to thank Arild Saasen for introducing me to this interesting subject and that he always was available if I needed any guidance or help.

Abstract

This report “Effects of temperature of the strength development of cementitious materials” has been prepared for the Master Thesis in Industrial Economics at the University of Stavanger (UiS).

A series of experiments has been performed using Aplite based cement slurries, Quartz based cement slurries and Liquid Stone delivered by Baker Hughes. The different cementitious materials have been compared regarding the compressive strength development at different temperatures. The various experiments show that at higher temperatures it could be beneficial to replace some of the cement with these materials. Measurements of the strength development of Ordinary Portland Cement at ambient temperature and 150 °C is also included in the thesis and used as a reference value.

Table of Contents

1 Introduction

When oil and gas wells have reached the end of their production life, they are required to be permanently plugged and abandoned (P&A). Ultimately, a well should be abandoned in the same condition it was from nature's side. This is practically impossible. The foremost goal is thus to achieve an abandoned well that will not leak to the surface. It has also been declared that the potential for leakage from surface to a depleted reservoir has not been given much attention, but should be covered when permanent P&A, because this is the most likely scenario in the first period after P&A.

On the Norwegian continental shelf (NCS) there are more and more fields approaching the end of their productive life. The number of wells that have been permanently P&A each year has increased from about 10 to 50-60 per year in a 10 year perspective as illustrated in Fig. 1 [1]. Estimates for the next 15 years shows that in the North Sea approximately 6000 wells including 1400 subsea wells need to be permanently P&A [2]. Of these are about 2200 wells on the NCS [3].

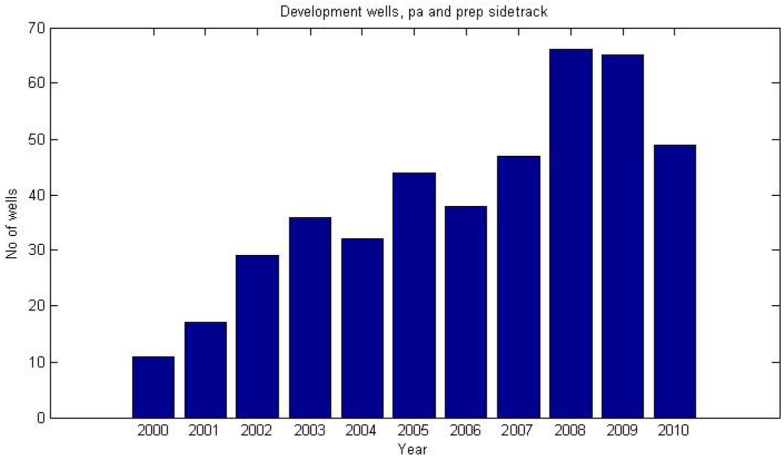

Figure 1 - The number of wells that has been permanently plugged and abandoned from year 2000 to 2010 [1].

Ordinary Portland Cement (OPC) has been the conventional plugging material when a well is being permanently P&A. OPC is widely used in concrete and beside water, one of the most used materials on earth. As OPC is the reactive component in concrete it is used in significant volume [4, 5]. Some estimates show that the cement industry is responsible for 5% of the total global CO_2 emissions [5]. The increased concentration of greenhouse gases like CO_2 is one of the causes for global warming and climate changes. During the process of producing cement the average gross specific CO_2 emissions were 866 kg CO_2 /tonne of clinker [4]. By replacing some of OPC with other material this will lead to a reduction in the CO_2 emissions.

A pozzolanic material such as Aplite or Quartz does not contain CO_2, and will not be liberating CO_2 in the development, such as in cement production. So by replacing some of Portland cement with Aplite or Quartz it will contribute to reducing greenhouse gas emissions. That’s why Bellona, a Norwegian environment organization, stated that Aplite is one of 101 solutions to the climate crisis [6].

Another aspect is the strength that is being achieved with OPC alone and with adding other materials. It is known in the oil industry for decades that OPC alone will literally brittle up and loose strength over time in high temperature environment. By adding other materials like Aplite or Quartz, the result may be stronger cement over time in these environments.

2 Background

In 2011 a comprehensive study related to temporary abandoned wells on the NCS was performed. The study was conducted by Petroleum Safety Authority Norway (PSA), Sintef and Wellbarrier [7, 8, 9]. The survey included 8 operating companies that were responsible for a total of 193 temporary abandoned wells on the NCS. The NORSOK regulations require two well barriers and the analysis of the survey showed that 38 percent of the temporary abandoned wells are not in accordance with these regulations. The analysis also shows that several of the wells have been temporarily abandoned for a long period of time. Temporary abandoned wells are defined as "all wells/wellbores, with the exception of active development wells (production/injection wells) and wells that have been permanently plugged and abandoned pursuant to regulatory requirements" [7]. The conclusion of the study is that the operators must define what is meant by temporary abandonment. The future focus to PSA is to reduce the number of temporarily abandoned wells.

The status of the temporary abandoned wells is presented in Fig. 2 [2].

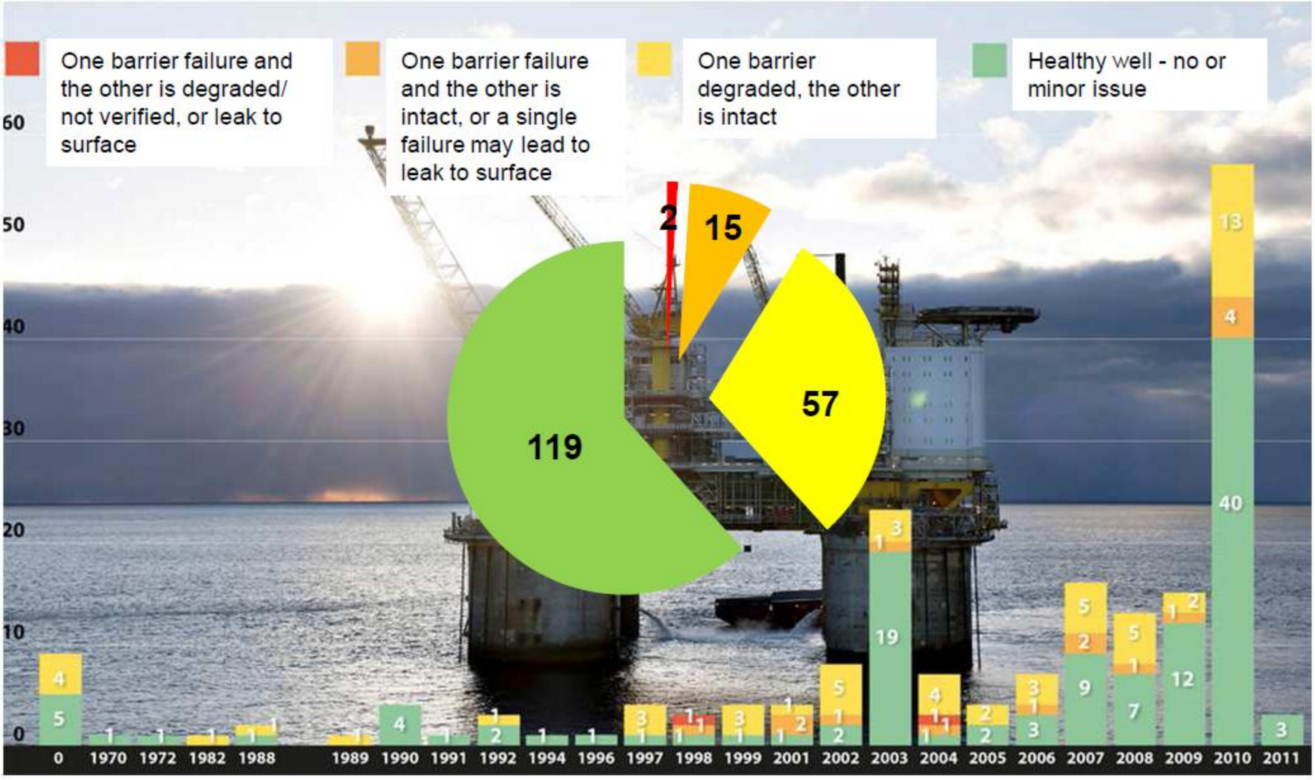

Figure 2 - The colors illustrate the status of the well integrity of temporary abandoned wells on the NCS. The figure also shows that wells have been temporarily abandoned for 40 years [2].

The Norwegian Oil Industry Association (OLF) Guideline no. 117 categorizes well integrity into "red, orange, yellow and green". In this context, "green" means that the well has no or minor issue. Furthermore, "red, orange and yellow" means that the well have various degrees of barrier failure.

According to Activities Regulations § 85 regarding well barriers:”If a barrier fails, activities shall not be carried out in the well other than those intended to restore the barrier”. According to this regulation, wells that are in category red and orange should be taken care of [10].

3 Regulations and requirements

Permanent plug and abandonment of wells on the NCS is governed by the Activities Regulations issued by the PSA Norway. These regulations states that the NORSOK D-010 standard should be used as a minimum requirement for well design, planning and execution of well operations in Norway [10,11]. Furthermore this implies that other alternatives to the standard may be used, as long as the solution can be proven equally or better than the NORSOK D-010 standard.

3.1 Well Barrier

A well barrier is defined in NORSOK D-010 as "an envelope of one or several dependent barrier elements preventing fluids or gases from flowing unintentionally from the formation, into another formation or to surface" [11]. The standard defines two types of well barriers; Primary and secondary well barriers. The primary well barrier is defined as: "the first object that prevents flow from a source", and the secondary well barrier is a back-up in case the primary barrier fails. Furthermore, a well barrier should be installed as close to the potential source of inflow as possible, covering all possible leak paths [11].

The NORSOK Standard states that a Well barrier element (WBE) is "objects that alone cannot prevent flow from one side to the other side of itself. The primary and secondary barrier is defined in NORSOK as being independent of each other, which means without common WBE. If there is a common well barrier, a risk analysis and risk reducing measures must be performed to reduce the risk in accordance to the ALARP (As Low as Reasonable Practicable) principle [3].

The facility regulations § 48 about well barriers states that "When a well is temporarily or permanently abandoned, the barriers shall be designed such that they take into account well integrity for the longest period of time the well is expected to be abandoned"[12]. And according to the Activity Regulations § 85 regarding well barrier; "there shall be tested well barriers with sufficient independence during well activities" [10].

Another reason for plugging a wellbore or reservoir section permanently is when sidetracking into a new reservoir, or drilling a new wellbore (slot recovery).

3.2 Permanent plug and abandonment

The definition of permanent abandonment is according to NORSOK D-010: "well status, where the well or part of the well, will be plugged and abandoned permanently, and with the intention of never being used or re-entered again" [11].

Since permanently plugged wells shall be abandoned with an eternal perspective, the general principle of two well barriers is not sufficient for permanent P&A. It is also required with an open hole to the surface barrier and a well barrier between the reservoirs. The open hole to the surface barrier isolates the surface that is exposed after casing cut. It functions as the final barrier against flow.

3.2.1 Permanent well barrier requirements

A permanent well barrier shall include all annuli, extending the full cross section of the well and seal both vertically and horizontally, see Fig. 3. Therefore it must be set a WBE inside the casing, placed at a depth with a qualified WBE in all annuli.

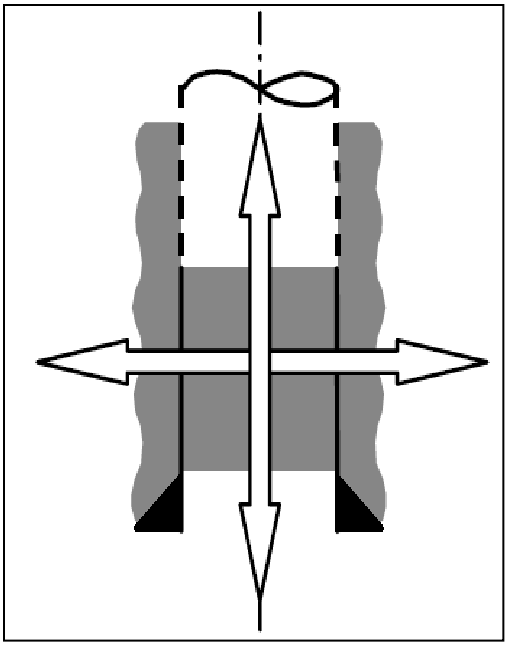

Figure 3 - The figure shows that a permanent well barrier shall seal both vertically and horizontally [10].

NORSOK D-010 states that: “a permanent well barrier should have the following properties:

a) Impermeable.
b) Long term integrity.
c) Non shrinking.
d) Ductile- (non brittle – able to withstand mechanical loads/impact.
e) Resistance to different chemicals/substances (H_2S, CO_2 and hydrocarbons).
f) Wetting, to ensure bonding to steel” [10]

These material requirements are also defined in the third issue of the British Guidelines for the Suspension and Abandonment of Wells, released in January 2009 [13].

Mechanical barriers are not suited for long term abandonment.

3.3 Temporary abandonment

Temporary abandoned wells are defined in NORSOK D-010 as: “well status, where the well is abandoned and/or the well control equipment is removed, with the intention that the operation will be resumed within a specified time frame (from days up to several years)” [10]. When a well is being temporary abandoned it shall be possible to re-enter the well in a safe manner.

4 Materials

The well barrier material has to withstand the load/environmental conditions it is exposed to for as long as the well will be abandoned [10]. A long term integrity test should also be performed on the plugging materials that are used. The standard does not recommend a specific material, but different requirements the material should fulfill.

4.1 Sample preparation

The composition of the different cement samples is shown in Table 1. The preparation of the different slurries was in accordance with American Petroleum Institute (API) [14] and the samples were prepared at ambient temperature. Baker Hughes' Liquid Stone (LS) was prepared at their laboratory and the specific gravity (s.g) was 1.68. Before LS was applied to the Ultrasonic Cement Analyzer (UCA) curing chamber, a liquid activator was added, see Table 2. When the activator was added, the mixing speed on the Warring Blender was 4000 rpm. Thereafter, the mixing speed was increased to 12000 rpm for 30s.

Table 1 – Composition of the cement samples. The specific gravity of the cement samples is 1.90

	G Cement	**Aplite**	**Quartz**
Cement [g]	792,00	333,33	333,33
Aplite [g]		450,00	
Calcitt Franzefoss Miljø VK150 [g]		50,00	50,00
Quartz [g]			450,00
H_2O [g]	349,00	316,43	316,43
Water/Cement - ratio	0,441	0,949	0,949

Table 2 - Composition of premix Liquid Stone. The specific gravity is 1.68.

Days after mixing	**Temperature [°C]**	**Premix LS [kg]**	**Activator [g]**
5 days	170	0,96	35,8
12 days	150	0,96	35,8
19 days	100	0,96	35,8
32 days	80	0,951	42,24

4.2 Ordinary Portland cement (OPC)

OPC is the most important binding material and the most common example of hydraulic cement. OPC sets and develop compressive strength due to hydration. A chemical reaction occurs between the water and the compounds present in the cement. The setting and hardening of OPS also occur under water. The development of strength is predictable, uniform and relatively quick. The set cement has low permeability and is nearly insoluble with water. Therefore, exposure to water will not destroy its hardness. Such properties are essential to achieve and maintain zonal isolation [15].

OPC is produced by pulverizing clinker. Clinker is the calcined (burned) material existence of the rotary kiln in a cement factory. The clinker consists mainly of hydraulic calcium silicates, calcium aluminates, and calcium aluminoferrites. Calcium sulphate (usually gypsum) is added to prevent flash set of the cement. Flash set is phenomenon where C_3A and C_4AF hydrates in contact with water and results in early stiffening. This can prevent proper placement of the cement slurry in the annulus [15].

Table 3 - Mineralogical Composition of Classic Portland cement Clinker

Oxide Composition	Cement Notation	Common Name	Concentration (wt%)
$3CaO\cdot SiO_2$	C_3S	Alite	55-65
2CaO	C_2S	Belite	15-25
$3CaO\cdot Al_2O_3$	C_3A	Aluminate	8-14
$4CaO\cdot Al_2O_3\cdot Fe_2O_3$	C_4AF	Ferrite phase	8-12

Currently there exist eight classes of API-ISO Portland cements, designated A to H. They are arranged according to the depths, at which they are placed, and the temperatures and pressures to which they are exposed [15].

4.2.1 Tobermorite

Cement contains tobermorite and the mineral is the reason for the increasing compressive strength development. According to Well Cementing C-S-H phase has a variable C/S ratio, averaging about 1,5. The conversion to α-C_2SH at 110°C can be prevented by the addition of 35% to 40% silica (by weight of cement [BWOC], reducing the C/S ratio to about 1,0. At this level, a mineral known as tobermorite ($C_5S_6H_5$) is formed. Tobermorite preserves high compressive strength and low permeability. When the curing temperature increases to 150°C, tobermorite converts to xonotlite (C_6S_6H) and a smaller amount of gyrolite ($C_6S_3H_2$) with minimal deterioration of cement performance [15].

4.3 Aplite

In accordance with ASTM International designation C-219-55 a pozzolan is defined as: “A silicious or siliceous and aluminous material, which in itself possesses little or no cementitious value, but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties” [15].

Many great ancient structures, such as the Pantheon, the Colosseum and other ancient buildings were built of a natural pozzolan-lime mixture. They are still standing and many of them have lasted for almost two thousand years. It is known that when a natural pozzolan-lime mixture is hydrated, a pozzolanic reaction is initiated and will continue for many years. This is probably the reason why these ancient structures have lasted as long as two thousand years.

There are two types of pozzolans:

1. Natural pozzolans, including volcanic ashes and diatomaceous earth
2. Artificial pozzolans, such as fly ashes

Aplite is a natural pozzolan, which develops compressive strength by mixing with cementitious materials, watered lime and water. The material can replace more than 80% of the cement content in concrete[16]. The material is a light and very fine-grained granitic dyke where Quartz and feldspar are the dominant minerals [17]. The Aplite used in this thesis is collected from a quarry in Finnvolldalen, Nord Trøndelag, Norway. The composition is shown in Table 4.

Table 4 - The Oxide composition of Aplite [18].

Oxide Composition	Cement Notation	Concentration (wt%)
SiO2	S	83,4
Al2O3	A	8,29
Fe2O3	F	0,9
CaO	C	0,92
MgO	M	0,06
Na2O	N	2,16
K2O	K	2,86
Loss on ignition		0,8
Other		0,61

The hydration of API cement produce calcium-silicate-hydrate (C-S-H) phases ($x\text{CaO}\cdot y\text{SiO}_2\cdot z\text{H}_2\text{O}$), which are responsible for the strength, and portlandite [Ca(OH)_2], which is a weak point in the cement matrix. When pozzolanic materials are added to the cement system it eliminates portlandite and allows lowering the water content in the cement system. These effects can reduce the permeability and also improve the mechanical properties of set cement [19]. A study performed by Baker Hughes compared pozzolan and conventional API cement exposed to CO_2-loaded water at 300°F (148,9°C) and 3000 psi (20,7 MPa) for several weeks. The analysis of the study showed significantly less carbonation and fewer negative impacts for the pozzolan system compared with the conventional API cement design [19].

4.4 Liquid Stone™

LS is intended to be used as a permanent plugging material delivered by Baker Hughes. LS is defined as storable, pre-mixed cement slurry that can be kept in the liquid state from several days to over a year and made to set when required. According to Baker Hughes the LS system consists, mainly of six components: premixed slurry of conventional Portland cement (or other cementitious material) a set retarding agent, slag, a dispersant, a suspending agent and water as the carrier fluid. When the product will be used, a liquid activator is added to the slurry prior to pumping. The purpose of the activator is to re-initiate the cement hydration process. Then the LS are pumped down the well and it behaves as conventional cement [20].

Since LS is prepared onshore and shipped out as a bulk material in transport tanks, it will reduce the necessity of cement mixing facilities. This will further reduce waste and also minimize the environmental, human health and safety impact of the cementing operation. There is also cost savings due to fewer personnel required to perform the cement job [20].

4.5 Quartz

Silicates are the most abundant group of minerals in the earth's crust. Silicates such as Quartz, Beryl and Zircon are quarried as the source for specific elements (Si, Be, and Zr, respectively). They are used as industrial minerals, valued for their physical or chemical properties. The basic chemical structure of silicates is the (SiO_4) silicon tetrahedron. It consists of four O^{2-} anions in the corner of a tetrahedron with a Si^{4+} in the center [21].

5 Experimental procedure

5.1 Compressive strength measurements

For our measurements we used an UCA. An UCA makes it possible to cure cement slurries under simulated down-hole conditions. The travel time of ultrasonic sound waves through the cement sample is measured and the travel time is correlated to the compressive strength of the cement. This process takes place during the curing of the cement from liquid to set cement while the temperature and pressure are adjusted to down-hole conditions [22].

5.1.1 Temperature and pressure

When the curing chamber was filled with cement, the pressure was set to 3000 psi (20,7MPa), the temperature was increasing linearly from 20°C to the pre-set temperature with 1°F per minute. The pre-set pressure may fluctuate with +/- 100 psi (0,69MPa). The temperatures accordingly may fluctuate with +/- 2°C.

5.2 Shrinkage test

A shrinkage test was performed on neat class G cement (G cement) and an Aplite based cement slurry (Aplite). The mixture was poured in cubes for setting. The top of the cubes was covered with a plastic film to prevent evaporation. After the slurries had set and dried for 3 days at ambient temperature, the initial weight was measured. Thereafter, all the cubes were placed in water for 7 days. The volume and weight of the cubes were then measured. The volume was measured based on the weight of the cubes when submerged in water. Finally the cubes were placed in a pressure vessel. The pressure was set to 5 bar, to be above the boiling pressure at 150°C [23]. After 5 days in the pressure vessel the temperature was turned off. The volume and weight were then measured again.

6 Experimental results

6.1 Compressive strength measurements

6.1.1 G Cement

To obtain reference values for the project, experiments were performed on G cement at ambient temperature, approximately 20°C and 150°C, both at a pressure of approximately 3000 psi. The cement composition is shown in Table 1. The compressive strength development is shown in Fig. 4 and Fig. 5.

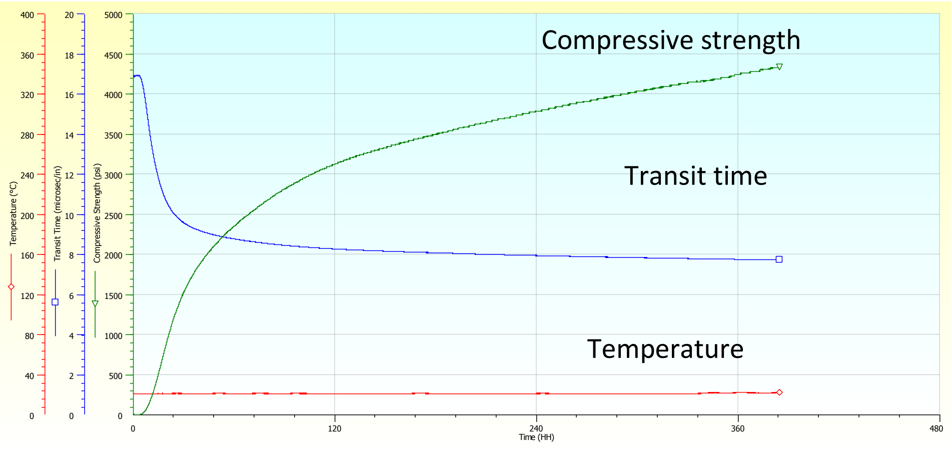

Figure 4 - The compressive strength development of a neat Class G cement cured at ambient temperature, approximately 20°C and approximately 3000 psi.

The compressive strength after 300 hours of curing was 4033 psi (27,8MPa). The experiment was stopped after 360 hours but the compressive strength was still increasing at this point. The compressive strength after 360 hours was 4241 psi (29,2MPa).

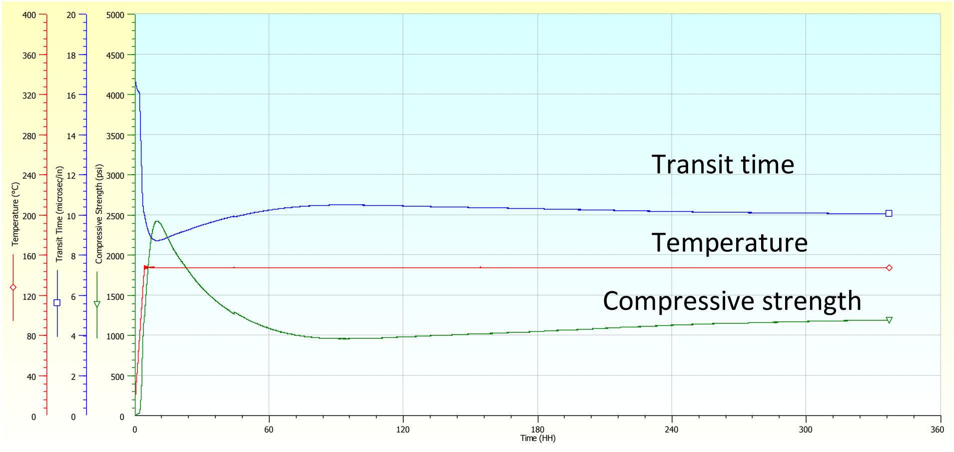

Figure 5 - The compressive strength development of neat Class G cement cured at 150°C and approximately 3000 psi.

The compressive strength for this cement reached a maximum of 2400 psi (16,55MPa) after 10 hours curing time. At this point the compressive strength started to decrease. A minimum of 955 psi (6,58MPa) was reached after 91 hours of curing. At this point the compressive strength started to slowly increase and it reached a maximum of 1185 psi (18,17MPa) after 337 hours, which was at the time the test was stopped.

6.1.2 Aplite

A series of experiments were performed on Aplite. The composition of all samples is the same and is shown in Table 1. The Aplite was tested at ambient temperature, 65, 100 and 170°C.

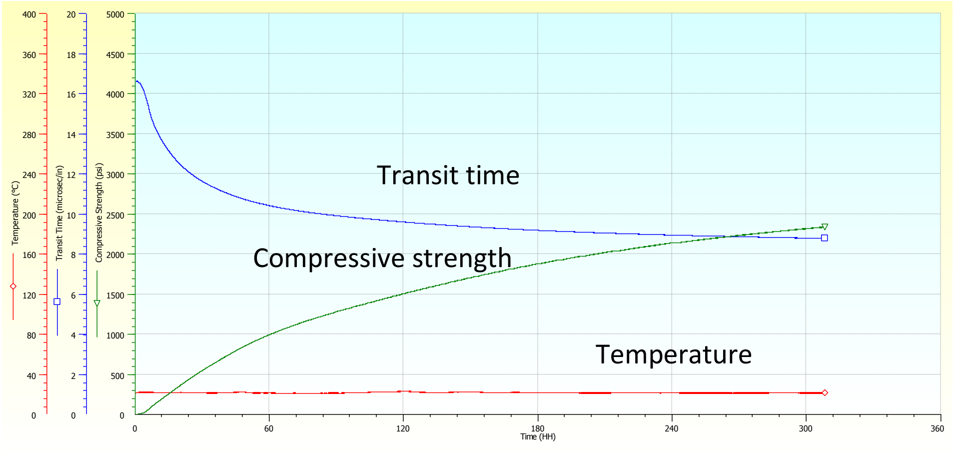

Figure 6 - The compressive strength development of an Aplite based cement slurry cured at ambient temperature, approximately 20 °C and 3000 psi.

The compressive strength development at ambient temperature, approximately 20 °C is shown in Fig. 6. After 300 hours of curing, the compressive strength of the Aplite was 2312 psi (15,9MPa). After 308 hours, while the compressive strength still had an increasing trend, the experiment was ended with a compressive strength of 2334 psi (16,1MPa) as the last reading.

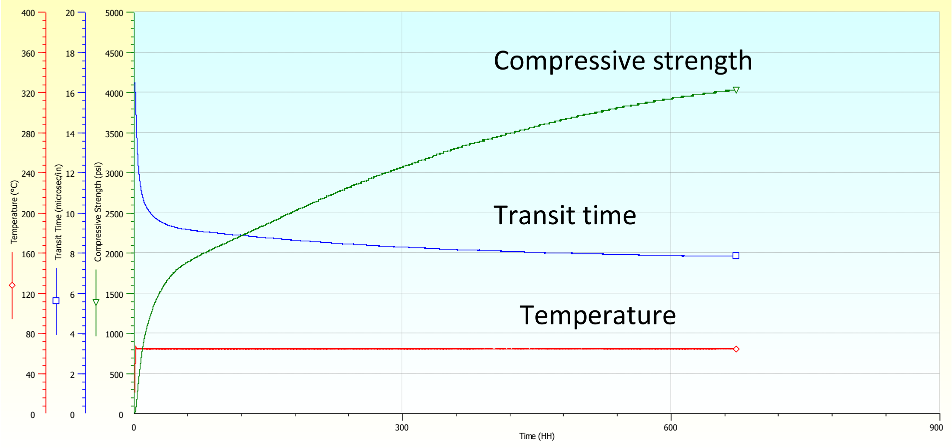

Figure 7 - The compressive strength development of an Aplite based cement slurry cured at 65°C.

The compressive strength development for Aplite cured at 65°C is shown in Fig. 7. The experiment was completed after 672 hours of curing and the compressive strength was at this point 4020 psi (27,7MPa). As seen in Fig. 7, the compressive strength at this point was still developing.

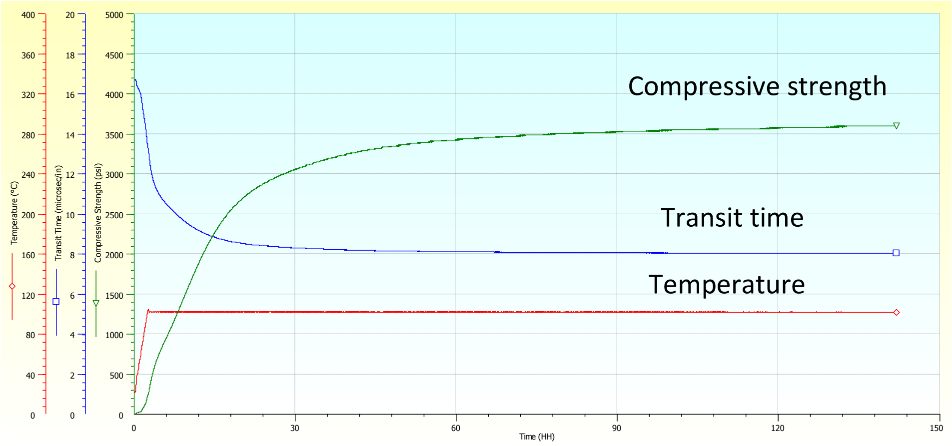

Figure 8 - The compressive strength development of an Aplite based cement slurry cured at 100°C.

The compressive strength development for Aplite cured at 100°C is shown in Fig. 8. After 60 hours of curing, the rapid strength development declines and at this point the compressive strength was 3420 psi (23,58MPa). After another 81 hours curing time (total time 141 hours) the experiment was completed and the compressive strength had reached 3591 psi (24,76MPa) at this point.

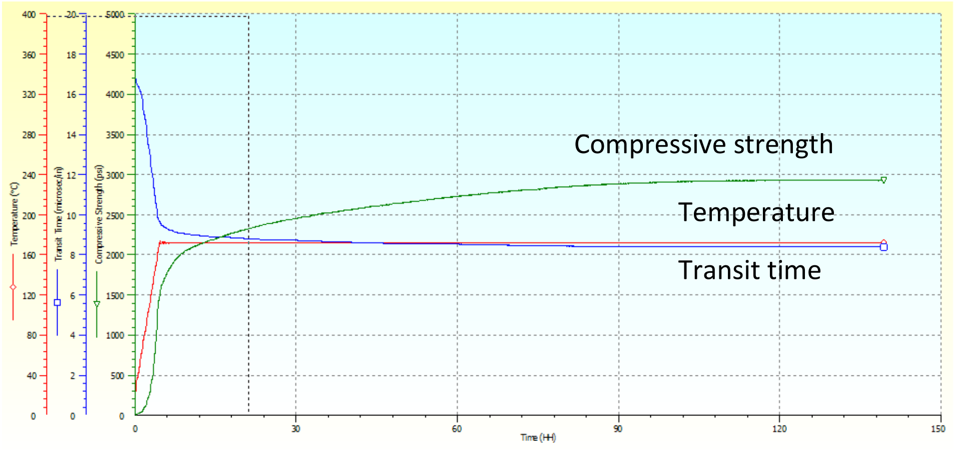

Figure 9 - The compressive strength development of an Aplite based cement slurry cured at 170°C.

The compressive strength of the Aplite cured at 170°C is shown in Fig. 9. The result shows that the compressive strength reached a maximum of 2924 psi (20,2MPa) after 116 hours curing time. Furthermore, it illustrates that the strength development levels of at this point.

6.1.3 Liquid Stone

A series of experiments was performed on 1.68 s.g. LS. LS were tested at 80, 100, 150 and 170°C. The LS supplied is not intended for lower temperatures than 80°C, therefore the slurry was not measured at ambient temperature.

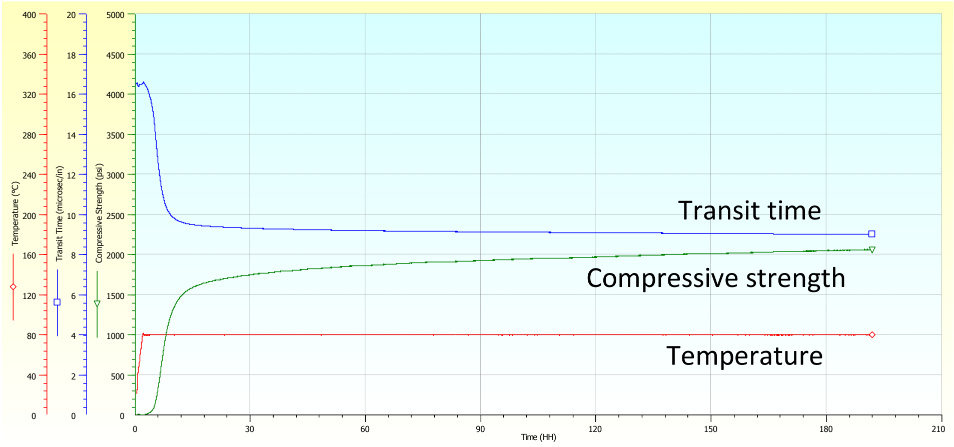

Figure 10 - The compressive strength development of Liquid Stone cured at 80°C.

The compressive strength development cured at 80°C is shown in Fig. 10. The measured values show that after 30 hours of curing the compressive strength reached 1743 psi (12,01MPa). After 192 hours the experiment was completed, with a compressive strength at 2052 psi (14,15MPa). At this point the compressive strength leveled off and only a slight increasing trend is indicated.

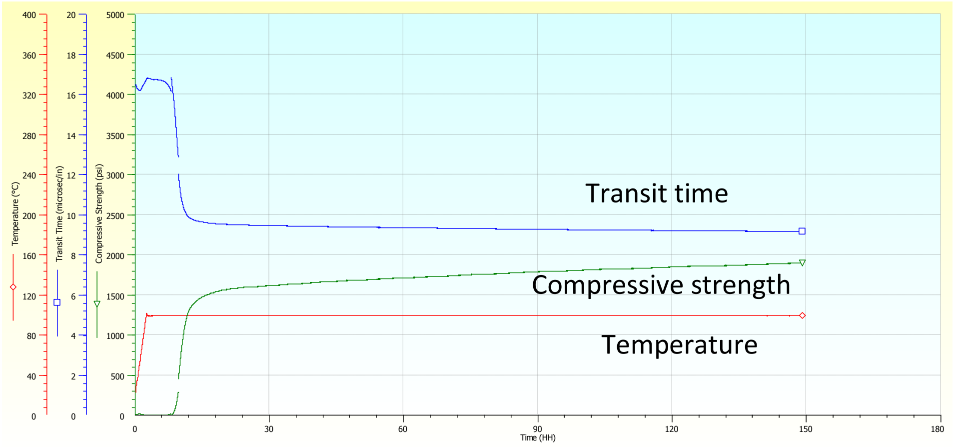

Figure 11 - The compressive strength development of Liquid Stone cured at 100°C.

Fig. 11 Illustrates the compressive strength for LS, which was cured at 100°C. After 21 hours of curing the compressive strength had increased to 1565 psi (10,79MPa). From this point until the experiment was ended after 149 hours, the compressive strength development showed an increasing trend. The compressive strength when the test was ended was 1889 psi (13,02MPa).

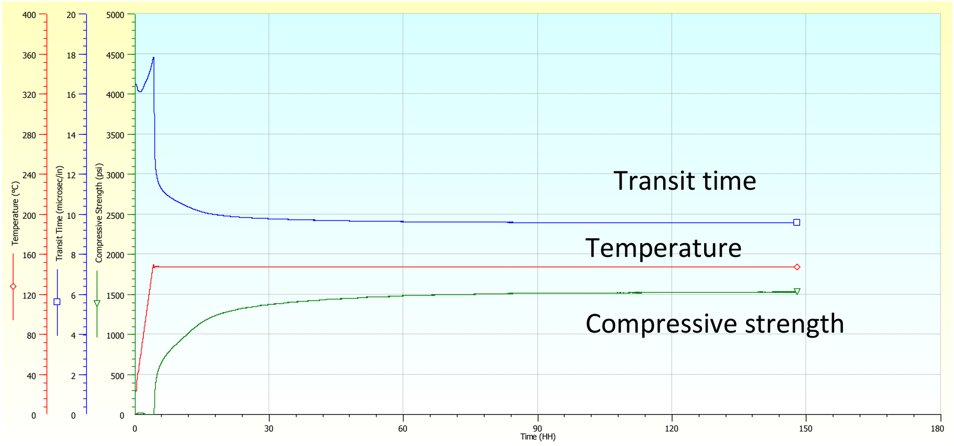

Figure 12 - The compressive strength development of Liquid Stone cured at 150°C.

The result of LS when it was cured at 150°C is shown in Fig. 12. After 30 hours of curing the compressive strength was 1366 psi (9,42MPa). After approximately 90 hours there was no further compressive strength development and the test was ended after 148 hours. The compressive strength at completion was 1522 psi (10,5MPa).

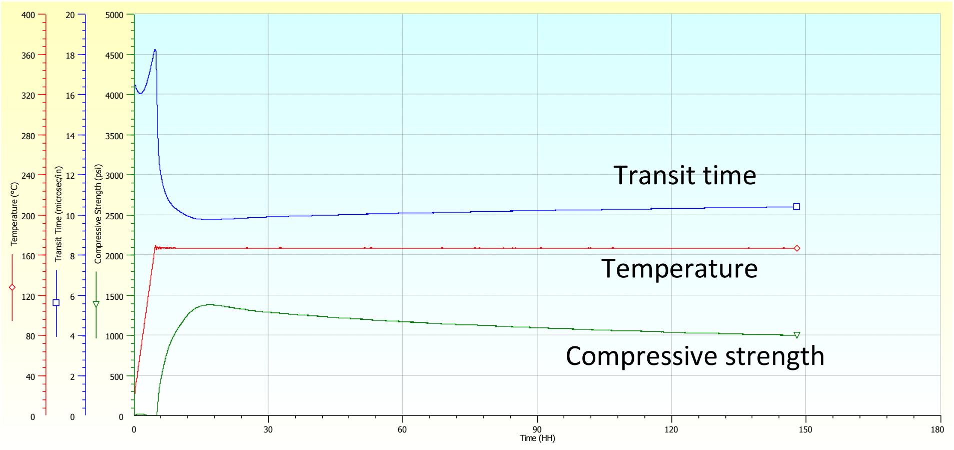

Figure 13 - The compressive strength development of Liquid Stone cured at 170°C.

The strength development of LS cured at 170°C is shown in Fig. 13. The result shows that the compressive strength reaches a maximum at 1380 psi (9,5MPa) after 17 hours of curing. When the maximum level was reached retrogression occurred. After 147 hours of curing the compressive strength was reduced by almost 400 psi (2,8MPa). In this point it seems to go to a constant value regarding to the compressive strength.

6.1.4 Quartz

The final experiments were performed on quartz. The mineral was tested at 100, 150 and 170°C. The composition of the slurry is found in Table. 1.

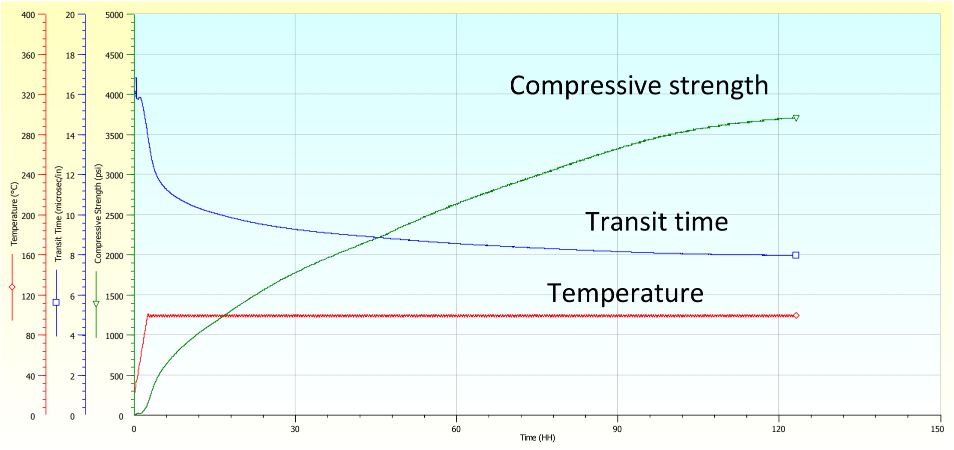

Figure 14 - The compressive strength development of Quartz based cement slurry cured at 100°C.

Fig. 14. Illustrates the compressive strength for Quartz cured at 100°C. When the experiment was ended after 123 hours of curing, the strength development was still increasing, however, at a lower trend curve. At this point the compressive strength was 3699 psi (25,5MPa).

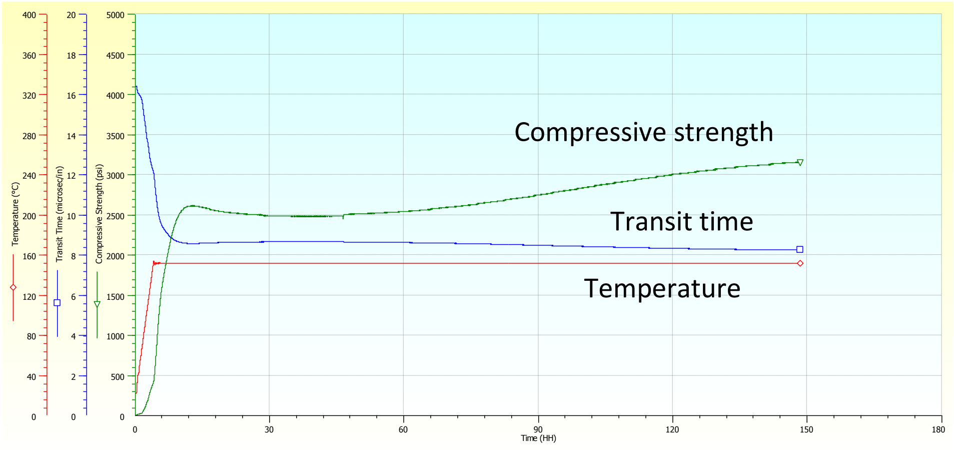

Figure 15 - The compressive strength development of Quartz based cement slurry cured at 150°C.

The strength development of Quartz cured at 150°C is shown in Fig. 15. The compressive strength reaches a maximum at 2608 psi (17,98MPa), after almost 13 hours of curing. This point is followed by retrogression. The compressive strength was reduced to 2483 psi (17,11MPa), after 34 hours of curing. After the minimum level occurred, the compressive strength starts to increase. The strength is still increasing when the experiment was ended after 148 hours of curing. The compressive strength was at this point 3149 psi (21,71MPa).

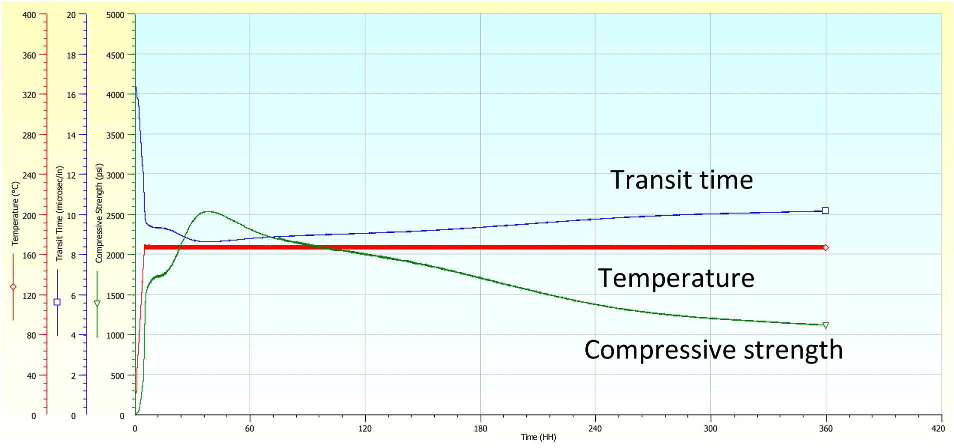

Figure 16 - The compressive strength development of Quartz based cement slurry cured at 170°C.

The compressive strength of the Quartz cured at 170°C is shown in Fig. 16. After 10 hours of curing the compressive strength was 1698 psi (11,71MPa). The compressive strength seems to decline in this point. The figure shows that the compressive strength starts to increase again after further 4 hours of curing. A maximum occurred at 2531 psi (17,45MPa), after 36 hours of curing. The maximum is followed by a decrease in the compressive strength. The experiment was ended when the compressive strength was 1117 psi (7,70MPa), after 360 hours of curing.

6.1.5 Compressive strength of 50 and 500 psi (0,345 and 3,45 MPa)

The oil industry defines 50 psi (0,345MPa) in compressive strength as initial setting of the cement slurries[24]. 5oo psi (3,45MPa) in compressive strength is often used in the oil industry as the strength required for sufficient conductor support [25].

Table 5 - Shows the time needed for the respective strength to reach a compressive strength of 50 and 500 psi (0,345 and 3,45MPa) respectively.

	Temperature	50 psi (0,345MPa)	500 psi (3,45MPa)
Cement	Ambient temperature	7h	14h
	150 °C	2h	3h
Aplite	Ambient temperature	5,5h	27,5h
	65 °C	1,5h	5,5h
	100 °C	1,5h	3,5h
	170 °C	1,5h	3h
Quartz	100 °C	1,5h	4,5h
	150 °C	1,5h	4h
	170 °C	1,5h	4h

It was not found to be comprehensible to include the result of LS in this context. As described earlier, how rapid LS build compressive strength depends on how much activator that is added.

6.2 Shrinkage test

As described earlier, the procedure for curing Aplite and G cement was performed at ambient temperature and normal pressure and the cubes were covered with plastic film during the first 24 hours. Thereafter, the cubes were submerged in water for 7 days, before set under pressure for 5 days. Fig. 24 and 25 shows the samples after setting.

Figure 17 - Result of the shrinking test for Aplite and G cement. More detailed data can be found in Appendix A and B.

The pictures clearly show that shrinkage of the samples of G cement had already taken place while the slurry set. It seems like Aplite is more stable than the G cement since those cubes did not show the same amount of shrinkage as the G cement cubes.

Figure 18 - The picture shows the samples 24 hours after setting and before the cubes were exposed to water.

Volume and weight was measured to investigate for volume change (indicating shrinking, or expansion) of the two products. Both slurries were designed to have a density of 1,90 kg/ltr. The result of the shrinking test for Aplite and G cement is shown in Table 6.

Table 6 - Result of the shrinkage test for Aplite and G cement. More detailed data can be found in Appendix A and B.

	Aplite	Neat Class G Cement
Initial Weight [g]	235,39	236,33
Initial Volume [cm^3]	124,06	119,54
Calculated specific gravity	1,897	1,977
Weight after exposure to water for 7 days [g]	238,34	240,9
Volume after exposure to water for 7 days [cm^3]	124,53	120,35
Calculated specific gravity	1,914	2,002
Weight after 5 days in a pressure vessel [g]	238,32	239,48
Volume after 5 days in a pressure vessel [cm^3]	124,32	120,33
Calculated specific gravity	1,917	1,990

The result shows that the volume for the Aplite and G Cement is increasing, respectively 0,38 and 0,68 %, after the cubes was exposed to water for 7 days. After being in the pressure vessel for 5 days, the result shows that the Aplite and the G Cement has shrunk 0,17 and 0,02 %, by volume respectively. Further it shows that the weight increased with respectively 1,25 % (Aplite) and 2% (G Cement) after exposure to water. A possible reason for the increasing weight is that evaporation occurred when the slurry was setting and prior to the submersion in water. The cubes then absorbed water when they were exposed to water. This led to an increase in weight.

The result shows that the G cement was very unstable after mixing, as the density increased from 1,90 kg/ltr to 1,977 kg/ltr after curing. This can also be seen in Fig.25 by the lower level of cured cement in the cubes with G cement. In the industry this is well known and is normally rectified by using gel, or other material as anti settling agent in cement slurries made from Class G cement. This should not be mixed together with shrinking. If shrinkage occurs, cracks or slippage to the cube sides would be expected. However, cracks were not observed on neither of the samples.

The Aplite slurry was fairly stable as the density after curing was as designed.

As the weights of both materials increased after submersions in water it is not recommended to qualify this procedure to be adequate for the purpose of checking for volume change of cements.

7 Discussion

In this study it has been found that G cement had a magnitude higher compressive strength than Aplite cured under ambient conditions. With an increasing temperature, G cement will achieve a more rapid increase regarding the compressive strength. However, when the temperature is increased to 150 °C, initially a rapid increase occurred followed by a decrease in the compressive strength. After 91 hours of curing the compressive strength starts slightly to increase again.

LS is dependent on an activator to start building compressive strength. How rapid it develops depends on how much activator that is added. The final result should, however, be the same. When the temperature was increased to 170 °C retrogression in the compressive strength occurred, but when the test was stopped it seemed to approach to a constant value regarding to the compressive strength.

It is observed that at a temperature of 100 °C both Quartz and Aplite had an increasing compressive strength. However, when adding Aplite to the G cement there is a more rapid increase in the compressive strength then when adding quartz. When the temperature was increased to 150 °C it was observed retrogression in the compressive strength for Quartz. The reason for this could be retrogression in the G cement and that the quartz was not able to build strength yet. So when the temperature was increased further to 170 °C quartz is first building compressive strength to 2531 psi (17,45MPa). After the maximum point there is a decrease in the compressive strength. Quartz is not able to build an increasing compressive strength again. Even though that the test was monitoring for 360 hours.

When the temperature was increased to 170°C for the Aplite, the compressive strength was significantly lower than the results at lower temperatures. The most likely reason is the mineral tobermorite which is only stable over a temperature range of approximately 80°C to 150°C [26].

8 Conclusion

It has been found that at lower temperature, OPC alone would be sufficient. However, there was not any negative effect observed when Aplite was added. Since the CO_2 emission would be less by adding Aplite this material could be a better alternative. Further it seems like Aplite will have a beneficial effect on the compressive strength of OPC with an increasing temperature.

These experiments have also found that LS could be a useful alternative to OPC in a temperature range of 80 to 170 °C, regarding the compressive strength.

Further it seems like Quarts should not be an alternative at temperatures above 150 °C.

The procedure used in the shrinkage test in this study did not give any sufficient data to make any conclusion on the difference in shrinkage between OPC and Aplite.

9 References

1. Statoil. 2011. *Extra well informed. Newsletter drilling and well.* Research and development results 2010. Published by Statoil in April 2011.
2. Det Norske Veritas (DNV). 2012. *Plug & Abandonment. How to safely secure and leave a well.* Module 7: Presented 29 January 2012.
3. Vignes, B. 2012. *Contribution to well integrity and increased focus on well barriers from a life cycle aspect.* PhD Thesis.
4. Cement industry energy and CO_2 performance. 2009. Getting the numbers right, in: World Business Council for Sustainable Development. The Cement Sustainability Initiative.
5. Gartner, E. 2004. Industrially interesting approaches to "low-CO2" cements, Cement and Concrete Research, 34 (2004) 1489-1498.
6. Bellona. [Online], Available: **http://101-solutions.org/norwegian.html** (accessed 15 April 2012)
7. Petroleum Safety Authority. 2011. *Environmental risk: Temporarily abandoned wells on the Norwegian shelf.* [Online], Available: **http://www.ptil.no/news/environmental-risk-temporarily-abandoned-wells-on-the-norwegian-shelf-article8100-79.html**
8. Totland N. and Carlsen I.M, Sintef Petroleum Research and Vignes B. Petroleum Safety Authority. 2011. *Temporary abandoned wells on the NCS.* [Online], Available: **http://www.ptil.no/getfile.php/Tilsyn%20p%C3%A5%20nettet/vrige/Forlatte%20br%C3%B8nner%20-%20Sintef.pdf**
9. Fjågesund T., Wellbarrier. 2011. *Evaluation of well barriers in temporary abandoned wells.* [Online], Available: **http://www.ptil.no/getfile.php/Tilsyn%20p%C3%A5%20nettet/vrige/Forlatte%20br%C3%B8nner%20-%20Wellbarier.pdf**
10. Petroleum Safety Authority. *The Activities Regulations § 85.*[Online], Available: **http://www.ptil.no/activities/category399.html**
11. NORSOK D-010, Well integrity in drilling and well operations, third edition. 2004. Stavanger: Norwegian Oil Industry Association (OLF)/Federation of Norwegian Manufacturing Industries (TBL).
12. Petroleum Safety Authority. *The Facilities Regulations § 48.*[Online], Available: **http://www.ptil.no/facilities/category400.html**
13. Oil & Gas UK, the Suspension and Abandonment of Wells, issue 3. 2009.
14. API RP 10B, Recommended Practice for Testing Well Cements, first edition. 2005. Washington, DC: API.
15. Nelson, E. B. and Guillot, D. 2006. *Well cementing.* Sugar Land, Texas: Schlumberger.
16. Seehusen, J. 2007. *Superbetong mot CO_2.* Teknisk ukeblad. [Online] Available: http://www.tu.no/bygg/article119349.ece
17. Wikipedia. 2012. *Aplite. (19 February 2012 revision),* [Online] Available: http://en.wikipedia.org/Wikipedia.org/wiki/Aplite (accessed 10 May 2012).
18. Telstø, L. Personal communication. Heli Utvikling.
19. Brandl, A., Cutler, J., Seholm, A., Sansil, M. and Braun, G. 2011. Cementing Solutions for Corrosive Well Environments. Paper SPE 132228 presented at the International Oil and Gas Conference and Exhibition, Beijing, China, 8-10 June 2010
20. Berg, E. Personal communication. Baker Hughes.
21. Nesse, W. D. 2000. *Introduction to Mineralogy*. Oxford, New York.

22. Collet, P. Halliburton Services. Ultrasonic Cement Analyzer, manual no. 458.9728. Duncan, Oklahoma.
23. The Engineering Toolbox. Pressure and boiling points of water. [Online], Available: **http://www.engineeringtoolbox.com/boiling-point-water-d 926.html**
24. Reinås, L., Hodne, H., Turkel, M,A. 2011. Hindered Strength Development in Oil Well Cement due to Low Curing. Paper SPE 149687 presented at the SPE Arctic and Extreme Environments Conference & Exhibition, Moscow, Russia, 18-20 October 2011.
25. Hodne, H. Personal communication. University of Stavanger.
26. Houston, J, R., Maxwell, J, R., Carroll, S, A. 2009. [Online], Available: **http://www.ncbi.nlm.nih.gov/pmc/articles/PMC2649027/**

10 Appendix

10.1 Appendix A (Result of shrinkage test for Aplite based cement slurry)

Aplite 1.9s.g		Initial Weight [g]	Initial Weight in water [g]	Measures [mm] after exposure to water for 7 days_ Average	Weight [g] after exposure to water for 7 days	Weight in water [g] after exposure to water for 7 days	Weight after pressure chamber [g]	Weight in water after pressure chamber [g]	Measures [mm] after pressure chamber_Average
1	A	236,99	124,81	50,045	240,03	125,34	239,89	125,05	50,11
	B	234,82	123,86	49,97	238,18	124,32	238,36	124,22	50,11
2	A	235,42	124,23	50,035	238,04	124,5	238,08	124,27	50,02
	B	234,33	123,35	49,91	237,1	123,95	236,95	123,73	50,24
		235,39	124,06	49,99	238,34	124,53	238,32	124,3175	50,12

10.2 Appendix B (Result of shrinkage test for Neat Class G cement)

Cement Neat Class G 1.9s.g		Initial Weight [g]	Initial Weight in water [g]	Measures [mm] after exposure to water for 7 days_Average	Weight [g] after exposure to water for 7 days	Weight in water [g] after exposure to water for 7 days	Weight after pressure chamber [g]	Weight in water after pressure chamber [g]	Measures [mm] after pressure chamber_Average
1	A	233,26	117,73	50	237,87	118,76	236,19	118,58	50,04
	B	229,23	116,57	50,1	233,36	117,02	232,58	117,29	50,1
2	A	240,23	121,66	50,91	245	122,66	243,69	122,54	50,97
	B	242,58	122,18	50,73	247,36	122,94	245,45	122,89	50,76
		236,33	119,54	50,435	240,90	120,35	239,4775	120,325	50,4675