AN EXPERIMENTAL STUDY ON THE EFFECTS OF DIFFERENT CHLORIDE SOURCES ON THE PROPERTIES OF API CLASS G CEMENT

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AN EXPERIMENTAL STUDY ON THE EFFECTS OF DIFFERENT CHLORIDE SOURCES ON THE PROPERTIES OF API CLASS G CEMENT

submitted by **ÖZGE RAMAZANOĞLU** in partial fulfillment of the requirements for the degree of **Master of Science in Cement Engineering Department, Middle East Technical University** by,

Prof. Dr. Gülbin Dural ÜNVER _____________________
Dean, Graduate School of **Natural and Applied Sciences**

Assoc. Prof. Dr. Sinan Turhan ERDOĞAN _____________________
Head of Department, **Cement Engineering**

Prof. Dr. İsmail Özgür YAMAN _____________________
Supervisor, **Civil Engineering Dept., METU**

Prof. Dr. Serhat Akın _____________________
Co-Supervisor, **Petroleum and Natural Gas Engineering Dept., METU**

Examining Committee Members:

Assoc. Prof. Dr. Sinan. Turhan ERDOĞAN _____________________
Civil Engineering Dept., METU

Prof. Dr. İsmail Özgür YAMAN _____________________
Supervisor, Civil Engineering Dept., METU

Prof. Dr. Serhat Akın _____________________
Petroleum and Natural Gas Engineering Dept., METU

Dr. Reha Özel _____________________
TPAO Research Center

Güray Karakaya, M.S. _____________________
Baker Hughes Incorporated

Date: 28.11.2014

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: Özge Ramazanoğlu

Signature :

ABSTRACT

AN EXPERIMENTAL STUDY ON THE EFFECTS OF DIFFERENT CHLORIDE SOURCES ON THE PROPERTIES OF API CLASS G CEMENT

Ramazanoğlu, Özge
M.S., Department of Cement Engineering
Supervisor: Prof. Dr. İsmail Özgür Yaman
Co-Supervisor: Prof. Dr. Serhat Akın
November 2014, 94 pages

In the petroleum industry, oil well cements are used in the form of slurries during the construction of oil or natural gas wells. Preserving the integrity of the well and the casing, providing zonal isolation are some of the uses of these special cements. Oil well cement slurries used in the petroleum industry are subjected to different exposure conditions than ordinary Portland cement slurries used in the construction industry. Therefore, oil well cements are required to possess different engineering properties than ordinary Portland cements.

During their usage, these cements often interact with various chloride sources either from the water that is being used in the preparation of the slurries, or sometimes intentionally used as an additive to achieve required properties. Therefore, there is a need to identify the effects of chlorides from different sources on the properties of oil well cements.

This study presents an experimental program that investigates the effects of different chloride sources on the properties of slurries prepared by class G cement. In the experimental program, a total of 22 cement slurries containing KCl, $CaCl_2$ and NaCl at various amounts are prepared. A control cement slurry with no salt addition is used as a reference. Cement slurries used in all experiments are prepared with the same water/cement ratio (0.44) as stated for Class G cement in API Specification 10A. The experiments that are carried out according to API Spec 10A for the conditions of medium depth oil wells include free fluid content, thickening time, compressive strength and rheology of cement slurries.

As a result of the experimental program, it was observed that different chloride sources have different effects on cement slurries’ properties. The effect of salt concentration is very clear on thickening time, compressive strength and rheological properties when compared with the free fluid properties. It is seen that, $CaCl_2$ is the most effective accelerator when compared to other chloride sources. However, when used in higher amounts, it negatively affects the flow properties of the slurries. NaCl is also an effective accelerator when used in lower amounts. On the other hand, when used in higher amounts it rather works as a retarder. KCl, on the other hand, works rather as a dispersant to improve the flow properties of the slurries. The optimum amount depends on the cement properties.

Keywords: Well cementing, API Class G cement, chlorides, free fluid, thickening time, rheological properties, compressive strength

ÖZ

FARKLI KLORÜR KAYNAKLARININ API G SINIFI ÇİMENTONUN ÖZELLİKLERİNE ETKİSİ ÜZERİNE DENEYSEL BİR ÇALIŞMA

Ramazanoğlu, Özge
Yüksek Lisans, Çimento Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. İsmail Özgür YAMAN
Ortak Tez Yöneticisi: Prof. Dr. Serhat AKIN
Kasım 2014, 94 sayfa

Petrol sektöründe, petrol ve doğal gaz kuyularının çimentolanması için petrol çimentoları ile hazırlanan çimento karışımları kullanılmaktadır. Bu özel çimento tiplerinin kullanım alanlarından bazıları kuyunun ve koruma borusunun sağlamlığını korumak ve bölgesel yalıtımı sağlamaktır. Yapı sektöründe kullanılan Portland çimentolarından farklı olarak, petrol sektöründe kullanılan çimentolar daha farklı koşullara maruz kalmaktadır. Bu nedenle, petrol çimentolarının Portland çimentolardan farklı özelliklere sahip olması gerekmektedir.

Petrol çimentoları, karışım için kullanılan sulardaki ya da karışım özelliklerini iyileştirmek için eklenen katkılardaki farkı klorür kaynaklarına maruz kalmaktadır. Bu nedenle, farklı klorür kaynaklarının petrol çimentosu özellikleri üzerindeki etkilerini belirlemek gerekmektedir.

Bu çalışma, farklı klorür kaynaklarının, G sınıfı çimento ile hazırlanmış karışımlar üzerine etkisini araştıran deneysel bir program sunmaktadır. Deneylerde farklı oranlarda KCl, $CaCl_2$ ve NaCl kullanılarak toplam 22 çimento karışımı hazırlanmıtır. Referans olarak kullanılmak üzere tuz katkısız bir kontrol numunesi hazırlanmıştır. Deneylerin tamamında kullanılan çimento karışımları, G sınıf çimentonun API Specification 10A' da belirtilen su/çimento oranına (0.44) göre hazırlanmıştır. Hazırlanan çimento karışımlarının, serbest sıvı, basınç dayanımı, koyulaşma zamanı ve akış özellikleri, orta derinlikte bir petrol kuyusu göz gönüne alınarak, API Spec 10A’ da belirtilen koşullara göre incelenmiştir.

Farklı klorür kaynakları, çimento hamurları üzerinde farklı etkiler göstermiştir. Kullanılan tuz miktarlarının etkileri, serbest sıvı özelliğinde belirgin değilken, koyulaşma zamanı, basma dayanımı ve akış özellikleri deneylerinde, daha iyi gözlenmiştir. Diğer tuzlara kıyasla $CaCl_2$ 'nin çimento hamurlarının özellikleri üzerinde daha etkili olduğu ve diğer tuzlarla hazırlanan karışımlardan çok daha az oranlar kullanılarak benzer sonuçlara varılabileceği ve yüksek miktarlarda kullanılmasının akış özelliklerini olumsuz etkilediği görülmüştür. NaCl’ nin düşük miktarlarda kullanıldığında hızlandırıcı, yüksek miktarlarda kullanıldığında ise geciktirici olarak çalıştığı görülmüştür. Akış özelliklerini geliştirme bakımından KCl’ nin etkili olduğu gözlenmiştir. Kullanılan çimento özelliklerinin, optimum tuz oranları üzerinde etkili olduğu gözlenmiştir.

Anahtar kelimeler: Kuyu çimentolama, API G Sınıfı çimento, klorürler, serbest sıvı, koyulaşma zamanı, akış özellikleri, basınç dayanımı

To my future

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NOMENCLATURE

API	American Petroleum Institute
ASTM	American Society for Testing Materials
EN	European Standards
HPHT	High Pressure High Temperature
HSR	High Sulfate Resistance
LOI	Loss on Ignition
IR	Insoluble Residue
MPa	Mega Pascal
MSR	Moderate Sulfate Resistance
PC	Portland Cement
psi	Pounds per Square Inch
PV	Plastic Viscosity
RPM	Rotation per Minute
SEM	Scanning Electron Microscope
TPAO	Turkish Petroleum Corporation
UCA	Ultrasonic Cement Analyzer
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
YP	Yield Point

CHAPTER 1

INTRODUCTION

1.1. General

Well cementing is one of the most important operations performed on a gas, oil and geothermal well. Primary well cementing is the process of placing cement slurry in the annulus between casing (protective pipes) and the formations exposed to the wellbore. The main purpose of primary cementing is to provide zonal isolation in the wellbore of oil and gas wells, e.g., to exclude fluids such as water or gas in one zone to another zone. A hydraulic seal must be obtained between the casing and the cement, and between cement and the formations to gain zonal isolation.

In primary cementing, after drilling the well to the desired depth, the drill pipe is removed and the larger string of casing is pushed into the well. The cement slurry is pumped through inside of the casing to fill the annular column then out into the annular space, as shown Figure 1-1 [1].

When primary cementing is unsuccessful, it is necessary to do a squeeze cementing job. In squeeze cementing, a cement slurry is forced through into porous formations, voids or perforations in the casing or in to the formation from which the water or gas is flowing into the borehole, as shown Figure 1-2 [2]. The aqueous phase of cement slurry enters into the formation, while the solid particles are forced to filter out on the permeable formation surface [3].

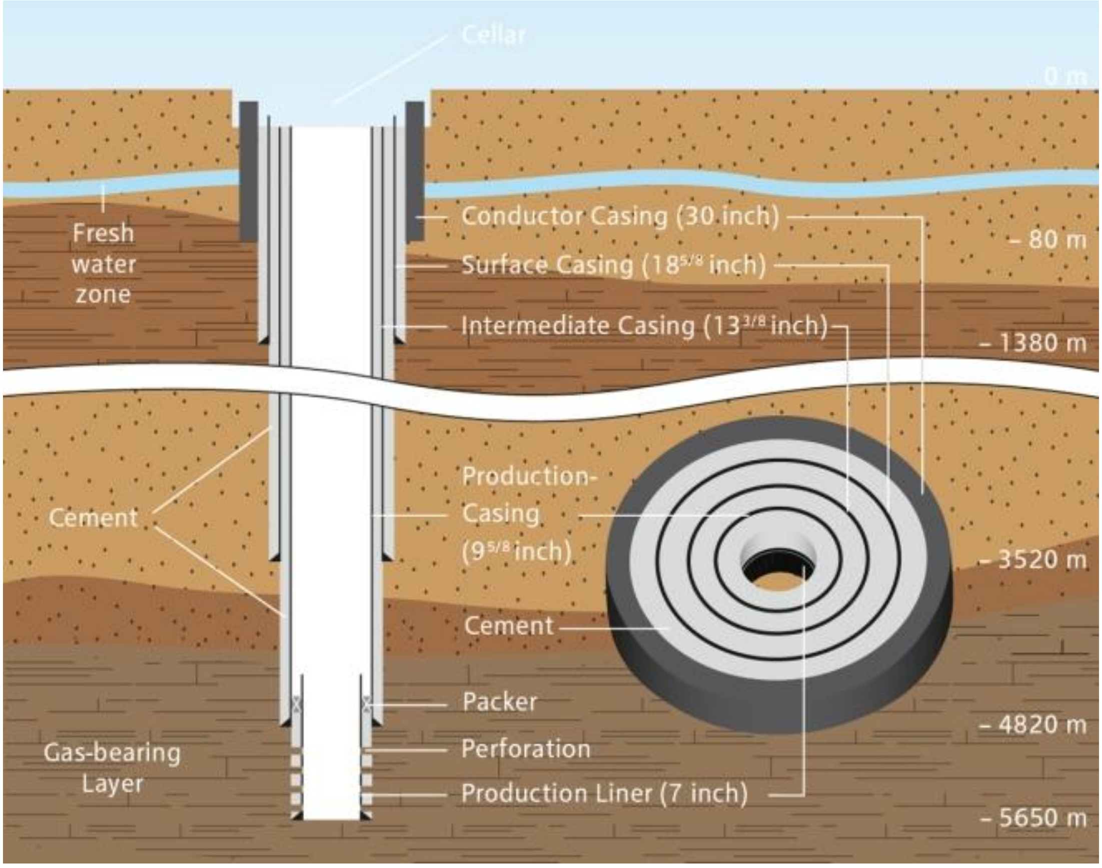


Figure 1-1 Primary cementing [1]

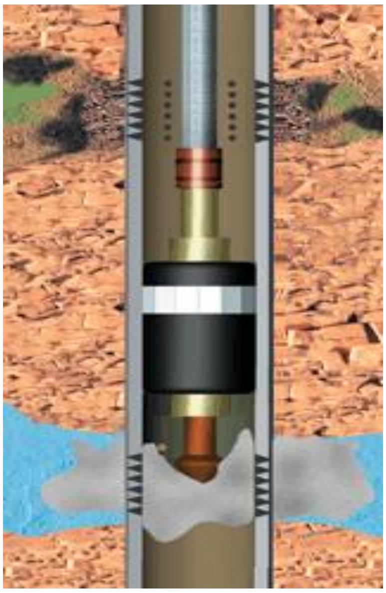


Figure 1-2 Squeeze cementing [2]

In wells, cement slurries are exposed to high temperatures and/or high pressures and sometimes to corrosive formation fluids. Therefore, cement slurries require some special properties.

There are always some problems on cement slurries that are used on primary cementing jobs performed across massive salt and evaporate formations. Unsatisfactory early compressive strength, which causes the collapse of the casing due to well enlargement from the highly plastic formations, poor zonal isolation between cement and formation are some of these problems [4].

Another problem that could be faced in designing the cement slurry is in Arctic regions. The cement slurry in these regions should not freeze before hardening around the casing in frozen formations. To decrease the freezing point under formation temperature, some chloride sources are often added to slurry, with some adverse affects on the setting and hardening characteristics.

Salts that are introduced into the cement slurry from formation dissolution during cementing operation will also affect the physical properties of the cement slurry. After the initial set, salts will continue to dissolve into the unsaturated cement and will result with micro- annulus between cement and salt formation [5].

Beach stated that, salt inhibited the swelling of montmorillonite particles in water-sensitive shales and sands [6]. Slagle and Smith showed after laboratory experiments that with the increasing salt concentrations, cement and formation bond is improving [7].

Moreover, sometimes salts are intentionally or unintentionally added in well cementing operations. Salts have been extensively used in well cementing for several reasons. One of them is the presence of salt in the available mixing water, especially when seawater is used in offshore drilling [8]. In some off-shore locations, it can be so expensive and hard to find suitable mixing water for the cementing operation [9].

It should be clarified that, all chemical additions to cement are called additives in the oil industry. On the contrary to construction industry the term admixture is not used in oil industry [10].

1.2. Objective

Chloride is the most widely used treatment agent in cementing that generally has economic and effective advantages. Sea water slurry is kind of salt water slurry that is used in offshore oil and gas cementing to decrease the cost of cementing operations [11].

The objective of this study is twofold, (i) to investigate the effects of different chloride sources (NaCl, $CaCl_2$, KCl) on the properties of API Class G cement, and (ii) to investigate the effects of NaCl on two different API Class G cements. As a result twenty-two (sixteen plus six) cement slurries were prepared. The same water/cement ratio (0.44) is used while preparing the cement slurries as stated at API Specification 10A for Class G cement [12]. The free fluid, thickening time, compressive strength and rheology of cement slurries are determined according to API Spec 10A for the conditions of medium depth oil wells.

1.3. Scope and Limitations

This thesis consists of five chapters,

Chapter 1 presents the introduction, shortly explaining main view of oil well cementing and gives objective and scope of this thesis.

Chapter 2 presents the literature review, about the oil well cements, special cement types used in oil well cementing, API cement types and their properties, chlorides and their effects on oil well cements.

Chapter 3 presents the experimental study, shortly describing the test materials and the procedures of the experiments.

Chapter 4 presents the results and discussion, concisely gives the test results and discussion of the results.

Chapter 5 presents the main conclusion and gives the recommendations for future researchers.

In this study:

- No other additive except salt was used**.**
- Only three different chloride sources were used,
- Contrary to the literature, $CaCl_2$ was used by weight of water to compare its effects with the others,
- The effects of chlorides on the microstructural properties of the cement slurries are not discussed.

CHAPTER 2

LITERATURE REVIEW

2.1. Oil Well Cement

In the exploration and production of oil and gas wells, there are various applications of well cementing. The main purpose and the types of well cementing are emphasized earlier in Chapter 1.

The temperature rises with the increasing borehole depth. Even this increasing temperature, the cement slurry has to be fluid to finish the cementing operation. In addition to high temperature, cement slurry is exposed to both hydrostatic pressure of drilling mud and/or cement slurry in the hole and the pumping pressure of cement slurry [10].

Because of the above- mentioned environmental and physical exposure regimes, oil well cement specifications are different than the Portland Cement types used in construction industry. According to the well conditions, American Petroleum Industry (API) determines the specifications for cement types. Besides the cements listed in API, there are also other cement types that are used in well cementing. In this section, there cement types will be briefly described.

2.1.1. API Cement Types

There are eight types of API Portland cements which are given from A to H. Depth of wells and sulfate resistance degrees are the main criteria for classification of API cements. These eight types of oil well cements illustrate the chemical and physical requirements that fulfill the most of the well conditions. Extremely hot and cold well conditions are excluded from API specifications. There are general descriptions for API class cements and their ASTM equivalent as below;

- Class A is intended for use from surface to 1830 m depth, when special properties are not required. Available only in ordinary (O) type (similar to ASTM C150, Type I cement).

- Class B is intended for use from surface to 1830 m depth, when conditions require moderate to high sulfate resistance. Available both moderate (MSR), and high sulfate-resistant (HSR) types (similar to ASTM C 150, Type II cement).

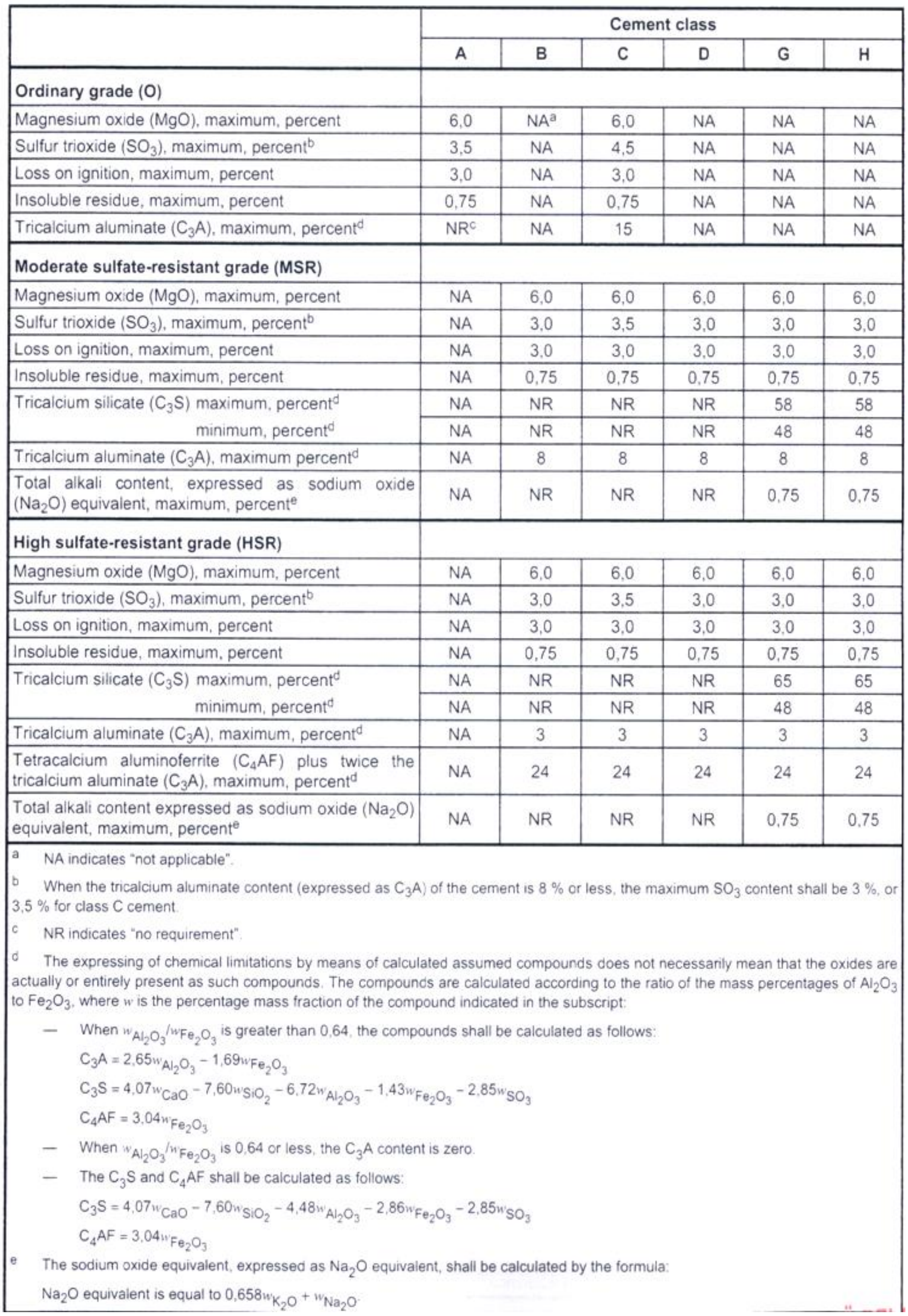
- Class C is intended for use from surface to 1830 m depth, when conditions require high early strength. Available in ordinary (O) and moderate (MSR) and high sulfate-resistant (HSR) types (similar to ASTM C 150, Type III cement).
- Classes D, E and F are intended for use in deeper wells, and also known as "retarded cements". C_3S and C_3A (faster-hydrating phases) amounts are reduced and particle size of cement grains are increased due to retard hydration. These classes are intended for use from surface to 1,830 m to 4880 m depth, under conditions of moderately high temperatures and pressures and available in both moderate (MSR) and high sulfate-resistant (HSR) types.

- Classes G and H are intended for use as basic well cement from surface to 2,440 m depth as manufactured, or can be used with accelerators and retarders to cover a wide range of well depths and temperatures. No additions other than calcium sulfate or water, or both, shall be interground or blended with the clinker during manufacture of Class G and Class H cement. They are available in both moderate (MSR) and high sulfate-resistant (HSR) types.

The chemical compositions of Classes G and Class H types are similar; their principal difference is the specific surface area of the cement. Class G is finer than Class H, and so has more water requirement than the Class H.

API made restrictions on cement types to fulfill the requirements of cement slurries according to the considerable depths. These depths are based on the conditions imposed by the casing-cement specification tests, and should be considered as approximate values. The chemical requirements, physical requirements of API cement types are listed in Table 2-1 and Table 2-2.

Table 2-1 Chemical requirements of API cement types [12]



	Cement class					
	A	B	C	D	G	H
Ordinary grade (O)						
Magnesium oxide (MgO), maximum, percent	6,0	NA[a]	6,0	NA	NA	NA
Sulfur trioxide (SO_3), maximum, percent[b]	3,5	NA	4,5	NA	NA	NA
Loss on ignition, maximum, percent	3,0	NA	3,0	NA	NA	NA
Insoluble residue, maximum, percent	0,75	NA	0,75	NA	NA	NA
Tricalcium aluminate (C_3A), maximum, percent[d]	NR[c]	NA	15	NA	NA	NA
Moderate sulfate-resistant grade (MSR)						
Magnesium oxide (MgO), maximum, percent	NA	6,0	6,0	6,0	6,0	6,0
Sulfur trioxide (SO_3), maximum, percent[b]	NA	3,0	3,5	3,0	3,0	3,0
Loss on ignition, maximum, percent	NA	3,0	3,0	3,0	3,0	3,0
Insoluble residue, maximum, percent	NA	0,75	0,75	0,75	0,75	0,75
Tricalcium silicate (C_3S) maximum, percent[d]	NA	NR	NR	NR	58	58
minimum, percent[d]	NA	NR	NR	NR	48	48
Tricalcium aluminate (C_3A), maximum percent[d]	NA	8	8	8	8	8
Total alkali content, expressed as sodium oxide (Na_2O) equivalent, maximum, percent[e]	NA	NR	NR	NR	0,75	0,75
High sulfate-resistant grade (HSR)						
Magnesium oxide (MgO), maximum, percent	NA	6,0	6,0	6,0	6,0	6,0
Sulfur trioxide (SO_3), maximum, percent[b]	NA	3,0	3,5	3,0	3,0	3,0
Loss on ignition, maximum, percent	NA	3,0	3,0	3,0	3,0	3,0
Insoluble residue, maximum, percent	NA	0,75	0,75	0,75	0,75	0,75
Tricalcium silicate (C_3S) maximum, percent[d]	NA	NR	NR	NR	65	65
minimum, percent[d]	NA	NR	NR	NR	48	48
Tricalcium aluminate (C_3A), maximum, percent[d]	NA	3	3	3	3	3
Tetracalcium aluminoferrite (C_4AF) plus twice the tricalcium aluminate (C_3A), maximum, percent[d]	NA	24	24	24	24	24
Total alkali content expressed as sodium oxide (Na_2O) equivalent, maximum, percent[e]	NA	NR	NR	NR	0,75	0,75

[a] NA indicates "not applicable".

[b] When the tricalcium aluminate content (expressed as C_3A) of the cement is 8 % or less, the maximum SO_3 content shall be 3 %, or 3,5 % for class C cement.

[c] NR indicates "no requirement".

[d] The expressing of chemical limitations by means of calculated assumed compounds does not necessarily mean that the oxides are actually or entirely present as such compounds. The compounds are calculated according to the ratio of the mass percentages of Al_2O_3 to Fe_2O_3, where w is the percentage mass fraction of the compound indicated in the subscript:

- When $w_{Al_2O_3}/w_{Fe_2O_3}$ is greater than 0,64, the compounds shall be calculated as follows:

$$C_3A = 2{,}65w_{Al_2O_3} - 1{,}69w_{Fe_2O_3}$$

$$C_3S = 4{,}07w_{CaO} - 7{,}60w_{SiO_2} - 6{,}72w_{Al_2O_3} - 1{,}43w_{Fe_2O_3} - 2{,}85w_{SO_3}$$

$$C_4AF = 3{,}04w_{Fe_2O_3}$$

- When $w_{Al_2O_3}/w_{Fe_2O_3}$ is 0,64 or less, the C_3A content is zero.
- The C_3S and C_4AF shall be calculated as follows:

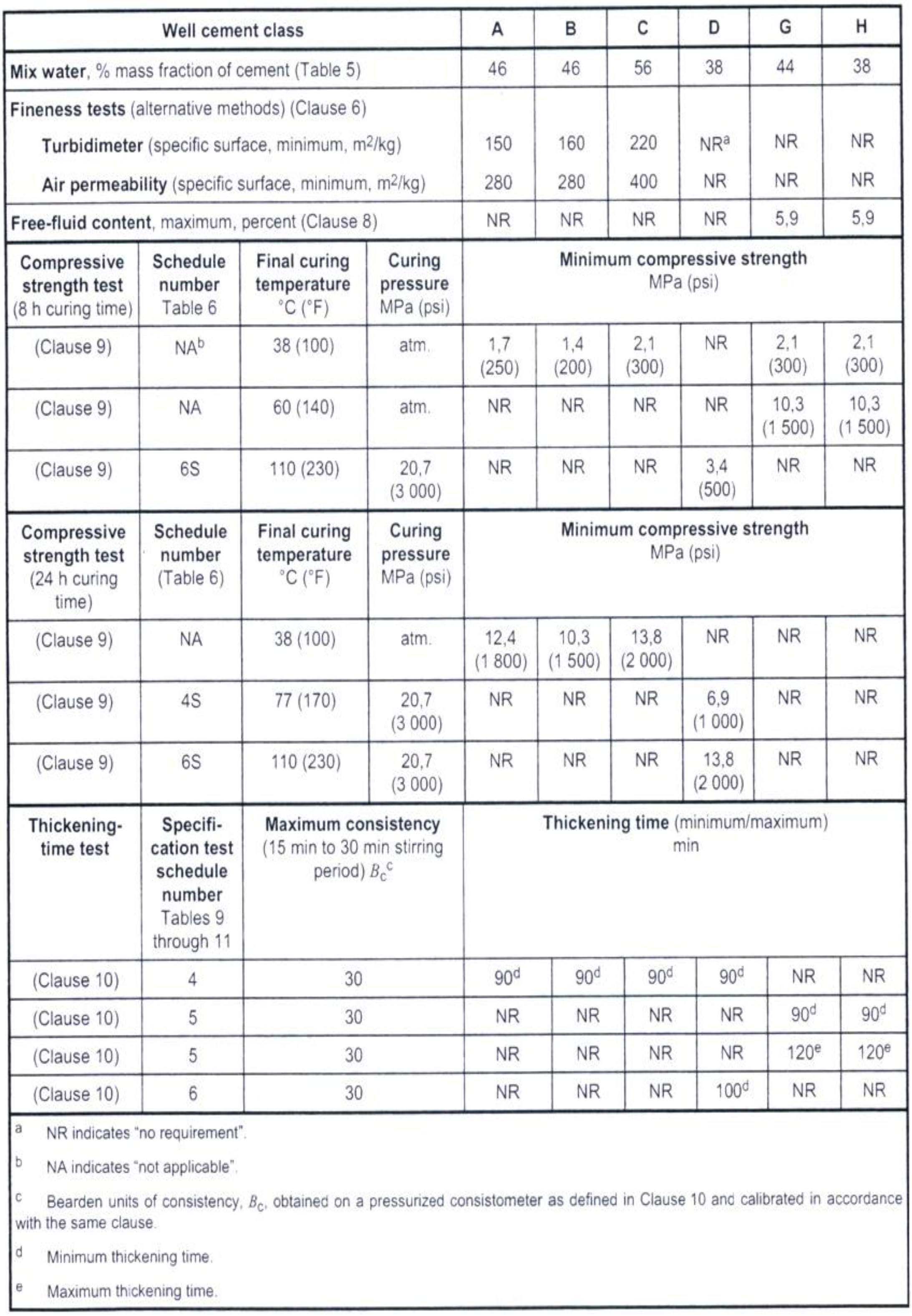
$$C_3S = 4{,}07w_{CaO} - 7{,}60w_{SiO_2} - 4{,}48w_{Al_2O_3} - 2{,}86w_{Fe_2O_3} - 2{,}85w_{SO_3}$$

$$C_4AF = 3{,}04w_{Fe_2O_3}$$

[e] The sodium oxide equivalent, expressed as Na_2O equivalent, shall be calculated by the formula:

Na_2O equivalent is equal to $0{,}658w_{K_2O} + w_{Na_2O}$.

Table 2-2 Physical requirements of API cement types [12]



Well cement class	A	B	C	D	G	H
Mix water, % mass fraction of cement (Table 5)	46	46	56	38	44	38
Fineness tests (alternative methods) (Clause 6)						
Turbidimeter (specific surface, minimum, m^2/kg)	150	160	220	NR[a]	NR	NR
Air permeability (specific surface, minimum, m^2/kg)	280	280	400	NR	NR	NR
Free-fluid content, maximum, percent (Clause 8)	NR	NR	NR	NR	5,9	5,9

Compressive strength test (8 h curing time)	**Schedule number** Table 6	**Final curing temperature** °C (°F)	**Curing pressure** MPa (psi)	**Minimum compressive strength** MPa (psi)					
(Clause 9)	NA[b]	38 (100)	atm.	1,7 (250)	1,4 (200)	2,1 (300)	NR	2,1 (300)	2,1 (300)
(Clause 9)	NA	60 (140)	atm.	NR	NR	NR	NR	10,3 (1 500)	10,3 (1 500)
(Clause 9)	6S	110 (230)	20,7 (3 000)	NR	NR	NR	3,4 (500)	NR	NR

Compressive strength test (24 h curing time)	**Schedule number** (Table 6)	**Final curing temperature** °C (°F)	**Curing pressure** MPa (psi)	**Minimum compressive strength** MPa (psi)					
(Clause 9)	NA	38 (100)	atm.	12,4 (1 800)	10,3 (1 500)	13,8 (2 000)	NR	NR	NR
(Clause 9)	4S	77 (170)	20,7 (3 000)	NR	NR	NR	6,9 (1 000)	NR	NR
(Clause 9)	6S	110 (230)	20,7 (3 000)	NR	NR	NR	13,8 (2 000)	NR	NR

Thickening-time test	**Specification test schedule number** Tables 9 through 11	**Maximum consistency** (15 min to 30 min stirring period) B_c[c]	**Thickening time** (minimum/maximum) min					
(Clause 10)	4	30	90[d]	90[d]	90[d]	90[d]	NR	NR
(Clause 10)	5	30	NR	NR	NR	NR	90[d]	90[d]
(Clause 10)	5	30	NR	NR	NR	NR	120[e]	120[e]
(Clause 10)	6	30	NR	NR	NR	100[d]	NR	NR

[a] NR indicates "no requirement".

[b] NA indicates "not applicable".

[c] Bearden units of consistency, B_c, obtained on a pressurized consistometer as defined in Clause 10 and calibrated in accordance with the same clause.

[d] Minimum thickening time.

[e] Maximum thickening time.

2.1.2. Thixotropic Cements

The term “thixotropy” is used for a system that is fluid under shear, but it develops a gel structure when at rest [13]. Thixotropic cement slurries are thin and fluid while mixing, pumping and displacement, but dramatically form a rigid gel structure when mixing or pumping stops as shown in Figure 2-1[8].

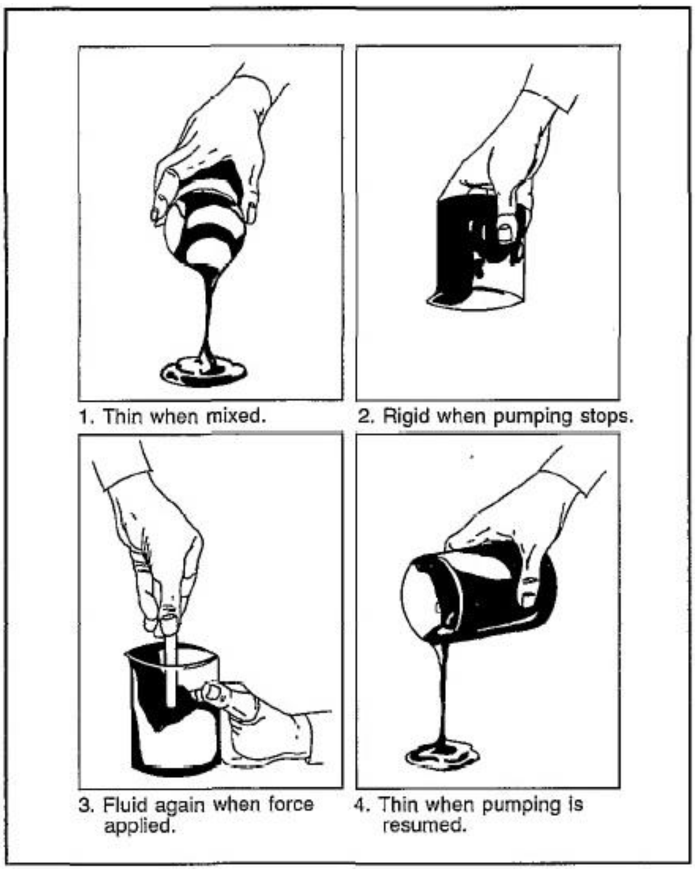


Figure 2-1 Thixotropic Behavior [8]

Thixotropic cement systems are used in wells when excessive fallback of the cement column is a common event [14]. Some wells fracture even under low hydrostatic pressure because of weak zones. Thixotropic cements prevent the fallback by reducing the hydrostatic pressure when gel strength increases [8].

Other important application of thixotropic cements is the treatment of lost circulation while drilling. A gel structure begins to arise after slurry enters the loss circulation zone. With the increasing flow resistance, zone becomes plugged and after cement sets, zone is effectively consolidated [8].

2.1.3. Foamed Cement

Foamed cement is generally used to solve cementing problems which are caused by fractured, highly permeable, vuggy or cavernous formations. Some formations are able to support the hydrostatic pressure from only very light fluids and some of them will not even support a column of water. Ultra low- density cements have been developed to solve this cementing problem [8].

Foamed cement has a low density with a relatively high compressive strength with these characteristic will give less damage to water-sensitive formations [15].

Increasing well productivity by decreasing cement loss to potential production zone because of its lower density is another advantage of foamed cement [16].

2.1.4. Thermal Cements

At elevated temperatures and pressures, the physical and chemical behavior of well cements change drastically. In thermal wells, formations with corrosive water and weak formations are common. Cement slurry design should be done carefully for these wells, otherwise it will result in strength loss, increased permeability and potentially loss of zonal isolation [8].

The deep oil and gas wells, geothermal wells and thermal recovery wells are three main well types of thermal cementing. Portland cement, Class J cement, silica-lime systems, and high-alumina cement are generally used in thermal cementing [8].

2.1.5. Latex- Modified Cement System

Latex is a common term that expresses an emulsion polymer. It is generally supplied as a milky suspension of very tiny polymer particles, often stabilized by surfactants to increase freeze/thaw resistance and inhibit coagulation when added to Portland cement [8].

In 1920s, natural rubber latex wad added to mortars and concretes. After that, latex-modified concretes have become common place because of its advantages. Better workability, decreased permeability, increased tensile strength, reduced shrinkage, increased elasticity and improved bonding between cement-casing and cement-formation are some of these advantages [17].

Rollins and Davidson stated that, latex improved the cement performance when it was added to the cement mix water [18]. Better bond to oil-wet and water-wet surfaces, improved resistance to contamination of formation fluids, lowered fluid-loss rate and increased durability are some benefits of latex in oil well cement.

Latex was identified as a suitable material for well cements and the preferred concentration of latex varied from 2.5% to 25% BWOC [19]. This system has been applied for many years but, application temperature is limited at under 50 ^{o}C (122 ^{o}F) [8].

2.2. Chlorides and Oil Well Cement

Cement systems which contain significant quantities of chloride are commonly called "salt cements" [8]. Salts have been extensively used in well cementing for several reasons. One of them is the presence of salt in the available mixing water, especially when seawater is used in offshore drilling [8]. In some off-shore locations, it can be so expensive and hard to find suitable mixing water for the cementing operation [9].

The usage of sea water for preparing cement slurries for down-hole cementing applications has improved considerably with the increase offshore drilling. Casing, liner and squeeze cementing operations have been made by salt cements that are prepared by sea water as mix water. Easy accessibility, lower costs because of eliminated transportation of mixing water, and decreased storage for fresh-water on offshore platforms are the remarkable advantages of using sea water on offshore cementing operations [20].

Also, when placing cements across massive formations or water-sensitive zones, addition of salts has proven to be effective [8]. Jones stated in 1964, that there is a tendency to stop clay blocking if salt concentration in water is increased [21]. Moreover, Hewitt stated that, if the salinity of the surrounding fluid reduces, the swelling of each clay usually increases. He also concluded, *"Therefore, a concentrated brine would cause the least damage; fresh water would cause the most"* [22]. In 1951, Ludwig stated that sodium chloride is added to the mixing water to decrease the action of cement slurry and formation salt where the well extends through a salt dome [9].

Lewis et. al., stated that, if the filtrated waters' salt concentrations are equal or exceeds the formation waters salt concentrations, there is no hydration between salt cement filtrate and water-sensitive formations, such as, montmorillonite, illite of chlorite. Salt cements do not allow poor bonding and channeling caused by swelling, or flowing of softened clay formations between the cement and formation [23].

After some laboratory tests, Cunningham et. al., stated that, samples that contain salt water had better bonding to a water-sensitive formation (Miocene) and no softening of the shale has occurred. On the other hand, samples that prepared are with fresh water tended to soften the shale. They also concluded that, the pH, ion content and the solubilities of calcium hydroxide and calcium sulfate are influenced by adding salt to cement slurries. The restriction of swelling and migration of water-sensitive clays and decreasing of the fracture of non-swelling shales are some of these influences [24].

Furthermore, salts are common and cheaper than other chemical additives that can modify the behavior of the cement system [8]. Using salt on oil well cementing improves flow properties, increases slurry weight and supplies better bonding between casing and swelling clays. Salt is also a good dispersant agent, compatible with other additives and it can be used as both accelerator and retarder [7]. Cunningham et al. also stated that, improving flow properties, being a fine dispersing agent, good compatibility with most other additives, acting like both an accelerator and a retarder with different concentrations, and increasing the slurry weight are some beneficial properties of using salt for oil well cementing [24].

In this section, the effects of various chloride sources on the properties of cements will be discussed.

2.2.1. Sodium Chloride (NaCl)

Sodium chloride is known as rock salt. It is readily soluble in water and it has a characteristic sharp taste [25]. Sodium chloride is an ionic compound made up of equal numbers of positively charged sodium and negatively charged chloride ions [26].

Sodium chloride has been used in oil well cementing more than decades. Salt is usually added to the mixing water before mixing with cement [7].

It is stated by Lea et. al. that, in cold weather, NaCl is added to Portland cement to decrease the setting time. Furthermore, they stated that NaCl is less effective than

$CaCl_2$ on the setting development of cement, and its effect is erratic [27]. Sodium chloride has two opposite effects on the setting properties of cement. It acts like an accelerator on low concentrations and like a retarder on high concentrations [6, 7, 9].

Test results conducted by Ludwig showed that, compressive strength is increased with increasing salt content of the mixing water and then decreased as the salt concentration increased [9]. It is also stated by Mattus et. al., that NaCl has an erratic effect on concrete; it causes set acceleration in some cements and retarding effects in others [28].

Abalaka et. al., stated in 2011 that, at early ages, NaCl has accelerating effects on compressive strength of concrete but it cannot be continued long term. There is a loss on compressive strength of concrete on long term because of saline solutions [29].

2.2.2. Potassium Chloride (KCl)

Hunter et al., recommended the use of KCl as an alternative to NaCl, in concentrations of 3% to 5% by weight of water. They also stated that, it is much easier to control the slurry properties with low KCl content than high NaCl content slurry. The 5% bwow KCl slurry is considered to supply some protection against formation of salt dissolution into the slurry [30].

According to Sweatman et al., cement slurry containing 3% KCl demonstrated properties such as thickening time, fluid loss, rheology, compressive strength superior to NaCl cement slurries with a lower cost [31].

Miranda et al., however stated that, there is an erratic behavior on the free fluid properties of cement slurries that contain KCl as shown Figure 2-2. The experimental studies also showed that, compressive strength increases with increasing KCl concentration up to7% bwow. However, compressive strength decreases, if KCl content increases from 7% to 20% bwow [32].

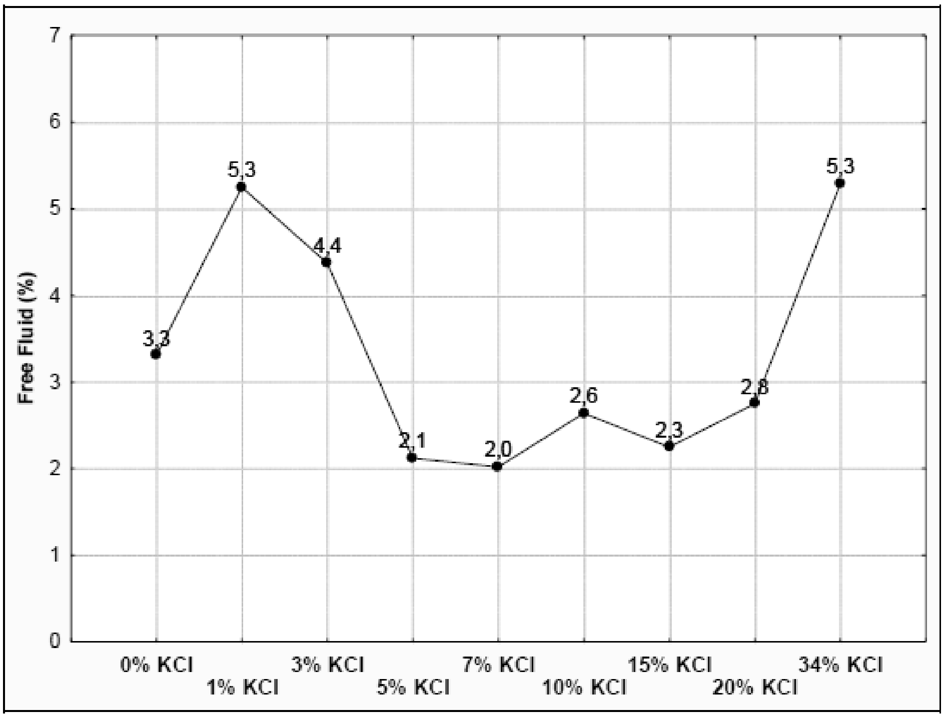


Figure 2-2 Free Fluid versus % KCl bwow, [32]

According to Cheng et. al., adding KCl to cement slurry increases the compressive strength up to 8%, and after 24% KCl cement paste structure is destroyed with compressive strength reductions as shown in Figure 2-3 [33].

Some experimental studies conducted by Venkateswara et. al., also showed an increase in compressive strength of the OPC concrete prepared with KCl at both 28 and 90 day ageing periods [34].

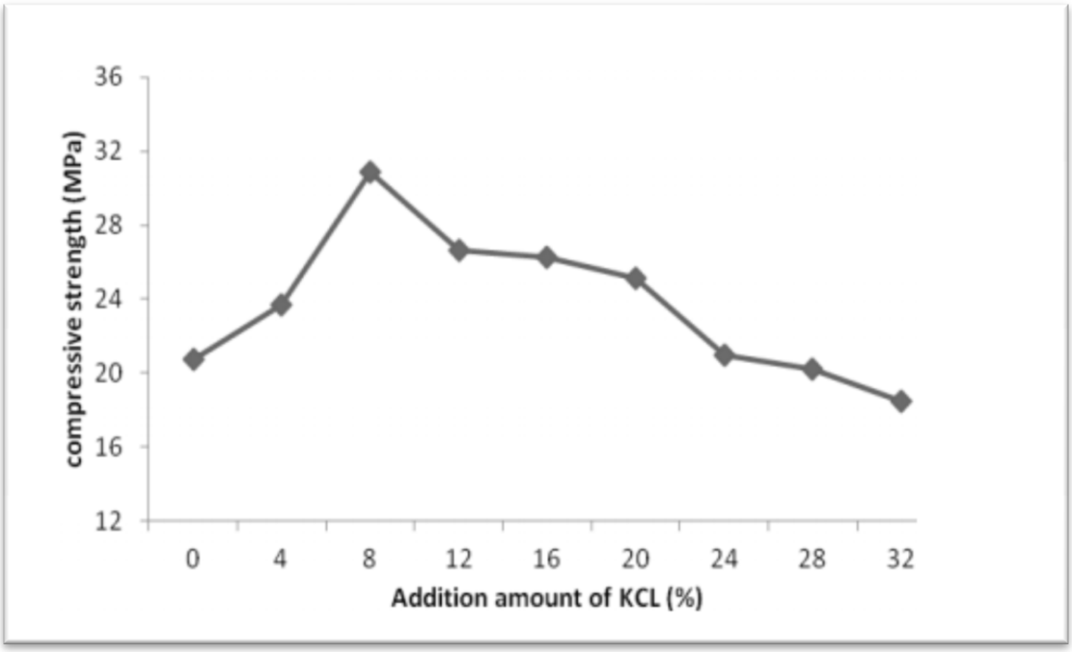


Figure 2-3 Compressive Strength versus % KCl bwow, [33]

Miranda et. al. stated that, KCl has an accelerating effect on the hydration of cement like NaCl at low concentrations and retarding effect at high concentrations. They also stated that retardation effects of high KCl content is less emphasized than the high NaCl content [32].

2.2.3. Calcium Chloride ($CaCl_2$)

Calcium chloride is undoubtedly the most efficient, readily available and the most economic of all accelerators [35]. The associated mechanisms of $CaCl_2$ on cementitious systems are complex, and still not completely understood [8, 36, 37].

In addition to acceleration of the initial set, there are several other effects of calcium chloride. The presence of $CaCl_2$ increases the rate of heat generation during the first hours after slurry mixing [8]. According to Ramachandran and Kishar et. al., $CaCl_2$ accelerates both setting and hardening of Portland cement concrete. They also stated that the hydration of system C_3A-$CaCl_2$-$CaSO_4.2H_2O$ shows that the $CaCl_2$

primarily accelerates the reaction between C_3A and gypsum. Sulfate reacts first followed by reaction of C_3A and chloride after the gypsum has been used up. $CaCl_2$ appears to stabilize the formation of trisulfoaluminate hydrate (ettiringite). After all $CaSO_4$ is consumed, conversion of trisulfoaluminate to monosulfoaluminate occurs [35, 36]. By contrast, it is concluded that, accelerators do not promote the hydration of C_3A, but mainly accelerate the hydration of C_3S [8].

Juenger et. al., stated that $CaCl_2$ accelerates the formation of "inner product" calcium silicate hydrate (C-S-H) with a low-density microstructure. The addition of $CaCl_2$ increases the pH of the Portland cement in the early period and at 24 hours [38]. Bortoluzzi et. al., stated that the addition of $CaCl_2$ reduces the setting time while the pH of cement increases in the initial period [39].

According to Torkittikul and Chaipanich, the hydration rate of Portland cement and the early strength of the cement pastes increases by adding $CaCl_2$. The compressive strength of neat cement paste is lower than all cement pastes that containing $CaCl_2$ [40].

Kishar et. al., stated after some X-ray diffraction analysis that the degree of hydration of $CaCl_2$ containing samples is higher than that of samples without $CaCl_2$. According to them, this result confirms the acceleration effect of $CaCl_2$ [35].

CHAPTER 3

EXPERIMENTAL STUDY

3.1. Materials

3.1.1. API Class G Cement

Class G cement is the most widely used type among API cements in various well conditions. It consists of mainly clinker with small amounts of gypsum. According to API, manufacturers are prohibited to use chemical admixtures, such as glycols or acetates to aid grinding. The clinker of this type of cement is coarsely ground to benefit from durability, lower porosity, and increased pumpability, superior resistance against chemical attacks, low hydration rate and decreased setting time in well conditions. It is available in moderate sulfate resistant (MSR) and high sulfate resistant (HSR) grades.

Two different API Class G cements were supplied by Bolu Cement plant and, the requirements for Class G cement with HSR grade and the properties of the cements used in the experiments are presented in Table 3-1. The cement labelled as “G1” represents the main cement that was used with all chloride sources. On the other hand the cement labelled “G2” represents the cement that was used to assess the effects of cement type with NaCl addition.

As seen in Table 3.1, the cements used in this study conform to the API Class G cement specifications. They both have a relatively high C_3S content and a low C_2S content. The G2 cement seems to be finer as can be observed from the Blaine fineness measurements.

Table 3-1 Properties of the cements used

Materials			
Chemical Analysis (%)	**G1**	**G2**	**API Limits (%)**
CaO	63.52	62.34	-
SiO_2	19.75	19.27	-
Al_2O_3	4.12	4.43	-
Fe_2O_3	5.69	6.15	-
MgO	1.74	2.76	Max. 6.00
SO_3	2.64	2.87	Max. 3.00
Na_2O	0.14	0.11	-
K_2O	0.45	0.47	-
Cl-	0.0079	0.011	-
LOI	1.87	1.32	Max. 3.00
Free CaO	0.56	0.56	-
IR	0.56	0.70	Max. 0.75
Total alkali cont. (Na_2O equivalent)	0.43	0.42	Max. 0.75
Compound Composition (%)	**API Class G Cement Clinker**		
C_3S	60.88	56.24	48-65
C_2S	10.69	12.82	-
C_3A	1.28	1.33	Max. 3.00
C_4AF	17.32	18.71	Max. 3.00
$2C_3A+C_4AF$	19.89	21.37	Max. 24
Physical Properties	**G1 Class G**	**G2**	**API Limits**
Specific Gravity	3.19	3.19	-
Thickening time, min	116	113	90
Max. consistency between 15-30 minute, Bc	12	18	30
Free Fluid, %	5.7	5.62	5.9
Specific Surface, cm^2/g	2843	2969	NR
Residue on 45 m sieve,%	21.1	14.8	-
Compressive Strength 8 hours curing at atm. pressure, 38 °C), MPa	3.7	3.0	Min. 2.1
Compressive Strength 8 hours curing at atm. pressure, 60 °C), MPa	10.9	10.4	Min. 10.3

NR: No Requirement

3.1.2. Chloride Sources

Chloride sources are supplied from TPAO Batman District, Well Completion Department. The chemical properties of sodium chloride, potassium chloride and calcium chloride are determined and the main elements are summarized as shown in Table 3-2. As seen in that table, the purity of the chloride sources are different for each source, with $CaCl_2$ having a rather low purity when compared to the others.

Table 3-2 XRF results of chloride sources

	% Elementary Concentration of Chloride Sources					
	NaCl		**KCl**		**$CaCl_2$**	
	Na	Cl	K	Cl	Ca	Cl
#1	64.90	36.09	47.36	54.98	28.15	41.34
#2	60.00	40.94	46.89	55.33	30.65	43.39
Mean	**62.45**	**38.52**	**47.13**	**55.16**	**29.40**	**42.37**

The salt specimens are analyzed with both SEM and XRD. The crystal structure of NaCl and KCl can be clearly seen in Figure 3-2 and Figure 3-4. Also, Figure 3-6 shows the $CaCl_2$ structure.

3.1.2.1. NaCl

NaCl salt has one peak on the XRD result as shown in Figure 3-1 and the SEM result in Figure 3-2. The result refers to halite mineral and it is the natural form of salt. It is commonly known as salt rock and it is the mineral form of NaCl.

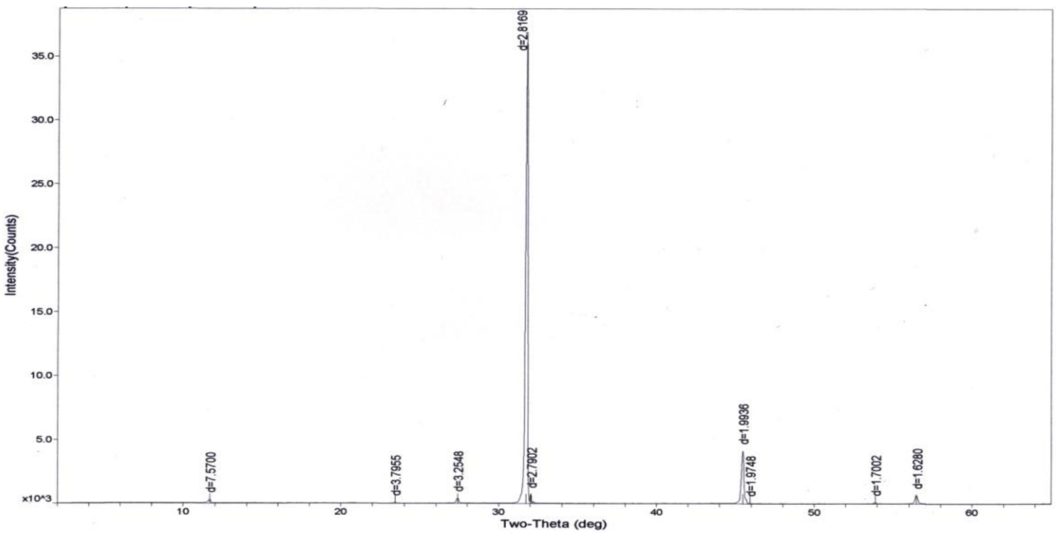


Figure 3-1 XRD analysis for NaCl

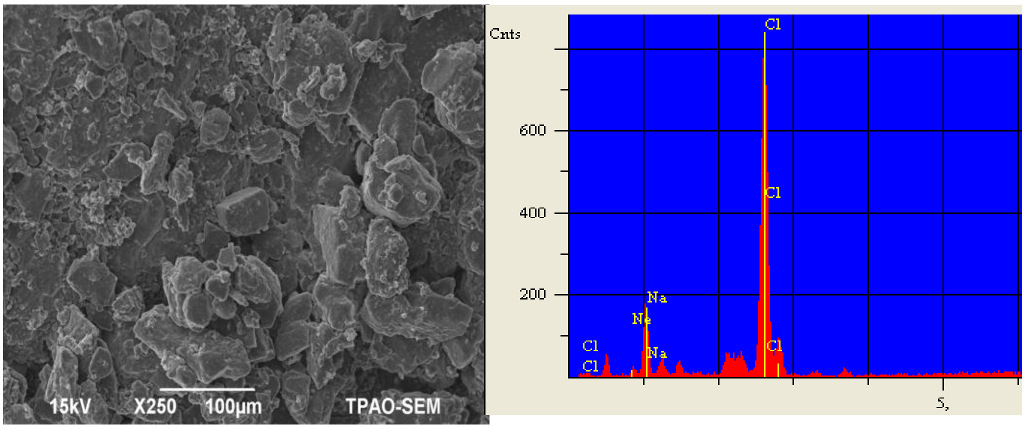


Figure 3-2 SEM micrograph of NaCl

3.1.2.2. KCl

In Figure 3-3, there is a peak that refers to sylvite mineral and Figure 3-4 shows the SEM analysis result. Sylvite is potassium chloride (KCl) in natural mineral form. It forms crystals in the isometric system very similar to normal rock salt, halite (NaCl).

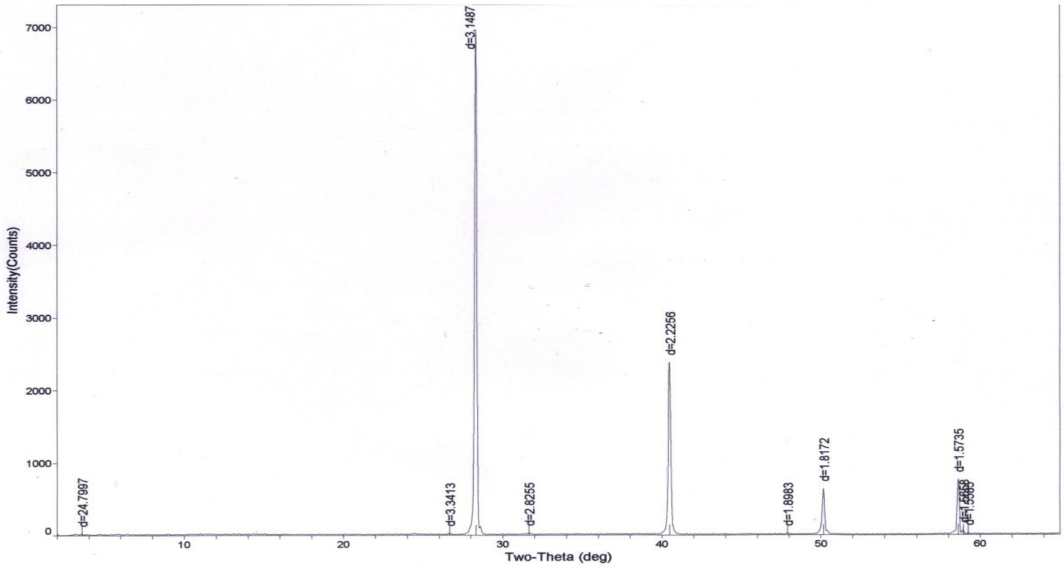


Figure 3-3 XRD analysis for KCl

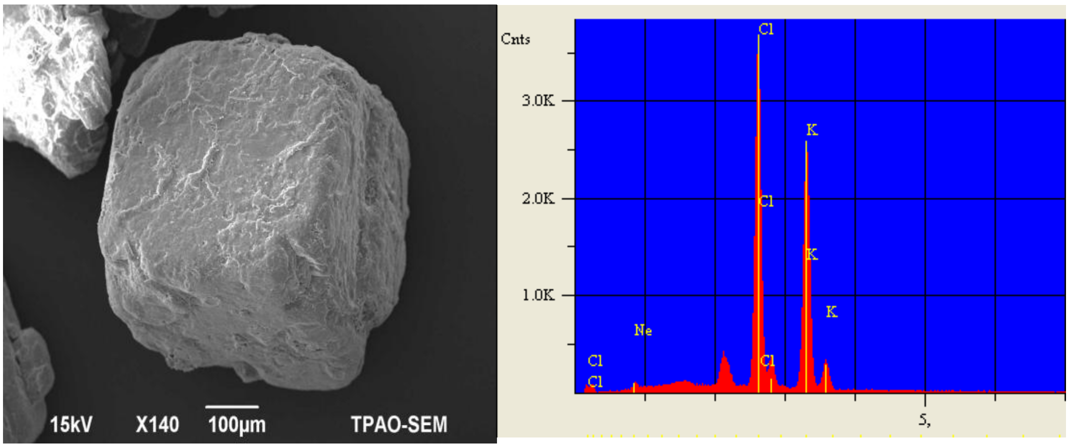


Figure 3-4 SEM micrograph of KCl

3.1.2.3. $CaCl_2$

XRD analysis result is not clear for $CaCl_2$ salt as it does have many impurities corresponding to more than one peak in the XRD diagram (Figure 3-5). The structure of $CaCl_2$ can be seen in SEM analysis (Figure 3-6).

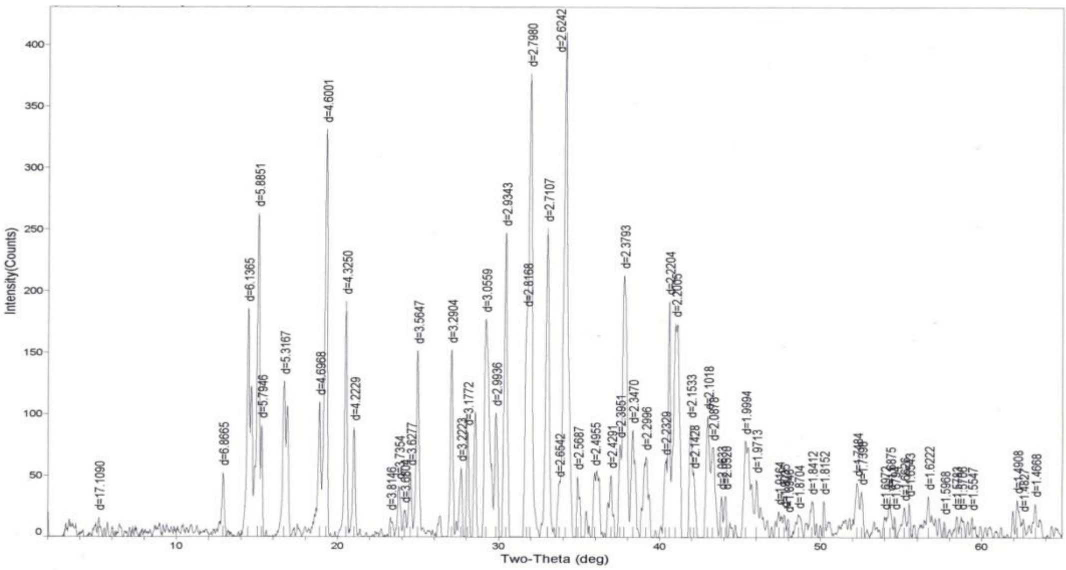


Figure 3-5 XRD analysis for $CaCl_2$

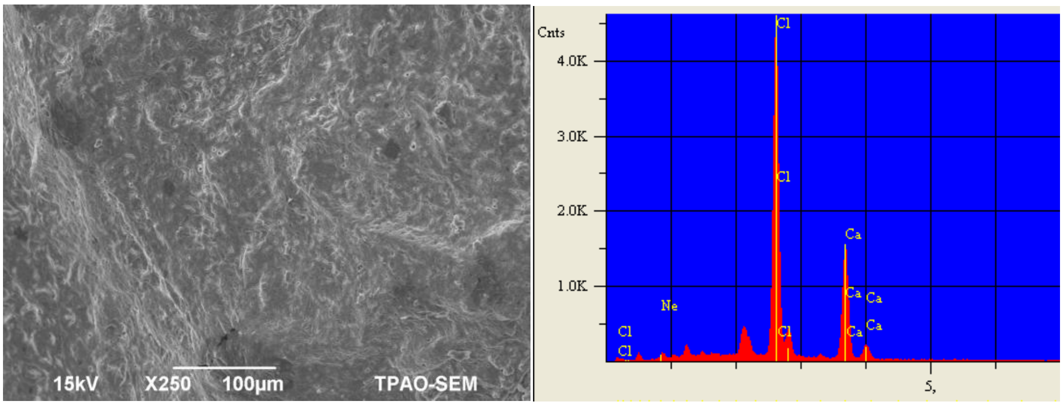


Figure 3-6 SEM micrograph of $CaCl_2$

3.1.3. Water

Tap water connected to the network in the Research Center of TPAO is used in this study for preparing the cement slurries.

3.2 Cement Slurry Compositions

With the G1 cement, a total of sixteen cement slurry compositions with salt addition including the reference slurry with no salt addition were prepared. For each salt type five different compositions are prepared with amounts of 1, 3, 5, 7, 10% for KCl and $CaCl_2$ and 3, 5, 10, 12, 15% for NaCl by weight of water. 800 g cement is used for preparing cement slurries for, thickening time, free fluid and compressive strength tests and 600 g cement is used for Ultrasonic Cement Analyzer and rheology tests. The w/c ratio required for Class G cement is 0.44 as specified in the API Spec. 10A, and thus all cement slurries are prepared with the same w/c ratio [12]. On the other hand, with G2 cement, a total of six cement slurry compositions with NaCl addition including the reference slurry without any NaCl were prepared.

3.3. Experimental Procedures

3.3.1. Slurry Preparation

Cement slurries are prepared in the TPAO Cement Laboratory according to the specifications in API Recommended Practice 10B [42]. After weighing the cement and salt, these components are mixed by a two speed mixer. This mixer, shown in Figure 3-7, cell is bottom-driven blade-type and has 1 liter size. The salts are added into water in the mixer and mixed at 4000 RPM. Later cement is added to slurry within 15 seconds. After the cement is added in to the mixer, the slurry is mixed at 12000 RPM for 35 seconds.

Figure 3-7 Mixer used in this study

3.3.2. Free Fluid

The free fluid is similar to the property of bleeding in fresh cement pastes. When cement slurry is allowed to stand for a period of time prior to setting, water may separate from slurry and accumulate at the top of the column [8]. All cement pastes bleed to some extent. Bleeding ends when either the movement of water is blocked by the growth of hydration products or by the solids effectively coming into contact with each other.

Specification tests for the free fluid of cement slurries apply only to Class G and Class H cements. In the free fluid test procedure, cement slurries are prepared according to API Specification 10A [12]. Then the slurry is conditioned at 27 ºC (80 ºF) in the atmospheric pressure consistometer for 20 minutes.

The atmospheric pressure consistometer, as shown in Figure 3-8, consists of a rotating cylindrical slurry container at a speed of 150 RPM with a temperature-controlled liquid bath.

Figure 3-8 Atmospheric consistometer

After conditioning of the cement slurry, 400 ml equivalent of cement slurry by mass is taken to a 500 ml conical flask that shown in Figure 3-9. The flask is then sealed to prevent evaporation and left undisturbed for 2 hours.

The supernatant fluid developed at the top of the flask is collected at the end of the 2 hours. The free fluid content of the slurry is calculated by volume fraction and expressed as percentage shown in Equation 3.1 as described by API Spec. 10A [12].

Figure 3-9 Free fluid test samples

$$\% FF = ((V_{FF} * \rho) / m_S) * 100 \qquad (3.1)$$

Where;

$\%FF$: is the free fluid content of the slurry, in percent

V_{FF} : is the volume of free fluid collected, expressed in millimeters

ρ : is the specific gravity of slurry

m_S : is the initially recorded mass of slurry, expressed in grams.

3.3.3. Early-age Compressive Strength Development

The cement slurries are placed into 50.8 mm (2 inch) cubic molds according to API Specification 10A [12]. The molds are then subjected to a curing regime appropriate to the simulated well temperature conditions for 7 hours and 15 minutes (Figure 3-10) .

With shallow well tests for Class A, B or C cements, simple water bath curing at atmospheric pressure and 38 ºC (100 ºF) is employed. For Class G and H cements, not only the same compressive strength test is used as for Class A, B or C cements, but also a higher temperature test at 60 ºC (140 ºF) is used at atmospheric pressure.

Later, they are cooled gradually in temperature-controlled water bath at 27 ºC for 45 minutes. After the cooling period, cubic specimens are removed from their molds. The compressive strengths of the specimens are tested by soil test equipment in the Cement Laboratory of TPAO Drilling Technology Department (Figure 3-11).

Figure 3-10 Temperature controlled water bath and the molds

Figure 3-11 Soil Test Equipment

3.3.4. Early-age Compressive Strength Estimation by Ultrasonic Cement Analyzer

The freshly prepared cement slurries are put into slurry cup and investigated for 24 hours at 20.7 MPa (3000 psi) of pressure. The curing temperature progressively reaches to 87.7 ºC (190 ºF) at 240 minutes.

The UCA (Ultrasonic Cement Analyzer) measures the transition time of the ultrasonic waves through the cement sample as it cures under simulated well conditions. The UCA actually directly measures the bulk compressibility of samples, but estimation is developed and correlated with compressive strength [8].

The UCA that was used for testing specimens is from Chandler Engineering with model 4262 in TPAO and shown in Figure 3-12. A sample output for UCA test is shown in Figure 3-13.

Figure 3-12 Model 4262 Ultrasonic Cement Analyzer (UCA)

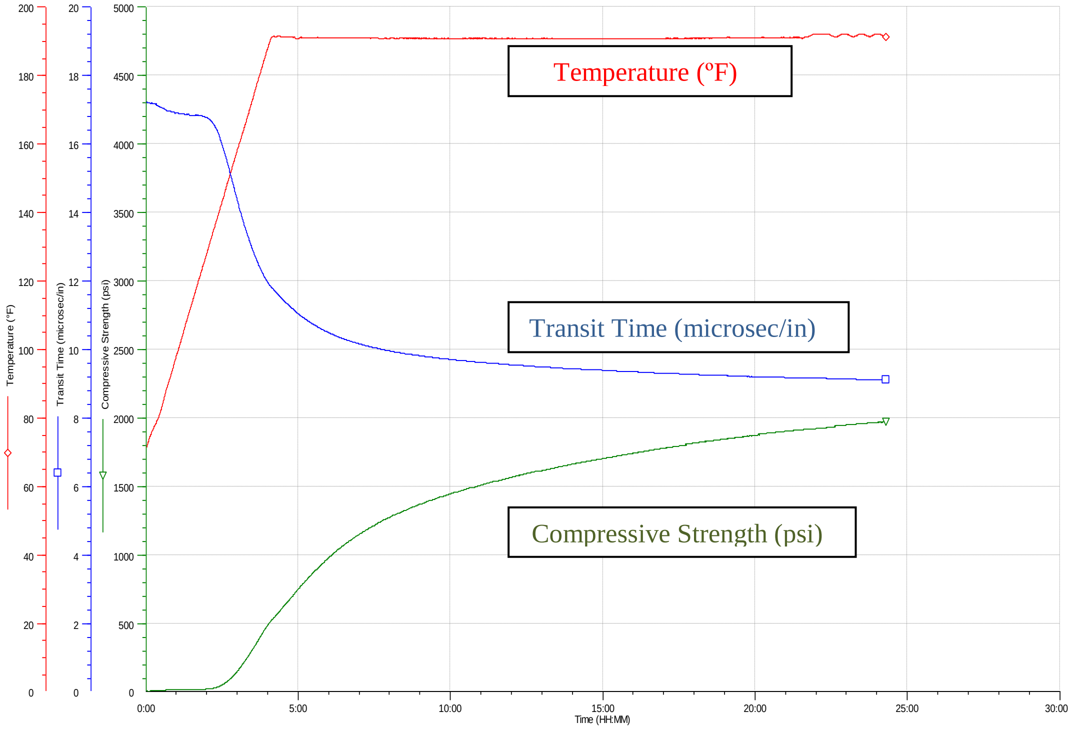


Figure 3-13 A sample output of Ultrasonic Cement Analyzer (UCA)

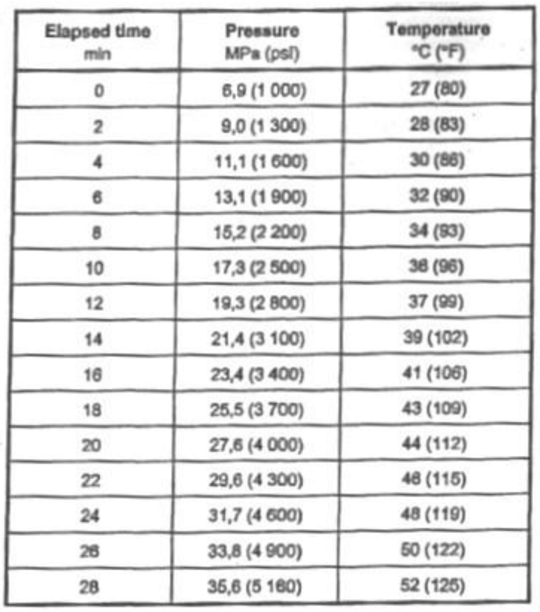
3.3.5. Thickening Time

Thickening time is essentially a setting time under conditions of controlled temperature and pressure ramps that simulate well conditions. It is defined as the time required for a cement slurry of given composition to reach a consistence of 100 Bearden units of consistence (Bc), determined by the methods outlined in API Specification 10A [12].

The high pressure high temperature consistometer (HPHT) is used for thickening time measurements. This machine has a rotating cylindrical slurry container equipped with a stationary paddle assembly and enclosed in a pressure chamber. The HPHT consistometer that used for testing is from Chandler Engineering with model 7025 in TPAO and it is designed for a working pressure of 170 MPa (25,000 psi) at a maximum temperature of 204°C (400°F) (Figure 3-14).

Figure 3-14 Model 7265 HPHT Consistometer

The cement slurries are mixed according to API Specifications and placed in the HPTH consistometer. The temperature and the pressure are increased according to a suitable schedule, given in Figure 3-15 for Class G cement, and consistence of the cement slurries is monitored until 100 Bc. The time taken to achieve 100 Bc is the thickening time of the slurry. A sample output for thickening time test is shown in Figure 3-16.



Elapsed time min	Pressure MPa (psi)	Temperature °C (°F)
0	6,9 (1 000)	27 (80)
2	9,0 (1 300)	28 (83)
4	11,1 (1 600)	30 (86)
6	13,1 (1 900)	32 (90)
8	15,2 (2 200)	34 (93)
10	17,3 (2 500)	36 (96)
12	19,3 (2 800)	37 (99)
14	21,4 (3 100)	39 (102)
16	23,4 (3 400)	41 (106)
18	25,5 (3 700)	43 (109)
20	27,6 (4 000)	44 (112)
22	29,6 (4 300)	46 (115)
24	31,7 (4 600)	48 (119)
26	33,8 (4 900)	50 (122)
28	35,6 (5 160)	52 (125)

Figure 3-15 Schedule 5 specification test for Class G cement [12]

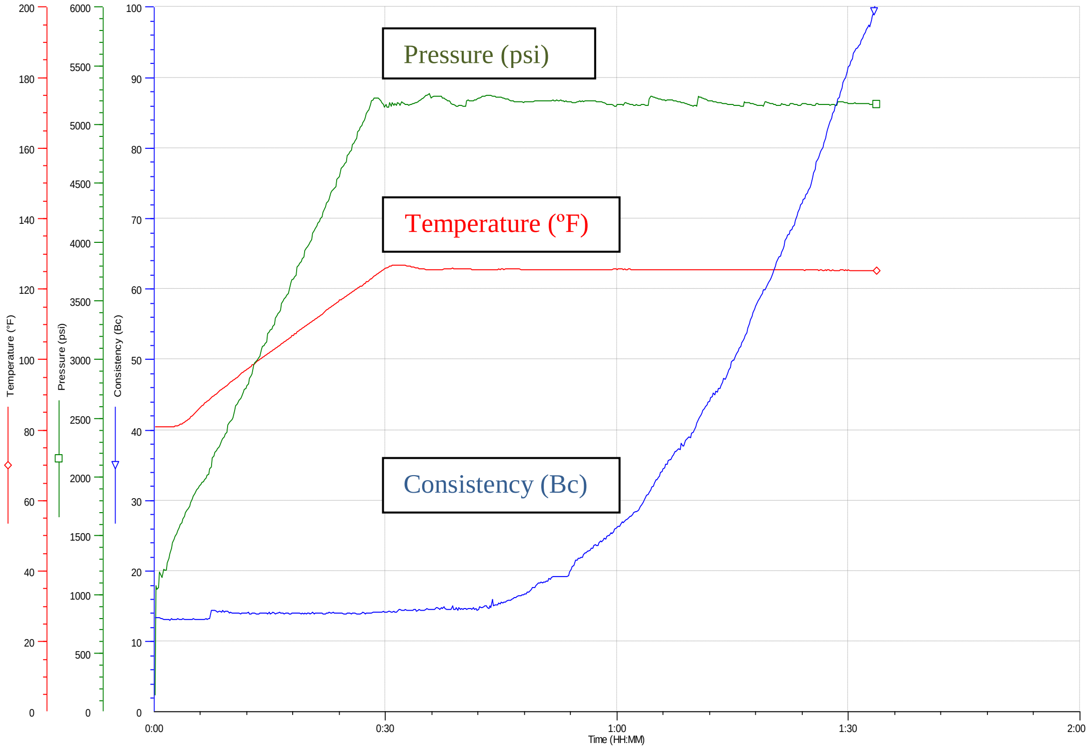


Figure 3-16 A sample output of HPHT consistometer

3.3.6. Rheological Properties

The cement slurries are prepared according to API Specification 10A for rheological property measurements [12]. Then the slurry is conditioned at 27 ºC (80 ^{o}F) in the atmospheric pressure consistometer for 20 minutes. After that, the rheological properties are measured by using the Chandler Engineering Model 3500 viscometer (Figure 3-17). The measurement fluid is contained within the annular space or shear gap between the rotor and bob. The rotor is rotated at known velocities (shear rates) and the viscous drag exerted by the test fluid creates torque on the bob. This torque is transmitted to a precision torsion spring, and its deflection is measured and related to shear stress.

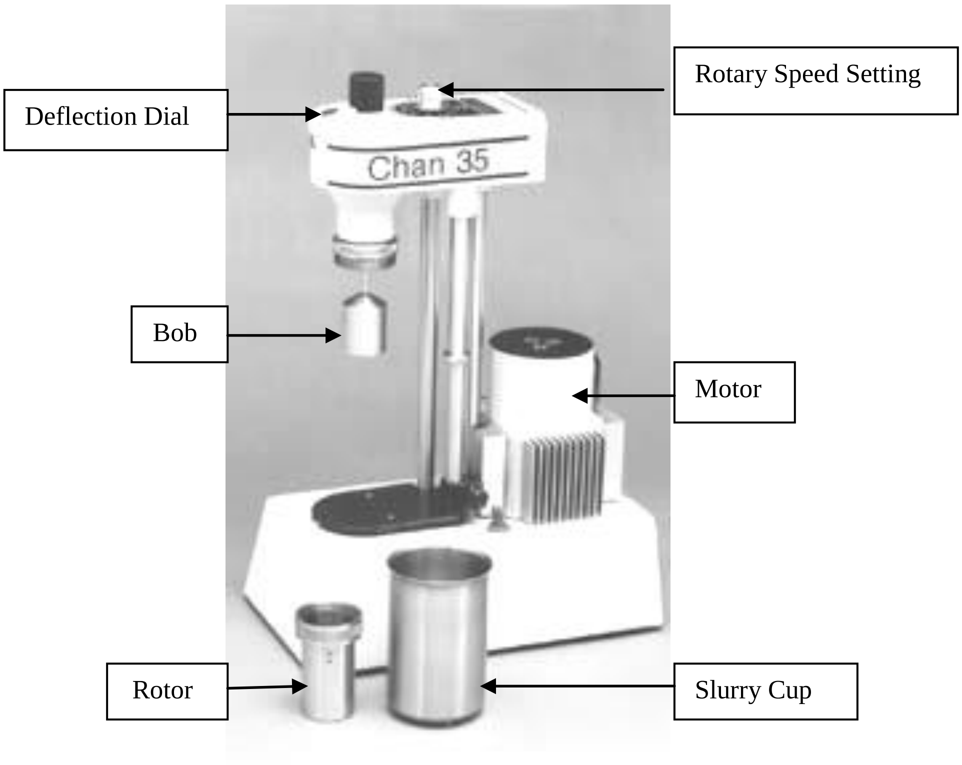


Figure 3-17 Model 3500 Viscometer

Measurements are carried out at 25 °C (80°F). Using the Bingham plastic model, Plastic Viscosity (PV) and Yield Point (YP) values are calculated according to these formulas:

$$PV = \theta_{600} - \theta_{300} \quad (3.3)$$

$$YP = \theta_{300} - PV \quad (3.4)$$

Where; PV is in centipoise (cp),

YP is in lb/100ft^2,

θ_{600} is the 600 RPM reading,

θ_{300} is the 300 RPM reading

After recording rheologies, samples are stirred for 1 minute at 600 RPM and motor is shut for 10 seconds and 3 RPM readings are recorded. This value is called 10 second gel strength. The readings for 10 minute gel strengths are also recorded with the same procedure the only difference being is the use of resting period for 10 minutes instead of 10 seconds.

3.3.7. XRD Analysis

X-Ray Diffraction (XRD) system from Rigaku D/Max-2200 Ultimate+/PC in TPAO (Figure 3-18) is used to reveal the crystal structure and mineral composition of chloride samples.

Figure 3-18 XRD instrument

The chloride specimens are dehydrated in temperature-controlled oven at 80 ºC for XRD analysis. X-Ray diffractograms are evaluated in Jade-7.0 software with control of PC directly linked to diffractometer by using the Inorganic Crystal Structure Database (ICSD) of International Center for Diffraction Data (ICDD).

3.3.8 SEM Analysis

Scanning electron microscope (SEM) system from Jeol with Model JSM-6490LV in TPAO (see in Figure 3-19) is used in high vacuum mode to investigate micro morphology of different chloride samples.

The chloride samples are first dried for 2 hours at 60 ºC prior to analysis and then are coated with gold using Polaran E5100 Serie-II. Then tests are conducted on the samples.

Figure 3-19 SEM instrument

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Free Fluid Content

The free fluid contents of different chloride sources for all ratios are given in Table 4-1. The maximum allowed amount of free fluid designated in API Specification 10A is 5.9 percent by volume [12]. It can be seen in Table 4-1 that all results are below the limit and there is a reduction in free fluid of the slurries i.e. a reduction in thickening time with salt addition.

Table 4-1 Free fluid content of cement slurries

	Free Fluid Content (%)							
	Amount of Salts, bwow							
Cement Slurry	**0%**	**1%**	**3%**	**5%**	**7%**	**10%**	**12%**	**15%**
NaCl	5.75	-	4.12	3.97	-	3.25	3.75	4.25
KCl	5.75	5.50	4.25	5.25	3.87	2.37		
$CaCl_2$	5.75	4.26	2.79	1.48	0.62	0.00		

To quantify the effect of salt addition on the free fluid content, the data in table 4-1 is normalized to show the relative change in free fluid content with different salt concentrations as shown in Figure 4-1.

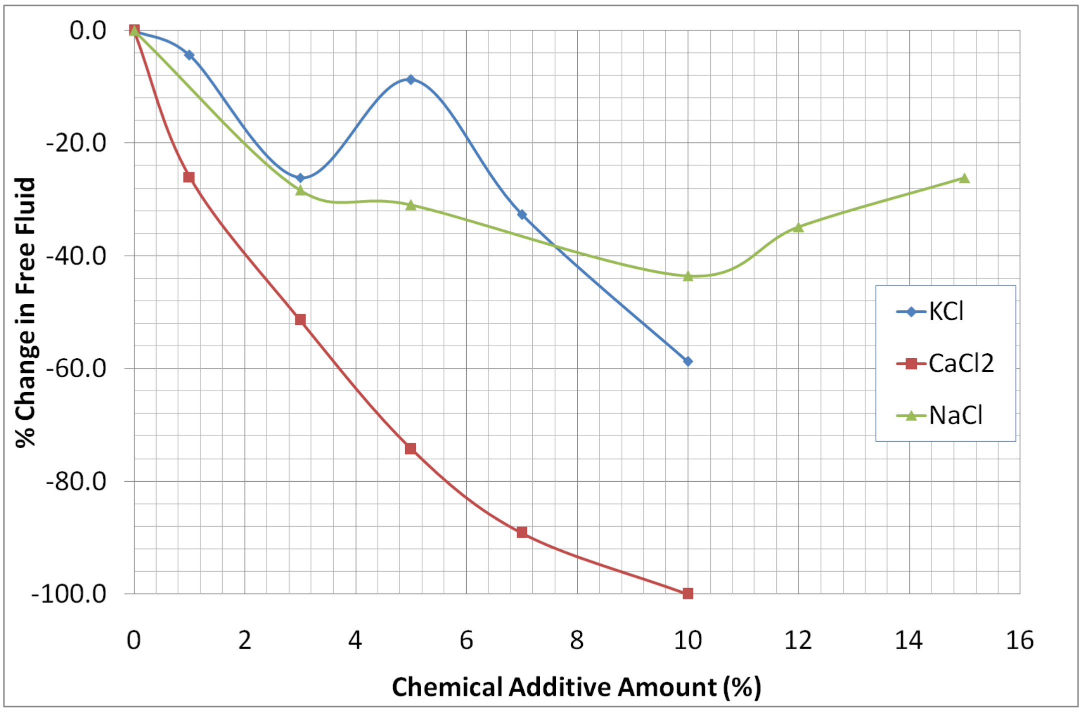


Figure 4-1 % Change in free fluids of cement slurries

As seen in Fig. 4-1, the addition of $CaCl_2$ dramatically reduced the free fluid content with increasing concentrations. For other salt additions there is also a reduction in the free fluid content but they were not as effective as $CaCl_2$.

Table 4-1 and Figure 4-1 also shows that the cement slurries prepared with KCl do not illustrate a regular trend as Miranda et al.(2012), the KCl containing slurries showed an erratic behavior [32].

It is also seen that, ratio of $CaCl_2$ content has an unignorable effect on the free fluid properties of cement slurry. Free fluids of slurries are decreasing dramatically with the increasing $CaCl_2$ ratio.

It can be seen that free fluid of slurries are decreasing at low NaCl content and increasing with higher NaCl content.

4.2. Early-age Compressive Strength Development

In Table 4-2, compressive strength analysis results are given for NaCl, KCl and $CaCl_2$. Also Figure 4-2 shows the relative change on compressive strength of slurries with different salt concentrations for 8 hours.

Table 4-2 Compressive strength of cement pastes for different compositions (8 hours)

		Compressive Strength (MPa)							
Cement slurry	**Sample No**	**Amount of Salts, bwow**							
		0%	**1%**	**3%**	**5%**	**7%**	**10%**	**12%**	**15%**
NaCl	#1	11.2	-	13.3	14.8	-	17.2	11.8	11.9
	#2	11.1	-	12.6	15.0	-	15.7	12.1	11.4
	#3	10.7	-	13.0	15.2	-	15.3	12.1	8.6
	Mean	**11.0**	**-**	**13.0**	**15.0**	**-**	**16.1**	**12.0**	**11.6**
KCl	#1	11.2	12.3	13.8	15.4	16.2	15.5		
	#2	11.1	12.9	12.6	15.4	15.2	15.9		
	#3	10.7	13.4	13.1	15.7	14.9	15.5		
	Mean	**11.0**	**12.9**	**13.2**	**15.5**	**15.4**	**15.6**		
$CaCl_2$	#1	11.2	14.1	16.7	19.3	21.0	21.4		
	#2	11.1	13.9	16.3	18.7	20.2	21.4		
	#3	10.7	14.1	16.7	18.1	20.1	21.4		
	Mean	**11.0**	**14.0**	**16.6**	**18.7**	**20.4**	**21.4**		

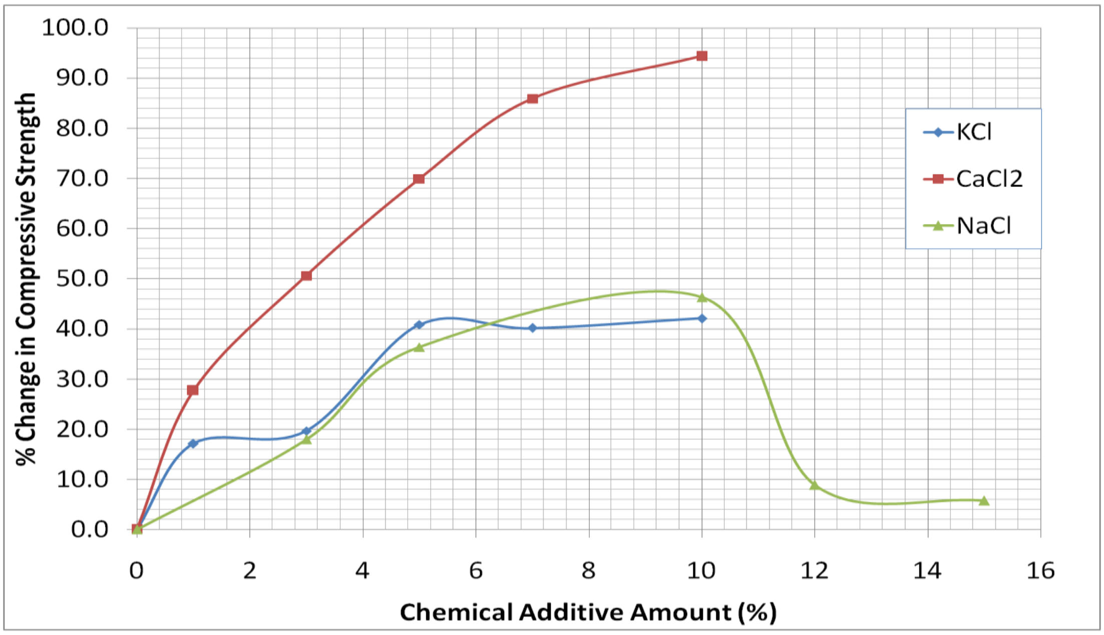


Figure 4-2 % Change in compressive strength of cement pastes (8 hours)

It is clear in Figure 4-2 that, adding salts to the Class G cement improves the compressive strength for short time period (8 hours) for all the salt used in this study.

It is observed that, the addition of $CaCl_2$ considerably improved the early age compressive strength with increasing concentrations as stated in literature [40].

For KCl, there is an optimum value of 5% KCl content and after that the compressive strength is not changed with further KCl addition.

On the other hand, some slurries containing NaCl show a different reaction than the other chloride containing slurries. While the compressive strength is rising with the adding NaCl, at 10% a sudden reduction is observed. Even though the higher NaCl addition decreases the compressive strength, these slurries have higher strengths than the reference slurry.

4.3. Early-age Compressive Strength Estimation by Ultrasonic Cement Analyzer

Ultrasonic cement analyzer (UCA) is used for estimating the compressive strength of the cement pastes through a period of time. All UCA graphs are presented in Appendix A.

In Table 4-3, all results of compressive strength analysis by UCA are given for different salt ratios and for 8, 12, 16 and 24 hours of ageing time. Also, Figure 4-3 shows the relative change of compressive strength with all salt concentration for 24 hours.

Table 4-3 Compressive strength of cement pastes by UCA (24 hours)

		Compressive Strength (MPa)							
		Amount of Salt, bwow							
Slurry	**Time (h)**	**0%**	**1%**	**3%**	**5%**	**7%**	**10%**	**12%**	**15%**
NaCl	8	10.9	-	9.4	9.1	-	11.2	10.8	9.7
	12	12.8	-	11.3	11.0	-	13.4	12.3	11.5
	16	14.1	-	12.5	12.3	-	14.5	13.1	12.5
	24	**15.5**	**-**	**13.9**	**13.6**	**-**	**15.9**	**15.1**	**13.5**
KCl	8	10.9	9.8	9.9	10.8	9.5	10.7		
	12	12.8	12.0	12.0	13.0	11.6	13.0		
	16	14.1	13.3	13.3	14.3	12.9	14.4		
	24	**15.5**	**14.9**	**14.7**	**15.7**	**14.3**	**15.9**		
$CaCl_2$	8	10.9	9.2	9.3	8.5	8.0	9.8		
	12	12.8	11.1	10.8	10.2	9.4	11.2		
	16	14.1	12.3	11.6	11.2	10.4	1.2		
	24	**15.5**	**13.8**	**12.9**	**12.2**	**11.5**	**13.2**		

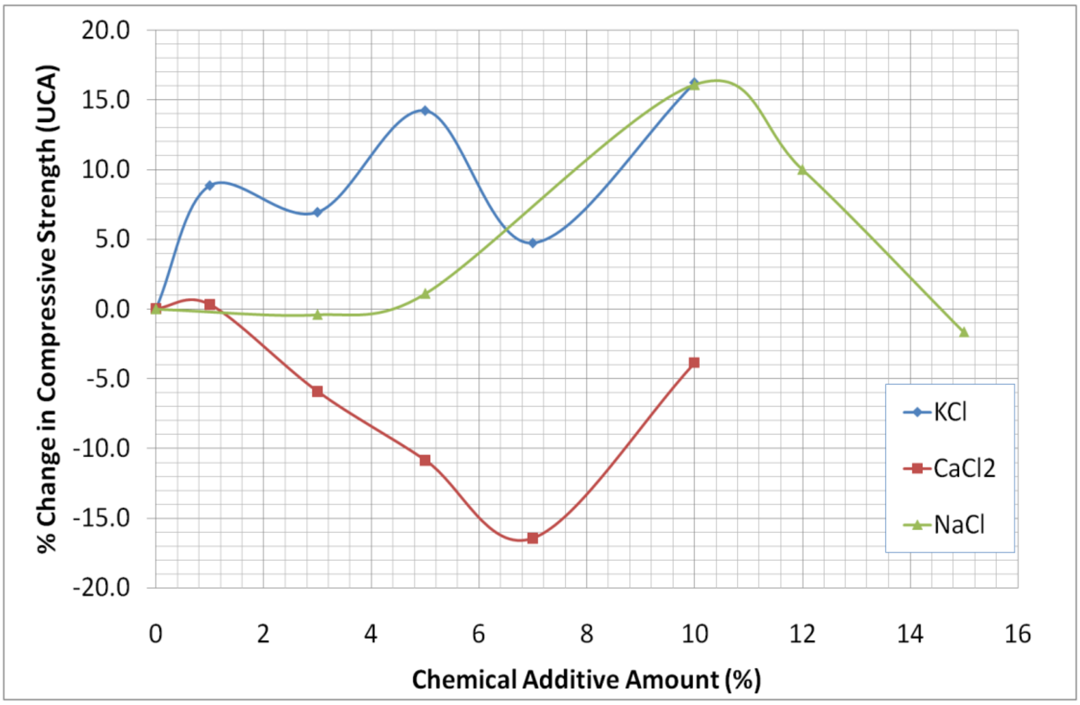


Figure 4-3 % Change in compressive strength of cement slurries by UCA (24 hours)

Heikal (2004) stated that, $CaCl_2$ addition accelerates both setting and hardening of Portland cement concrete but, due to the formation of chloroaluminate hydrates, compressive strength decreases with time and final strength can be reduced [41]. As stated in literature, the slurries prepared with $CaCl_2$ show the exact opposite behavior of cubic mold results and the compressive strength of samples is decreased with the increasing $CaCl_2$ concentration. Even it is started to increase again, the compressive strengths of $CaCl_2$ added samples are lower than the reference sample.

The compressive strength measured with UCA, of cement pastes containing KCl and NaCl shows the similar behavior with the cubic molds. On the other hand, reference sample has the higher compressive strength value than with the addition of 15% NaCl sample.

4.4. Thickening Time

The data is presented in Table 4-4 for the thickening time with different salts and ratios. The comparative change in thickening time for all salt concentrations can be seen in Figure 4-4. All thickening time graphs are presented in Appendix B.

Table 4-4 Thickening time results for cement pastes

	Thickening Time (min)							
	Amount of Salts, bwow							
Cement Slurry	**0%**	**1%**	**3%**	**5%**	**7%**	**10%**	**12%**	**15%**
NaCl	116	-	83	83	-	92	93	115
KCl	116	92	90	89	82	82		
$CaCl_2$	116	84	57	55	43	31		

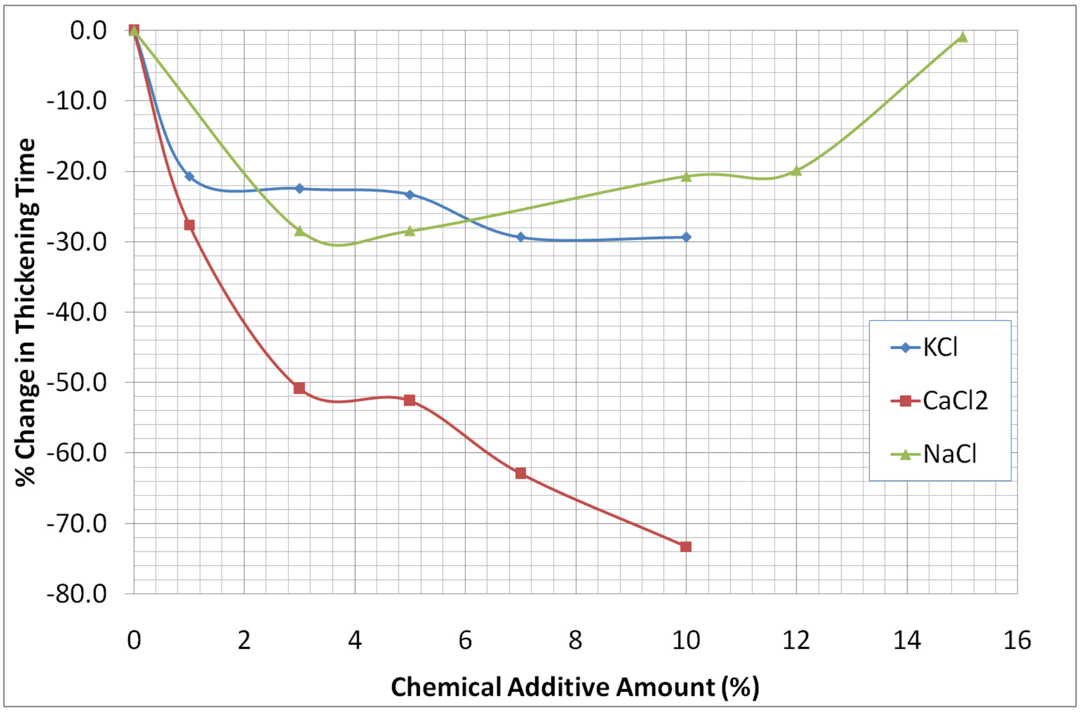


Figure 4-4 % Change in thickening time of cement slurries

As seen in Figure 4-4, $CaCl_2$ is the more efficient salt than other salts that reduces the thickening time. The other salt additions also decrease the thickening time but they were not as effective as $CaCl_2$.

As stated in literature, using NaCl at low concentrations accelerates the thickening time and it acts like a retarder at high concentrations [6, 7, 9, 27]. The thickening times of samples containing NaCl more than 5% bwow start to get longer again.

Even though there is no remarkable change in thickening time after 1% addition of KCl, the acceleration effects of KCl can be clearly seen in Figure 4-4.

4.5. Rheological Properties

The viscometer readings for all salts and concentrations are given in Appendix C. Table 4-5 shows the PV and PV values for all slurries. Figure 4-5 for PV and the Figure 4-6 for YP, illustrate the relative change in values for all samples.

Table 4-5 PV and YP values for cement slurries

		Amount of Salt, bwow							
Slurry		**0%**	**1%**	**3%**	**5%**	**7%**	**10%**	**12%**	**15%**
NaCl	**PV**	39	-	37	35	-	34	34	42
	YP	26	-	31	31	-	30	29	39
KCl	**PV**	39	38	35	35	36	40		
	YP	26	27	25	23	24	55		
$CaCl_2$	**PV**	39	35	35	38	41	-		
	YP	26	36	43	50	91	-		

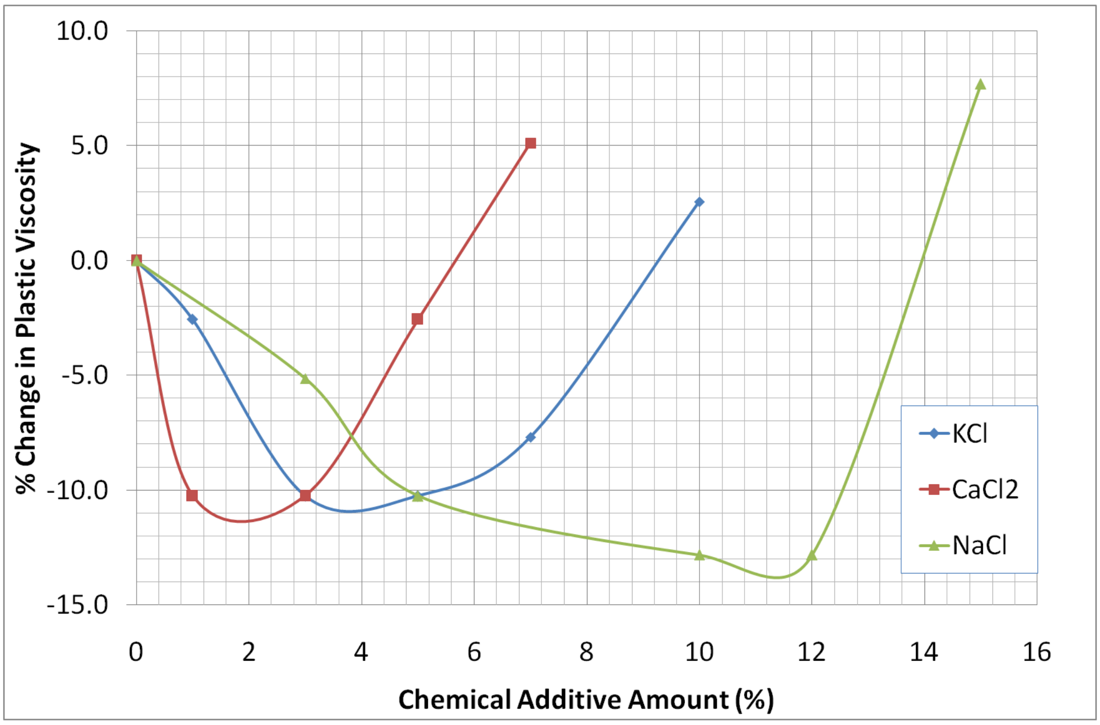


Figure 4-5 % Change in Plastic Viscosity

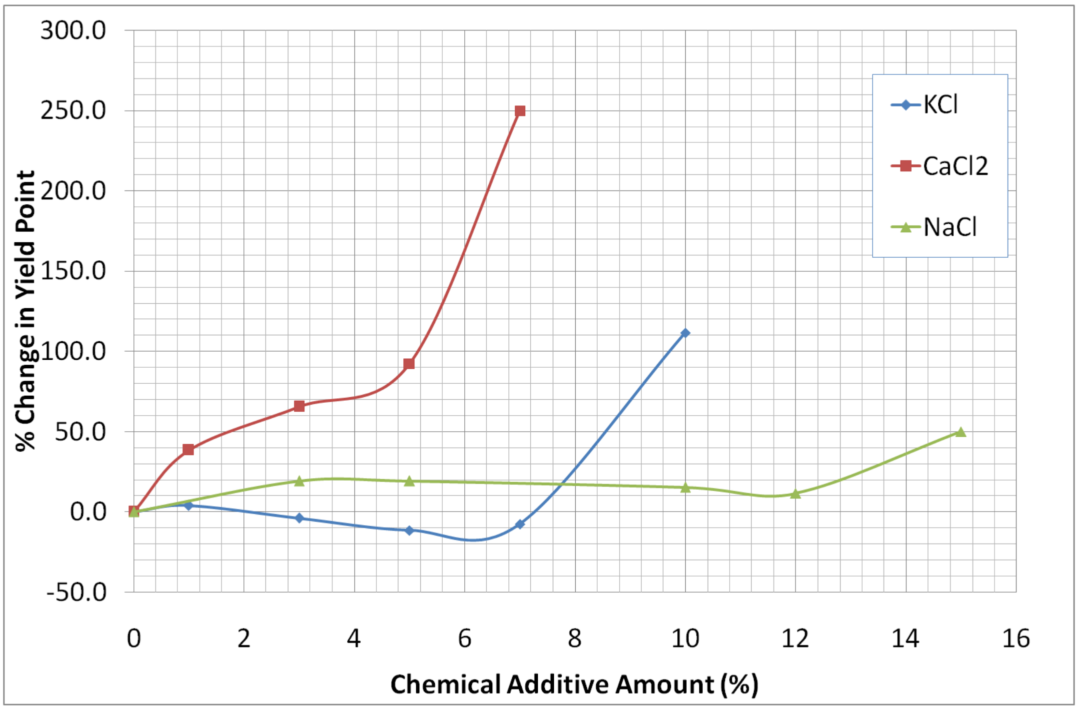


Figure 4-6 % Change in Yield Point

In Figure 4-5, it is clearly seen that the addition of the chlorides reduces the plastic viscosity up to a certain amount. Later, as that amount is increased there is an increase in PV. The optimum amount depends on the chloride type.

NaCl content reduces the viscometer readings and PV values in low concentration (Table 4-5). It is clear that, readings are decreasing with the increasing KCl content until 7%. The readings of 10% KCl containing slurry are above the reference slurry. It is observed for cement slurries containing KCl a decrease in PV with increase of KCl content until 7%. Further, increase on KCl concentration causes an increase in this parameter. It is barely shown that, $CaCl_2$ extremely affects the rheology of the slurries because, both viscometer readings and PV values are increasing with the increasing $CaCl_2$ content.

As for the yield point, the addition of $CaCl_2$ drastically increased the YP at all additions. The NaCl and KCl was not as effective as $CaCl_2$ in changing the YP.

For NaCl containing slurries, the YP values generally higher than reference slurry that can be seen in Figure 4-6. It is also observed that, there is a decrease in the YP for KCl containing slurries until 7% and after this amount, the YP increases The YP values for $CaCl_2$ containing slurries are increasing with the increasing amount of $CaCl_2$ same as other rheological parameters.

The gel values of slurries are given in Table 4-6, for 10 seconds and 10 minutes. Figure 4-7, Figure 4-8 also present the % changes of gel behaviors of cement slurries for 10 sec. and 10 min.

Table 4-6 Gel values of cement slurries

		Amount of Salts, bwow							
Cement pastes		**0%**	**1%**	**3%**	**5%**	**7%**	**10%**	**12%**	**15%**
Gel Values for NaCl (lbf/100 ft^2)	10 sec	10	-	10	12	-	13	10	13
	10 min	14	-	12	15	-	15	12	14
Gel Values for KCl (lbf/100 ft^2)	10 sec	10	11	11	11	12	13		
	10 min	14	14	14	14	15	16		
Gel Values for CaCl2 (lbf/100 ft^2)	10 sec	10	11	13	17	25	28		
	10 min	14	14	17	20	96	106		

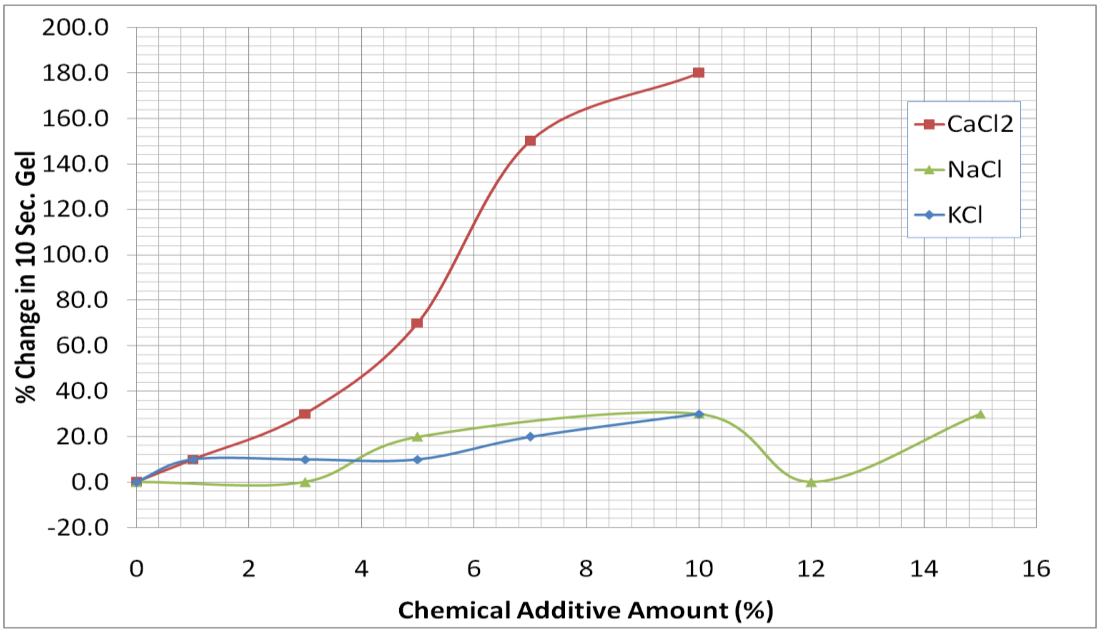


Figure 4-7 % Changes in 10 seconds gel values for cement slurries

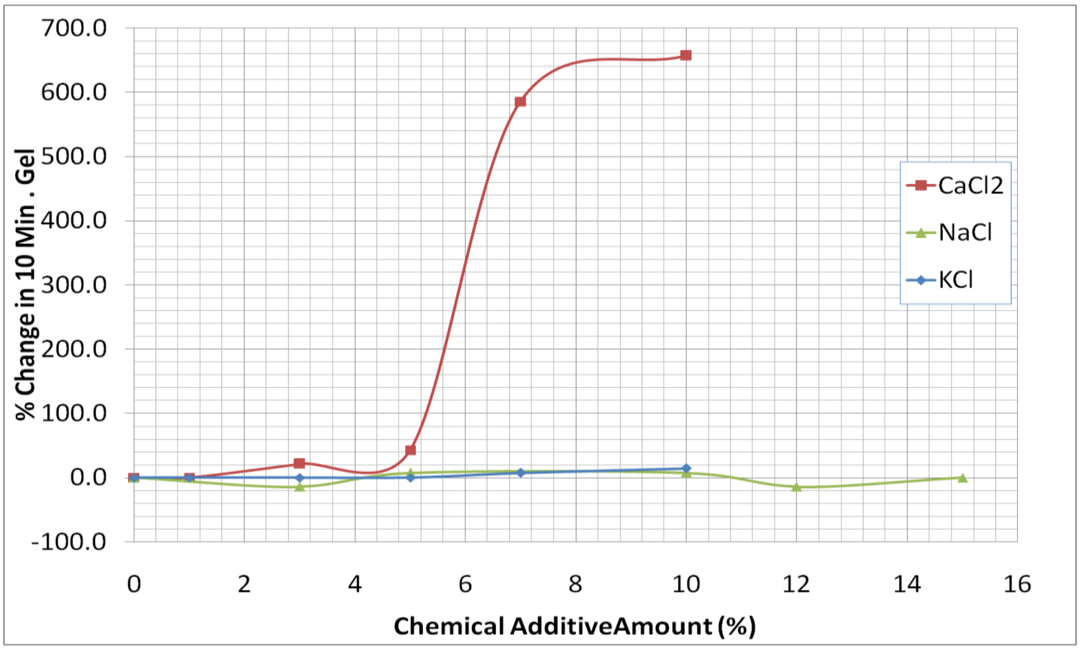


Figure 4-8 % Changes in 10 minutes gel values for cement slurries

The slurries containing KCl do not present a significant change in gel values for both 10 sec. and 10 min. Even the KCl content increase, the gel values are nearly the same with reference slurry.

On the contrary to KCl, $CaCl_2$ has a remarkable effect on cement gel values. Gel values are increasing with the increasing $CaCl_2$ content and especially after 5% addition gel values get considerably higher.

On the other hand, gel values of NaCl containing cements are not affected from NaCl concentration changes. The gel values are nearly the same with the reference slurry values both at low and high concentrations.

4.6 Effects of Cement Type

In order to observe the combined effects of cement type and salt addition, another API Class G cement labeled as “G2” with the properties that was presented in Table 3-1 is obtained. Using that cement and the NaCl additive, the free fluid, early age compressive strength development, early age compressive strength estimation by UCA, thickening time and the rhelogical properties tests are re-performed for cement slurries containing 1, 3, 5, 7, 10% amounts of NaCl. Therefore, all test conditions are kept the same as previous experiments except the cement.

4.6.1 Effects of Cement Type on Free Fluid

The free fluid contents of cement slurries for all NaCl contents that were prepared with different G Class cements are given in Table 4-8. Note that "*" represents the experiments that was conducted with the “G2” cement. It is clearly seen from Table 4-8 that all results are below the API limit and there is a reduction in free fluid content with NaCl addition in both cements. When the values presented in Table 4-8 are normalized to show the relative change in free fluid content for different cement types, the findings are presented as shown in Figure 4-9.

Table 4-7 Effects of different G class cement on free fluid properties

	Free Fluid Content (%)							
	Amount of Salts, bwow							
Cement Slurry	**0%**	**1%**	**3%**	**5%**	**7%**	**10%**	**12%**	**15%**
NaCl	5.75	-	4.12	3.97	-	3.25	3.75	4.25
NaCl *	5.62	5.49	4.98	3.75	4.12	4.75		

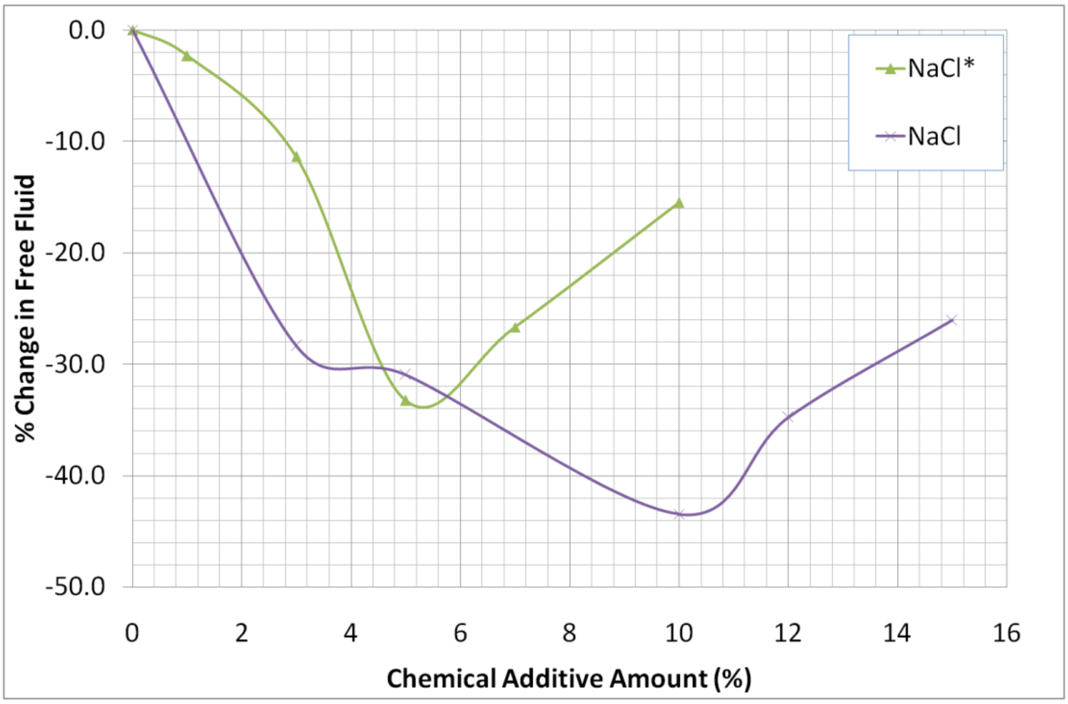


Figure 4-9 % Change in free fluids of different G class cement slurries

As seen in Figure 4-9, the addition of NaCl reduces the free fluid content of both cements until a certain limit. With the first cement (G1) which was a bit coarser, this optimum value is about 10%, whereas with the finer cement (G2) this value shifts to around 5%.

4.6.2 Effects of Cement Type on Early-age Compressive Strength Development

The compressive strength analysis results are given in Table 4-9 for 8 hours. The relative change in compressive strength of different cement slurries are given in Figure 4-10.

Table 4-8 Effects of different G class cement on compressive strength properties (8 hours)

		Compressive Strength (MPa)							
Cement slurry	**Sample No**	**Amount of Salts, bwow**							
		0%	**1%**	**3%**	**5%**	**7%**	**10%**	**12%**	**15%**
NaCl	#1	11.2	-	13.3	14.8	-	17.2	11.8	11.9
	#2	11.1	-	12.6	15.0	-	15.7	12.1	11.4
	#3	10.7	-	13.0	15.2	-	15.3	12.1	8.6
	Mean	**11.0**	**-**	**13.0**	**15.0**	**-**	**16.1**	**12.0**	**11.6**
NaCl *	#1	10.6	13.1	13.5	13.8	13.3	11.4		
	#2	10.1	12.6	13.6	13.7	13.1	10.9		
	#3	10.6	12.1	13.2	14.0	13.4	10.5		
	Mean	**10.4**	**12.6**	**13.4**	**13.8**	**13.3**	**10.9**		

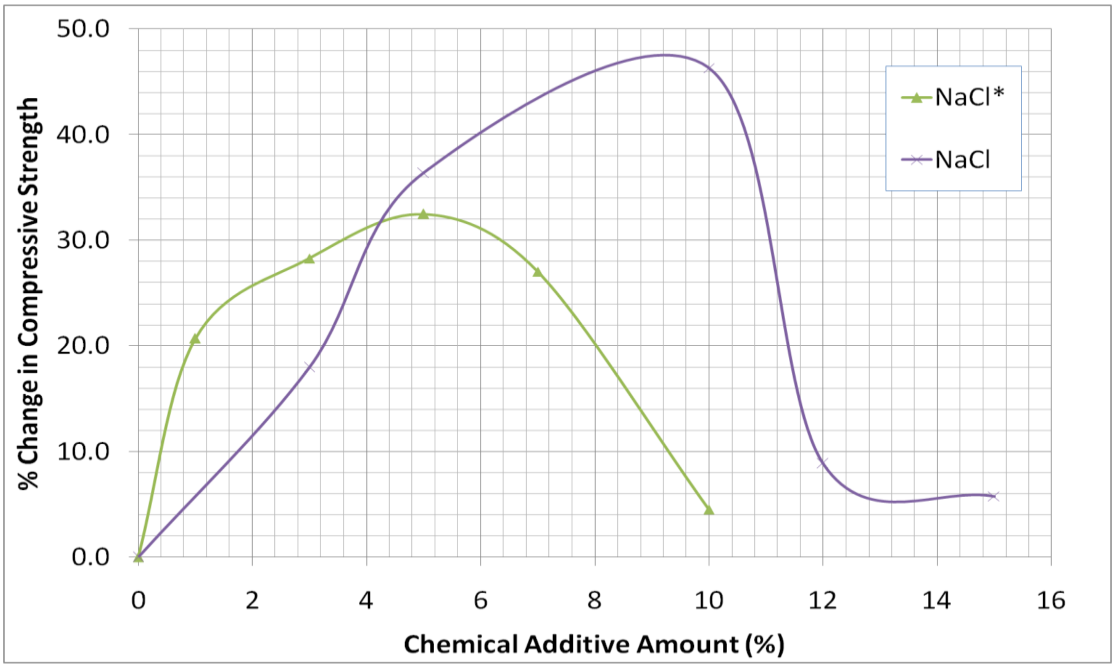


Figure 4-10 % Change in compressive strength of different G class cement slurries

As seen Figure 4-10, NaCl containing slurries have higher compressive strength than the reference slurries for both two cement types. It is also clear that, there are two peak points in Figure 4-10, one of for G1 and the other is for G2 type cement which corresponds to 10% and 5% addition of NaCl. The compressive strengths of the slurries are increasing until these peak points and decrease with further NaCl addition.

4.6.3. Effects of Cement Type on Early Age Compressive Strength Estimation by Ultrasonic Cement Analyzer

In Table 4-10, the results of compressive strength estimations by UCA are given for both G1 and G2 type cement for 8, 12, 16 and 24 hours of ageing time. All UCA graphs are given for G2 type cement with the "*" mark in Appendix A.

Figure 4-11 also shows the relative change in compressive strength for different cement types with NaCl addition.

Table 4-9 Effects of different G class cement on compressive strength properties by UCA

		Compressive Strength, MPa							
		Amount of Salt, bwow							
Slurry	**Time (h)**	**0%**	**1%**	**3%**	**5%**	**7%**	**10%**	**12%**	**15%**
NaCl	8	10.9	-	9.4	9.1	-	11.2	10.8	9.7
	12	12.8	-	11.3	11.0	-	13.4	12.3	11.5
	16	14.1	-	12.5	12.3	-	14.5	13.1	12.5
	24	**15.5**	**-**	**13.9**	**13.6**	**-**	**15.9**	**15.1**	**13.5**
NaCl*	8	8.8	10.8	11.8	10.2	9.5	8.9		
	12	10.7	13.1	14.6	12.7	12.0	11.3		
	16	12.0	14.6	16.3	14.1	13.3	12.6		
	24	**13.5**	**16.4**	**18.1**	**15.6**	**15.0**	**14.1**		

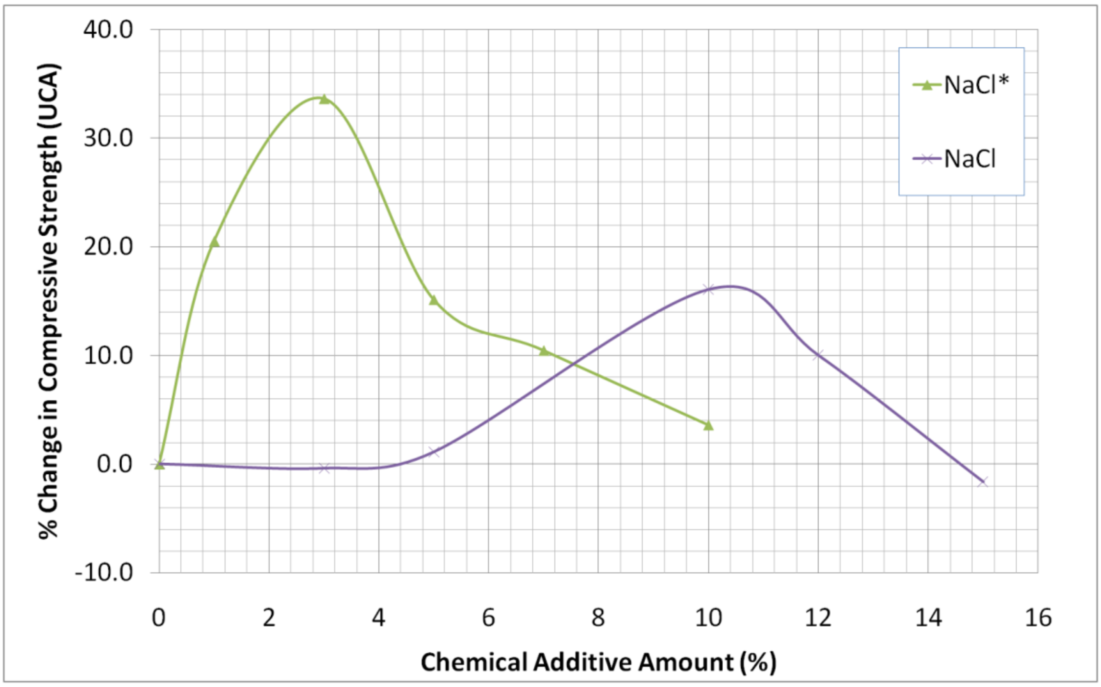


Figure 4-11 % Change in compressive strength of different G class cement slurries by UCA (8 hours)

It is clearly seen in Figure 4-11 that, adding NaCl increased the compressive strength of both cements until the optimum limits which are 10% for G1 and, 3% for G2. After these limits, more NaCl addition causes a reduction in compressive strength for both cements.

4.6.4. Effects of Cement Type on Thickening Time

The thickening time test results for G1 and G2 type cements with NaCl addition are given in Table 4-11. The proportional change in thickening time for these slurries can be seen in Figure 4-12. All thickening time graphs are given for G2 type cement with a "*" mark in Appendix B.

Table 4-10 Effects of different G class cement on thickening time

	Thickening Time (min)							
	Amount of Salts, bwow							
Cement Slurry	**0%**	**1%**	**3%**	**5%**	**7%**	**10%**	**12%**	**15%**
NaCl	116	-	83	83	-	92	93	115
NaCl *	113	99	91	90	92	107		

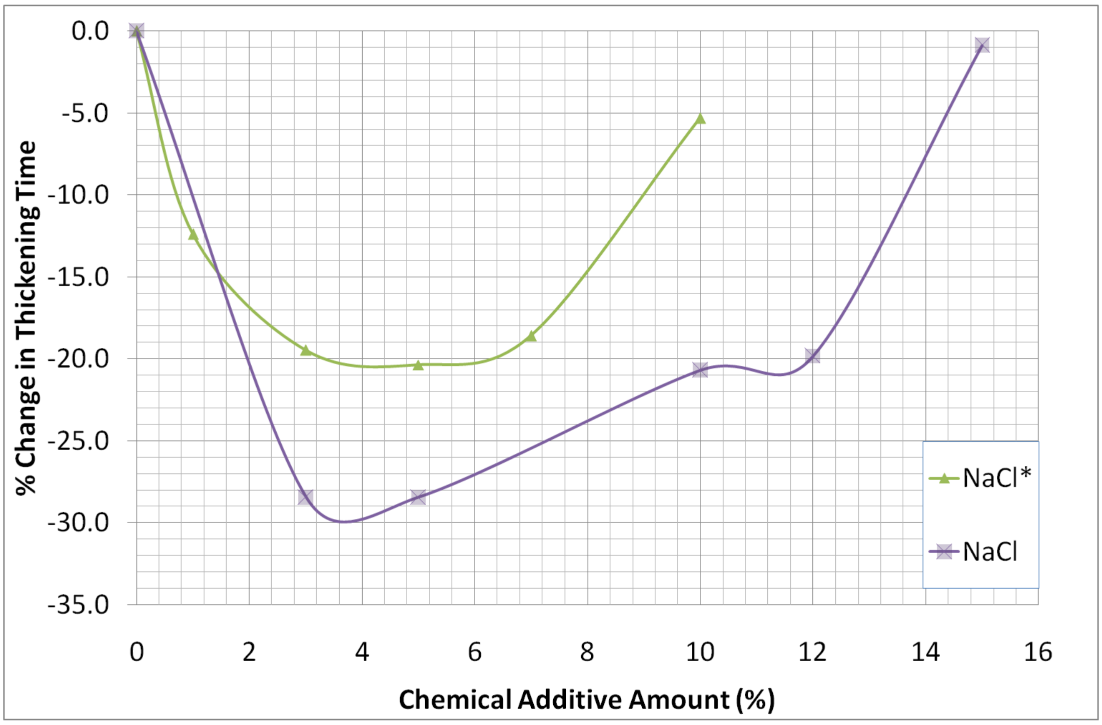


Figure 4-12 % Change in thickening time of different G class cement slurries

As seen in Figure 4-12, NaCl addition accelerates the thickening time in low concentration and retards it in high concentration for both cement types [6, 7, 9, 27]. This observation was also verified by the free fluid measurements. There is an optimum value for the thickening times of both G1 and G2 type cement samples at 5% NaCl addition. After this point, the thickening time gets longer with increased NaCl addition.

4.7.5. Effects of Cement Type on Rheological Properties

All viscometer readings are given for G2 type cement with a "*" remark in Appendix C. The PV and YP values for G1 and G2 type cements with NaCl addition are given in Table 4-12. The comparative change in PV and YP of these slurries can be seen in Figure 4-13 and Figure 4-14.

Table 4-11 Effects of different G class cement on PV and YP

		Amount of Salt, bwow							
Slurry		**0%**	**1%**	**3%**	**5%**	**7%**	**10%**	**12%**	**15%**
NaCl	**PV**	39	-	37	35	-	34	34	42
	YP	26	-	31	31	-	30	29	39
NaCl*	**PV**	38	43	39	39	38	43		
	YP	42	35	44	44	46	43		

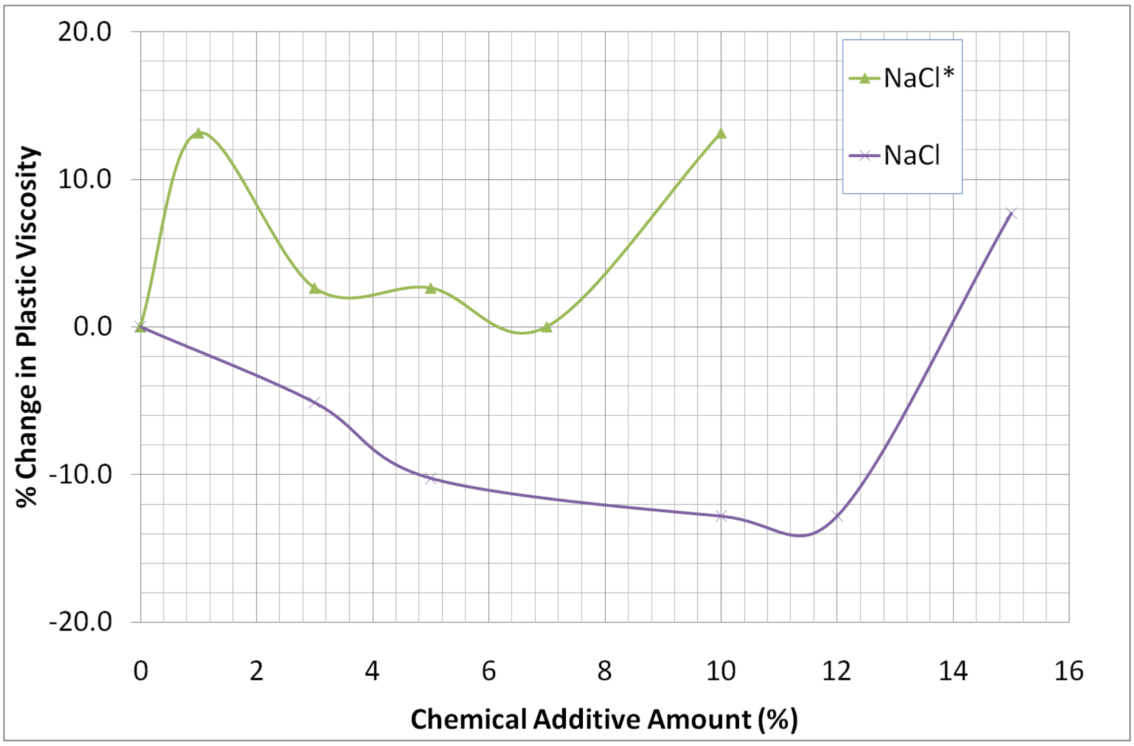


Figure 4-13 % Change in PV values of different G class cement slurries

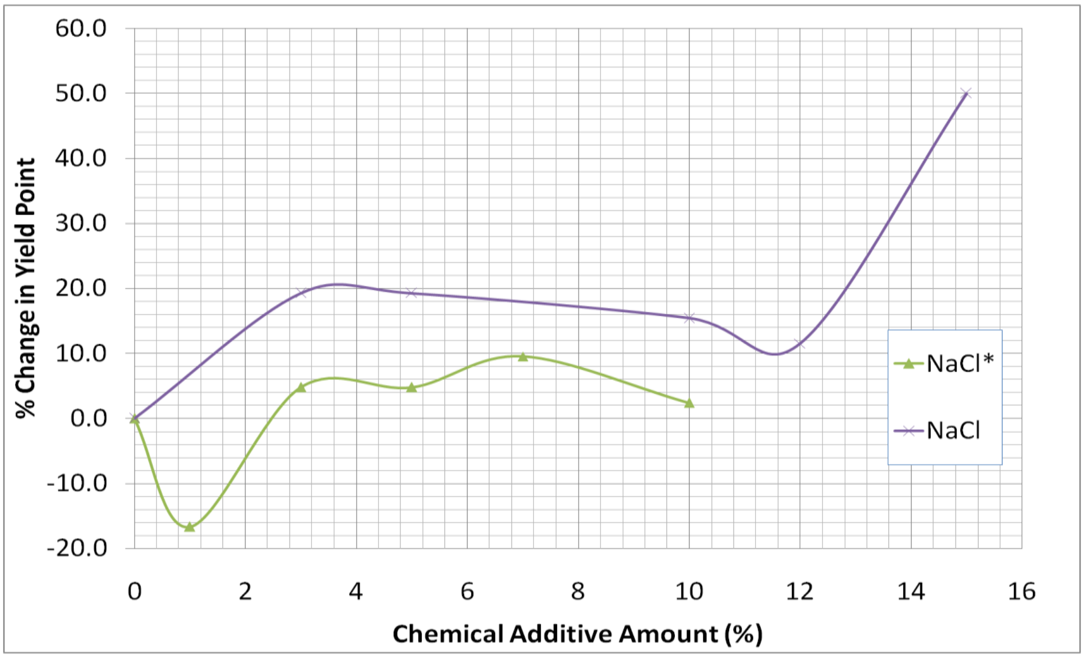


Figure 4-14% Change in YP values of different G class cement slurries

NaCl addition reduces the viscometer readings in low concentration until a certain value and this value shifts again for a different G class cement.

In Figure 4-13, it is seen that the addition of NaCl reduces the PV for the slurries prepared with G1 up to 12% and the PV increase with the further NaCl addition. The slurries prepared with G2 shows different behavior than G1 slurries. As shown in that graph except for the 1% NaCl addition the general layout of the graph is similar for both cement types. The PV is always higher than the reference slurry up to 7% addition and after this amount, it increases again. On the other hand, YP values of G2 slurries are relatively small when compared to G1 slurries.

Table 4-13 represents the 10 seconds and 10 minutes gel values for G1 and G2 slurries. As seen in Table-13, cement type does not show a considerable effect on gel values. All gel values are nearly same with reference gel values.

Table 4-12 Effects of different G class cement on gel values

Cement pastes		Amount of Salts, bwow							
		0%	**1%**	**3%**	**5%**	**7%**	**10%**	**12%**	**15%**
Gel Values for NaCl (lbf/100 ft^2)	10 sec	10	-	10	12	-	13	10	13
	10 min	14	-	12	15	-	15	12	14
Gel Values for NaCl* (lbf/100 ft^2)	10 sec	16	15	16	16	18	14		
	10 min	17	17	18	18	20	18		

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

5.1 Conclusions

At the end of this experimental investigation, it was seen that, the cement type, the chloride source and amount, and the environmental exposure regime (temperature, pressure, age) all affect the properties of the cement slurries. The specific findings are summarized as follows;

- All cement slurries are in the range of required specifications for free fluid analysis according to API Specification 10A. $CaCl_2$ is the most effective chloride source to reduce the amount of free fluid. Free fluid amount reduces dramatically with the increasing amount of $CaCl_2$ addition. KCl does not show a regular behavior with a change in concentration. Moreover, free fluid amount reaches to an optimum with a change in NaCl addition.

- Early-age compressive strength development analysis conducted according to API Spec 10A, results show that the samples prepared with $CaCl_2$ have the most remarkable increase in compressive strength. The samples containing KCl does not have a change in compressive strength after 5% (bwow). Although compressive strength increases with increasing NaCl content, similar to the free fluid content, there is an optimum amount.

- The compressive strength of the cement pastes at 1-day is also estimated by ultrasonic cement analyzer (UCA). However, destructive test method (DTM) and the UCA method are conducted for different temperature, pressure and curing conditions, the compressive strength of the pastes estimated by UCA is not in the same trend with DTM.

- All thickening time tests are conducted according to API Spec 10A, schedule 5 (5160 psi, 125 ºF). Test results indicate that, KCl has the lowest and $CaCl_2$ has the highest effect on thickening time between the three chloride sources. Also, it is observed that, NaCl acts as an accelerator in low compositions and as a retarder in high compositions as stated in literature.

- Rheological properties are examined at 27 ºC and atmospheric pressure as recommended API 10B-2 [42]. It is observed that the chloride addition reduces the PV and YP values until a certain amount which shows difference with chloride types. Cement slurries containing KCl have nearly the same PV and YP values with reference slurry until 7%. After 7%, YP value of sample increasing rapidly. $CaCl_2$ containing samples have the similar behavior with KCl containing samples and after 5% $CaCl_2$, YP value increases dramatically. Even PV, thus YP values cannot be calculated for 10% $CaCl_2$ containing slurry sample. For NaCl containing samples, there is nearly regular behavior with reference slurry but after 12% NaCl, both PV and YP values increase. The optimum amount changes with the chloride type.

- It is clearly seen that, $CaCl_2$ has a visible effect on both 10 seconds and 10 minutes gel values. KCl containing slurries has no remarkable change when compared to the NaCl and $CaCl_2$. 10 seconds gel values are more variable than 10 minutes gel values for all chloride sources.

- From the tests performed on NaCl with the G2 cement, it was observed that even the used cement type met the requirements of API Spec 10A, the optimum chloride amounts changed or shifted for all the performance tests.

- To sum up, calcium chloride is the most effective chloride sources on API Class G cement between three different sources. It can be used an effective accelerator even in low concentration, but other parameters should be optimized. KCl has the best results for flow properties both low and high concentrations. NaCl can be used as an accelerator in low concentrations and a retarder in high concentration. Right chloride sources and concentrations should be chosen according to the priorities and to formation properties.

5.2 Recommendations for Future Studies

- Increased salt ratio caused some difficulties on preparing cement slurries. Therefore, some additives like dispersant, could be used to get better results.

- Because no additives are used in tests, there is a lot of foam during mixing slurries. Therefore, an anti-foam agent could be used during mixing.

- In thickening time tests, limited amount of composition are used. Therefore, tests could be done for high concentrations to determine the effects of salts on high ratios.

- Compressive strength tests, conducted by UCA, are done for a medium depth oil well temperature and 24 hours. Hence, these tests could be performed for different temperatures and ageing times.

- Rheological measurements are done at room temperature and pressure. So, different temperature and pressure could be used to observe their effects on salty cement slurries.

- It was observed that a change in cement type affects the performance characteristics of the slurry. The interaction between the salt source and cement type can be studied.

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APPENDICES

A. COMPRESSIVE STRENGTH OF CEMENT SLURRIES BY UCA

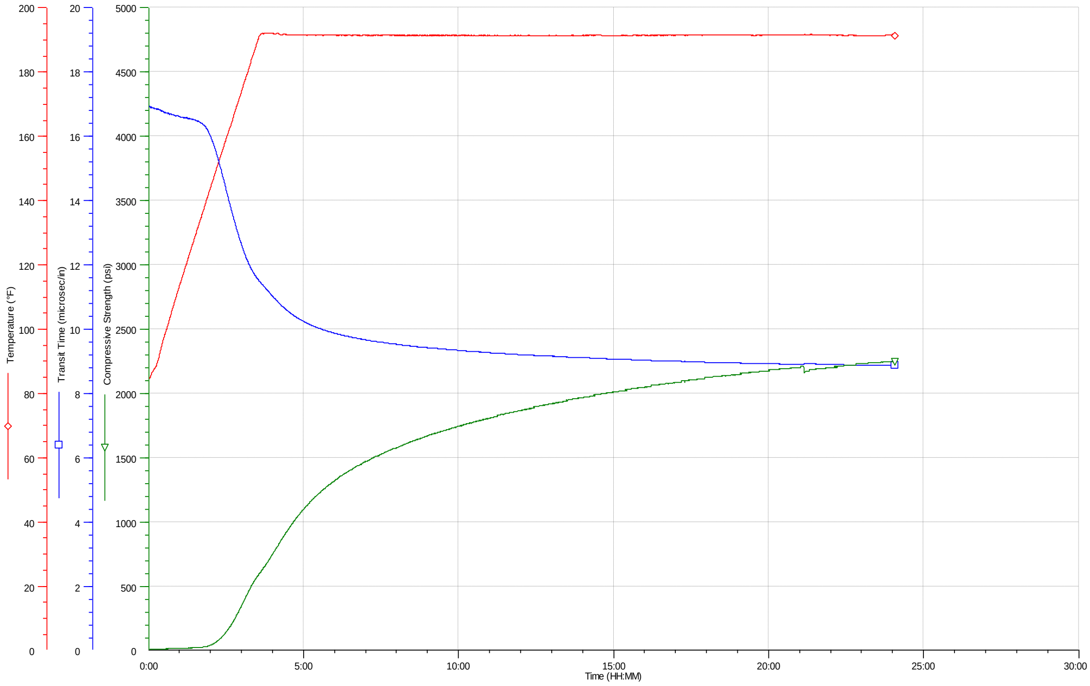

Figure A.1. Cement + 44% Water

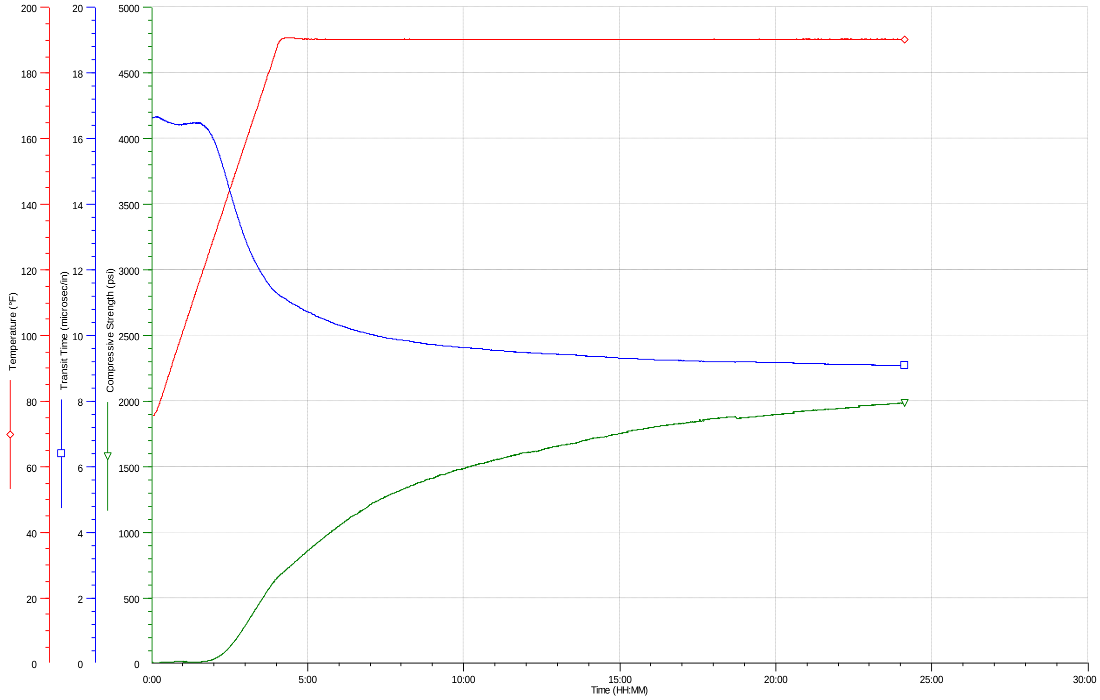

Figure A.2. Cement + 44% Water + 3% NaCl

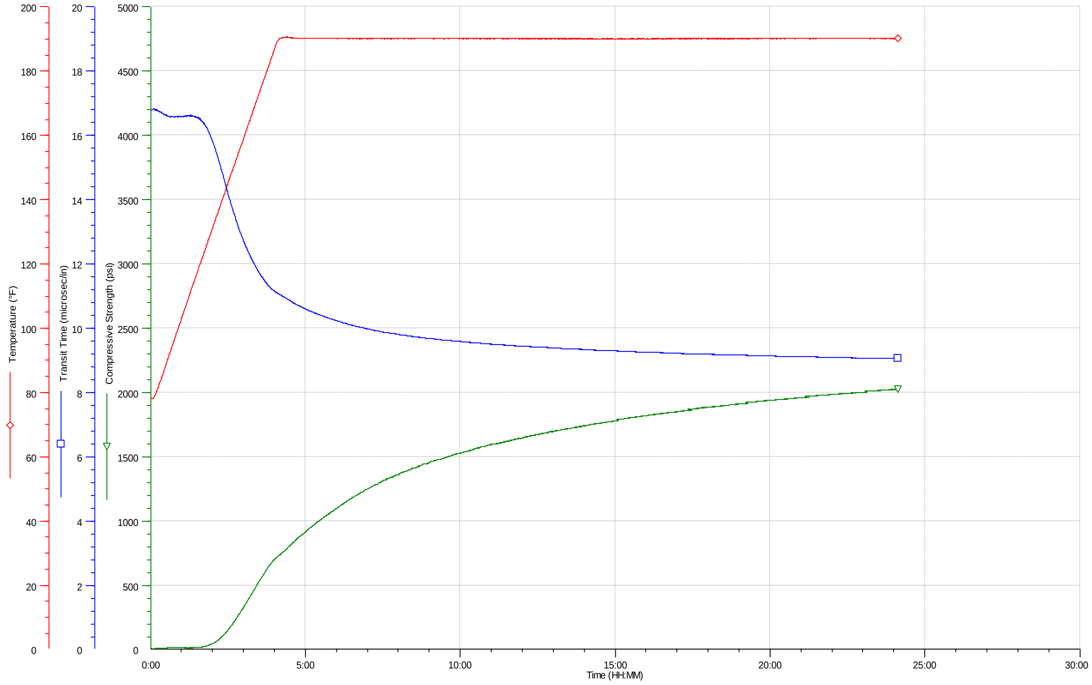

Figure A.3. Cement + 44% Water + 5% NaCl

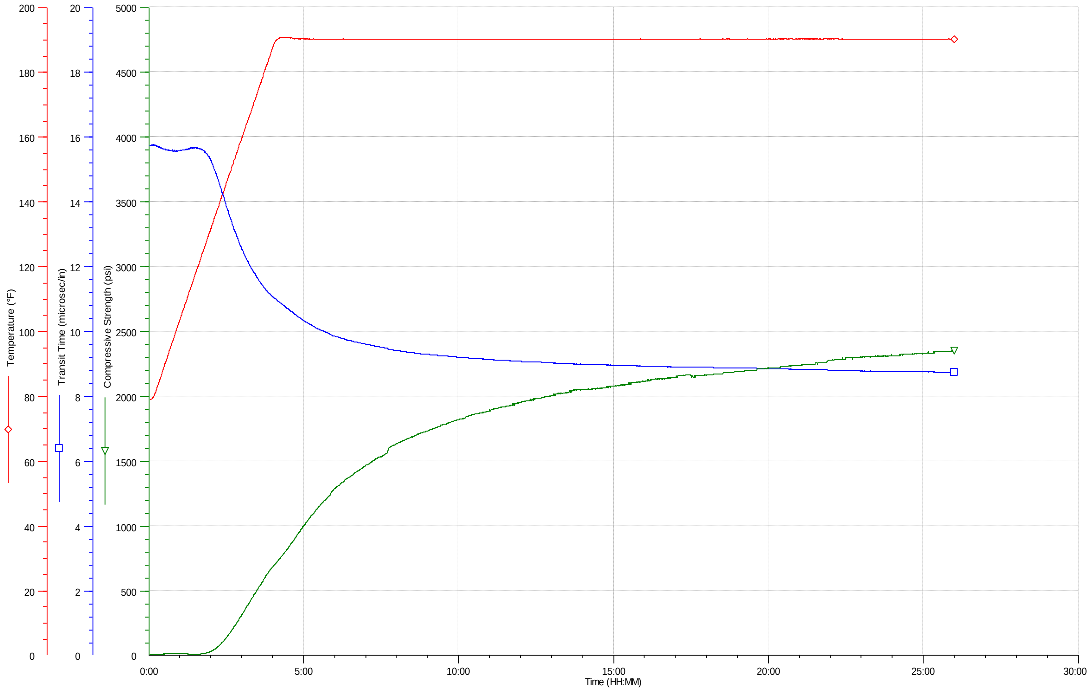

Figure A.4. Cement + 44% Water + 10% NaCl

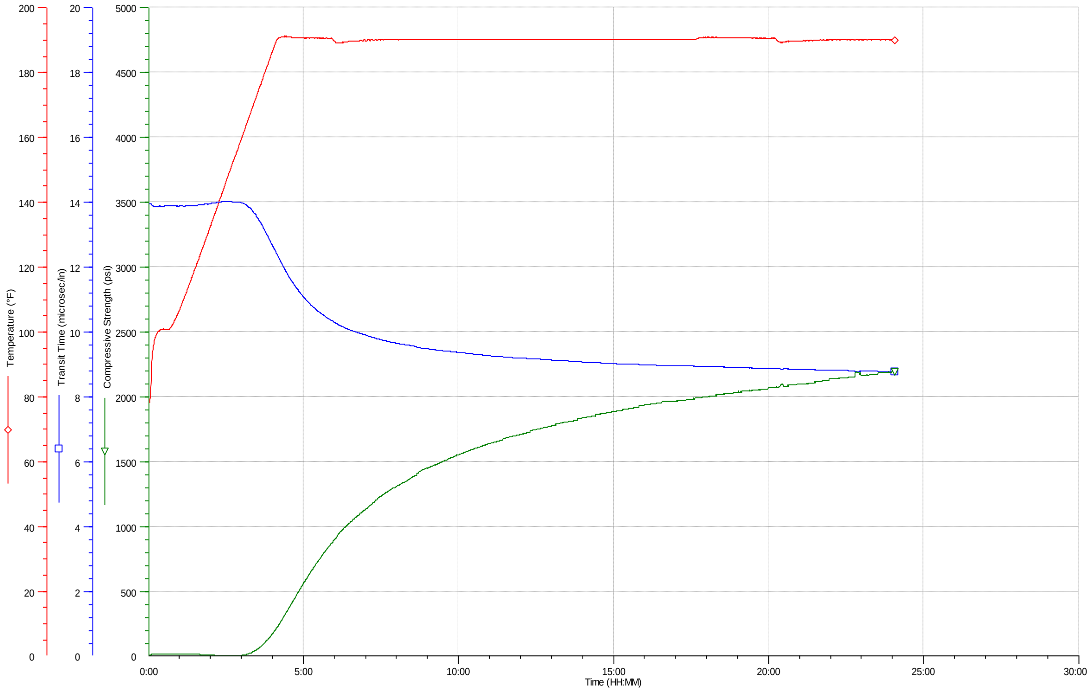

Figure A.5. Cement + 44% Water + 12% NaCl

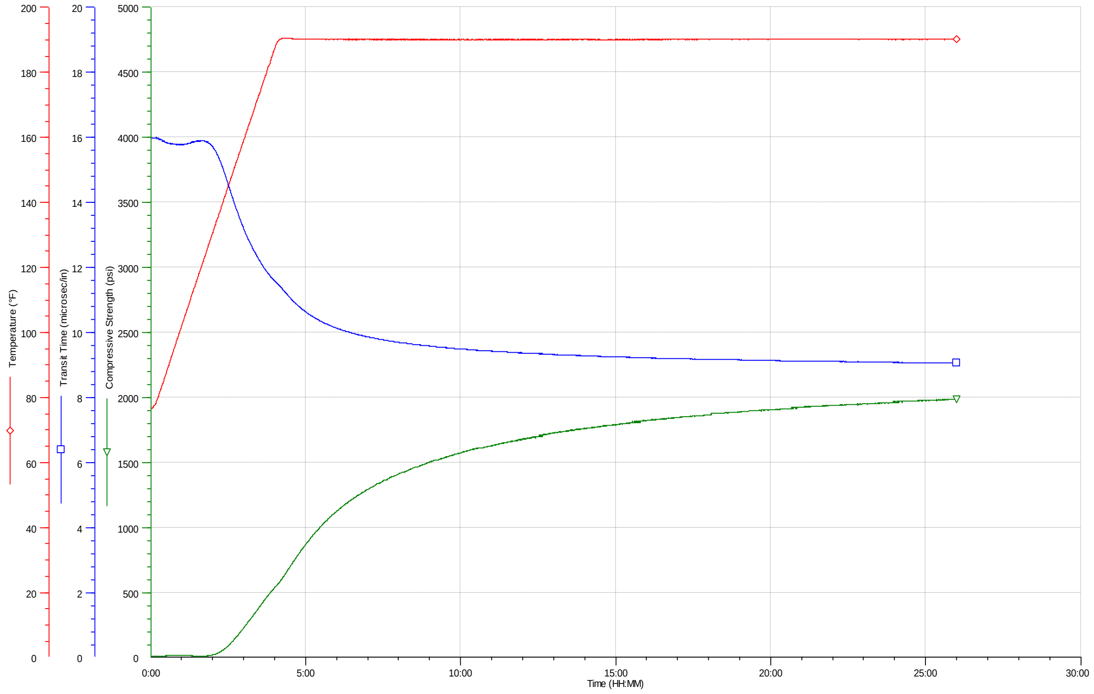

Figure A.6. Cement + 44% Water + 15% NaCl

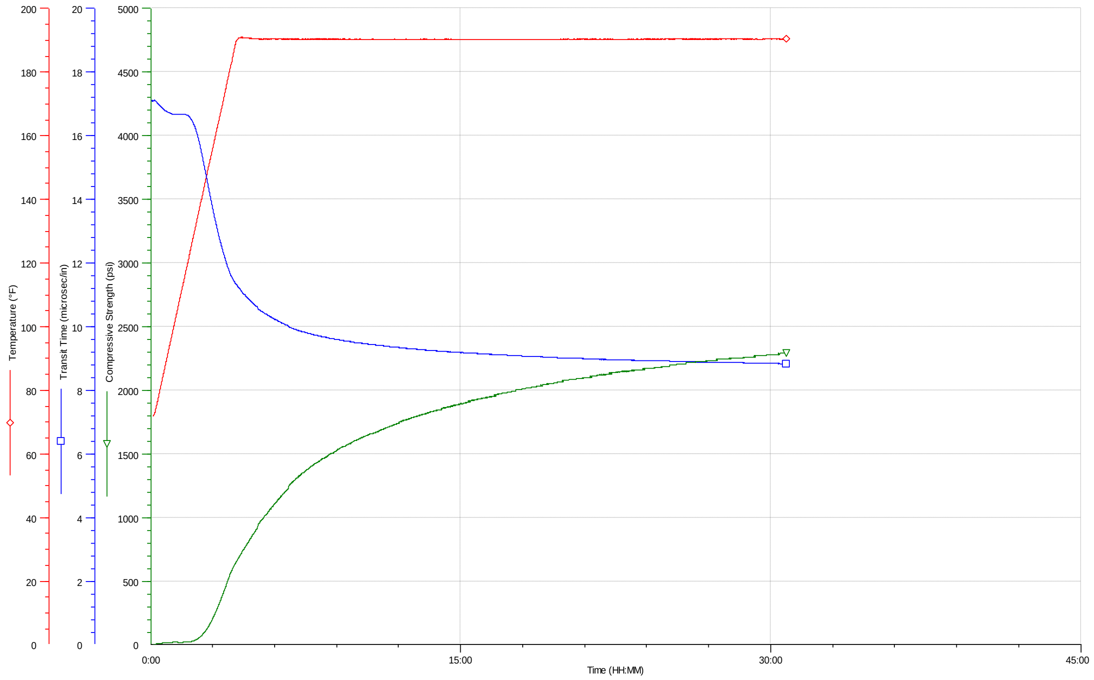

Figure A.7. Cement + 44% Water + 1% KCl

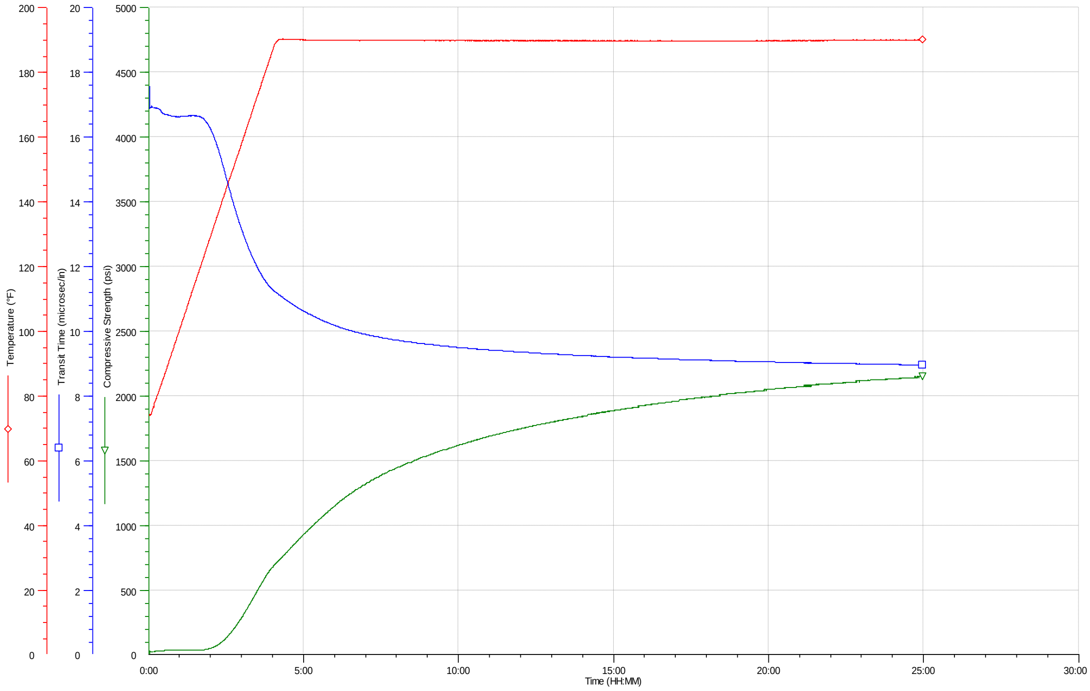

Figure A.8. Cement + 44% Water + 3% KCl

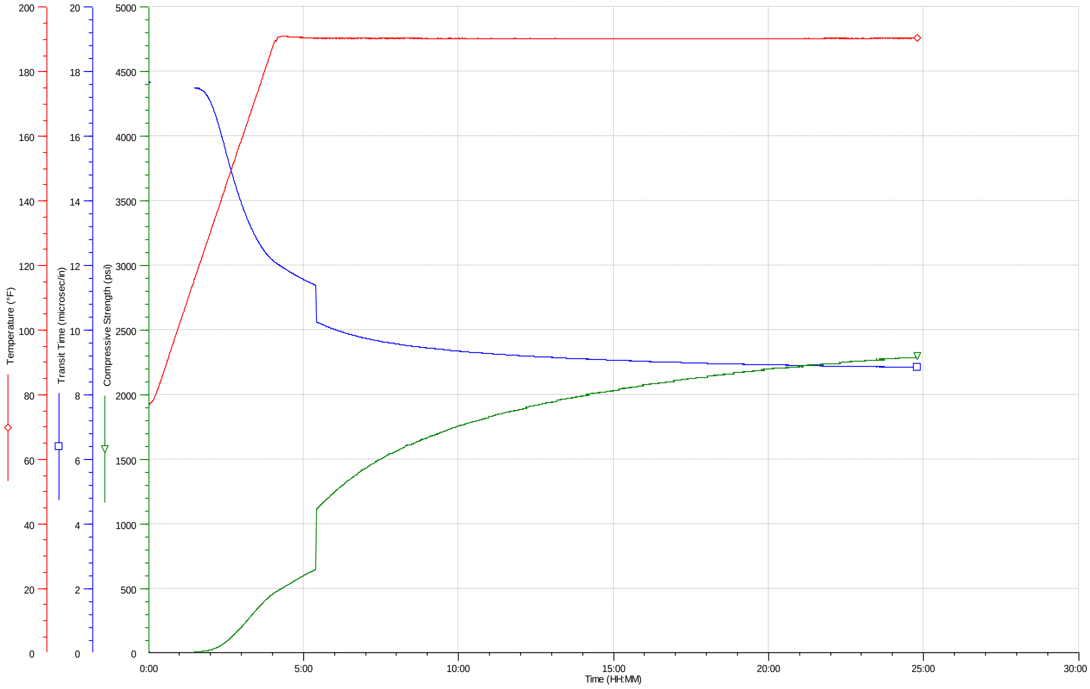

Figure A.9. Cement + 44% Water + 5% KCl

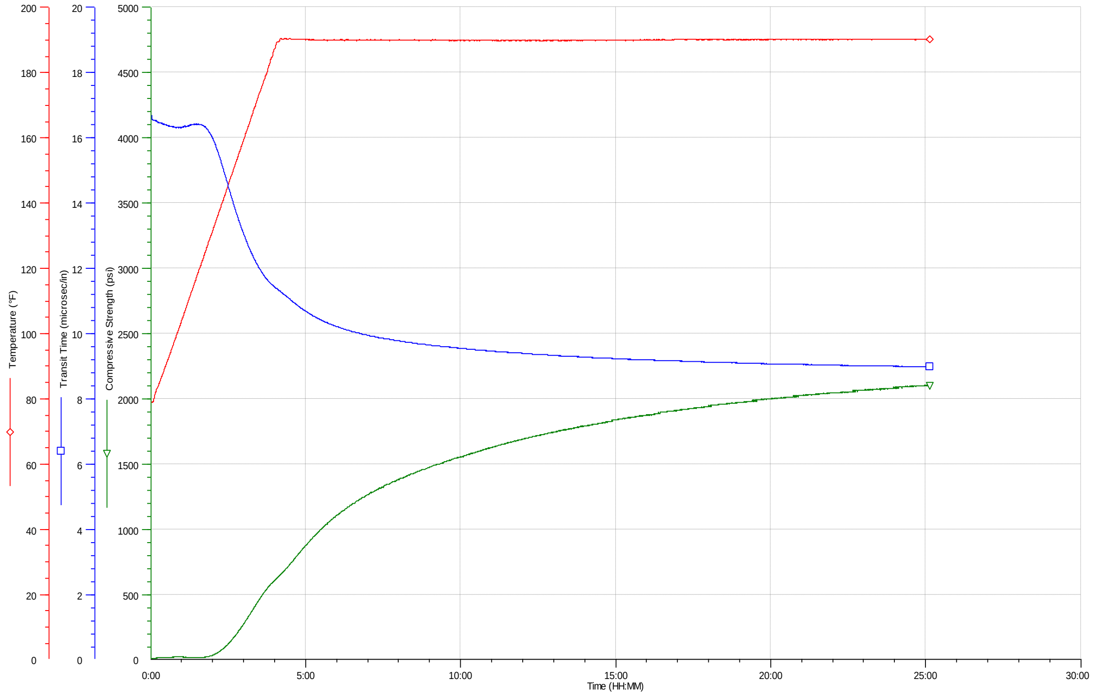

Figure A.10. Cement + 44% Water + 7% KCl

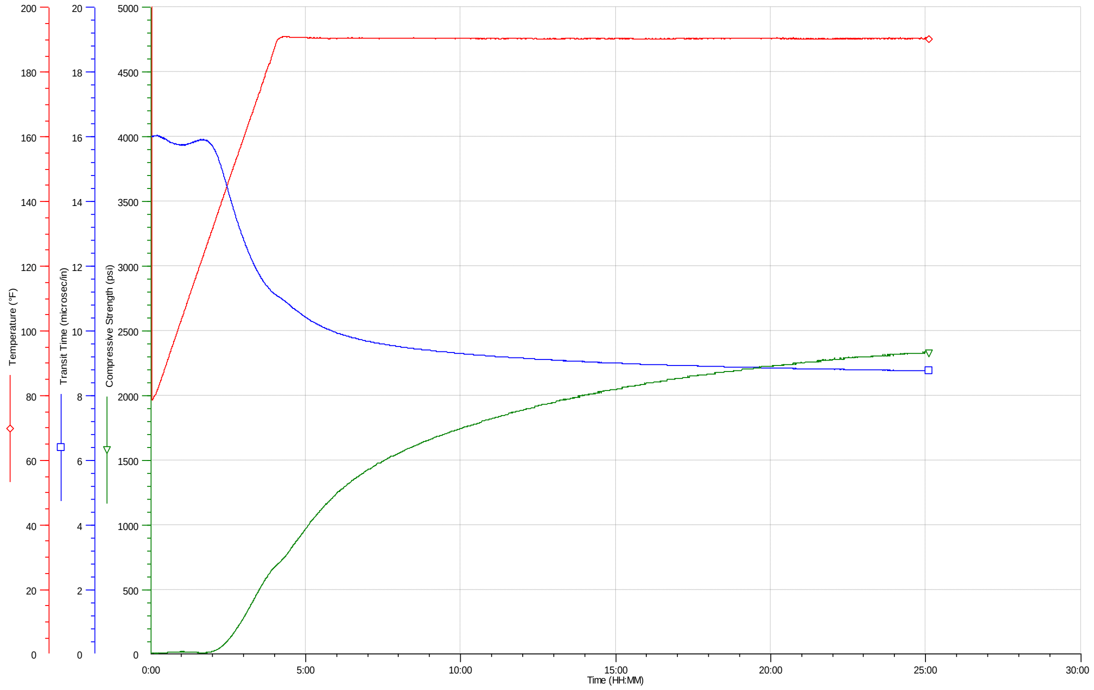

Figure A.11. Cement + 44% Water + 10% KCl

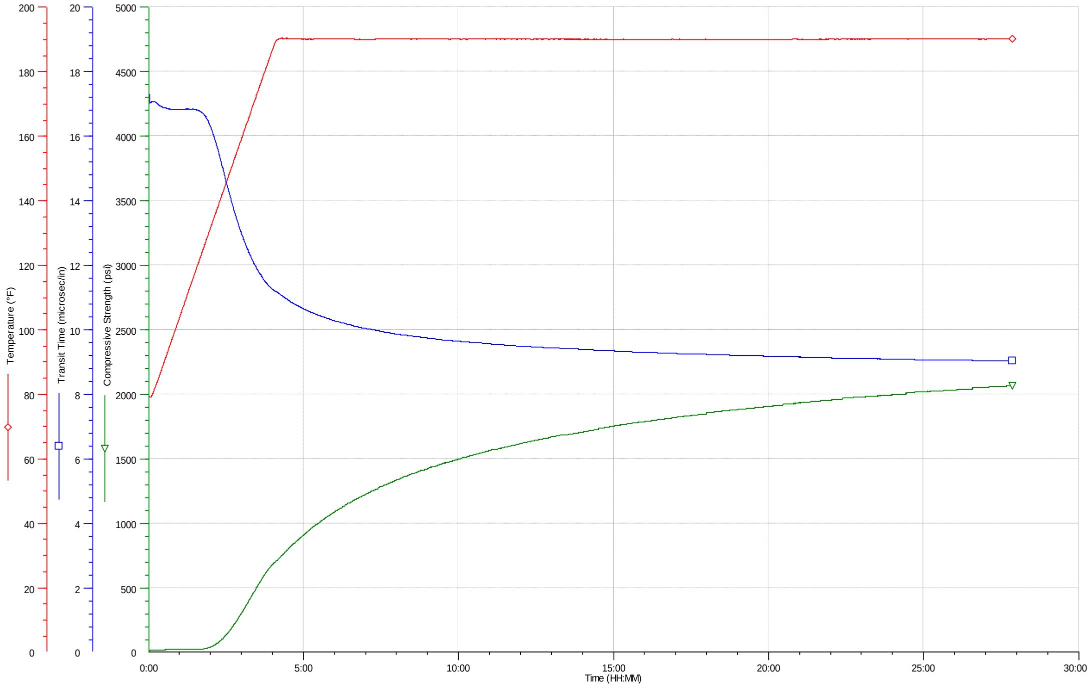

Figure A.12. Cement + 44% Water + 1% $CaCl_2$

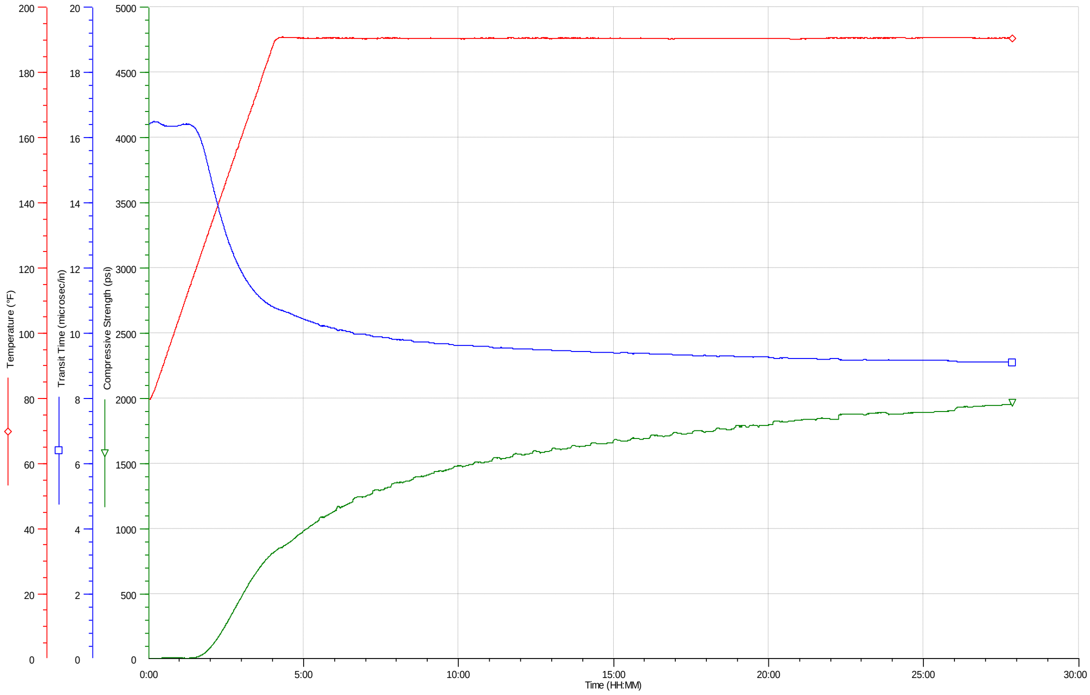

Figure A.13. Cement + 44% Water + 3% $CaCl_2$

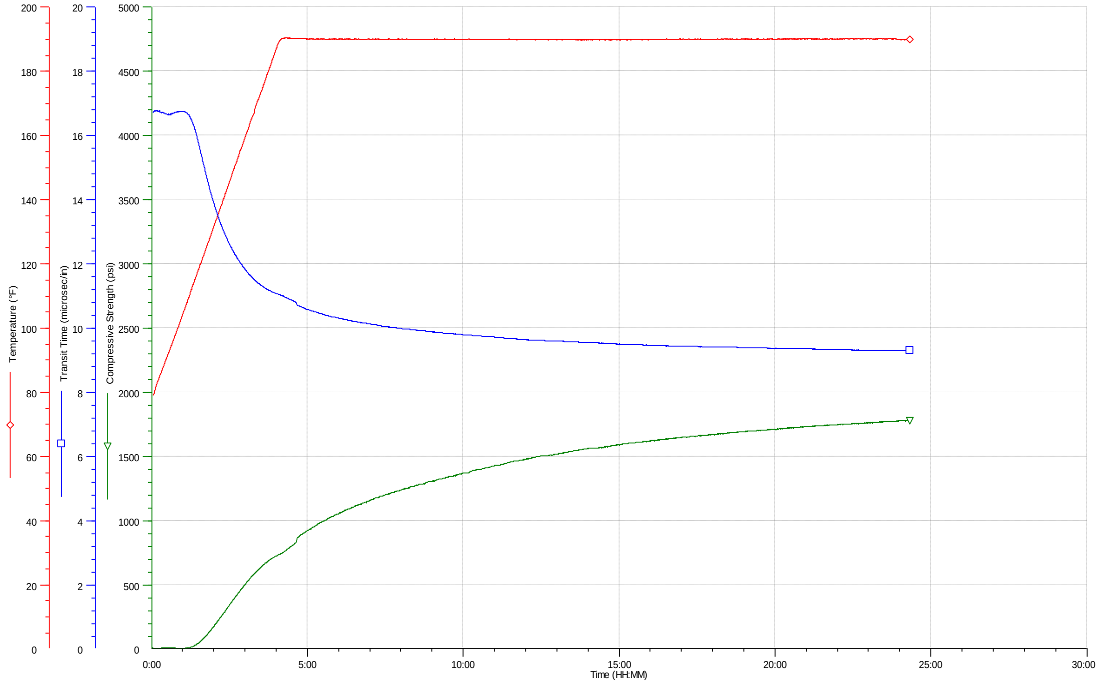

Figure A.14. Cement + 44% Water + 5% $CaCl_2$

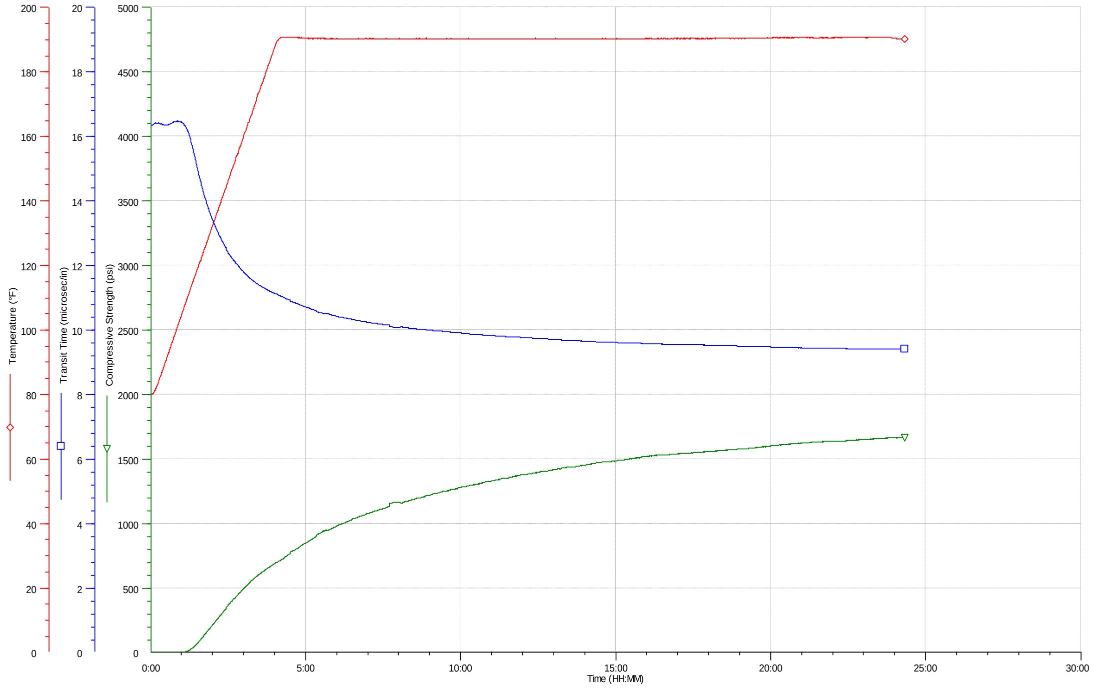

Figure A.15. Cement + 44% Water + 7% $CaCl_2$

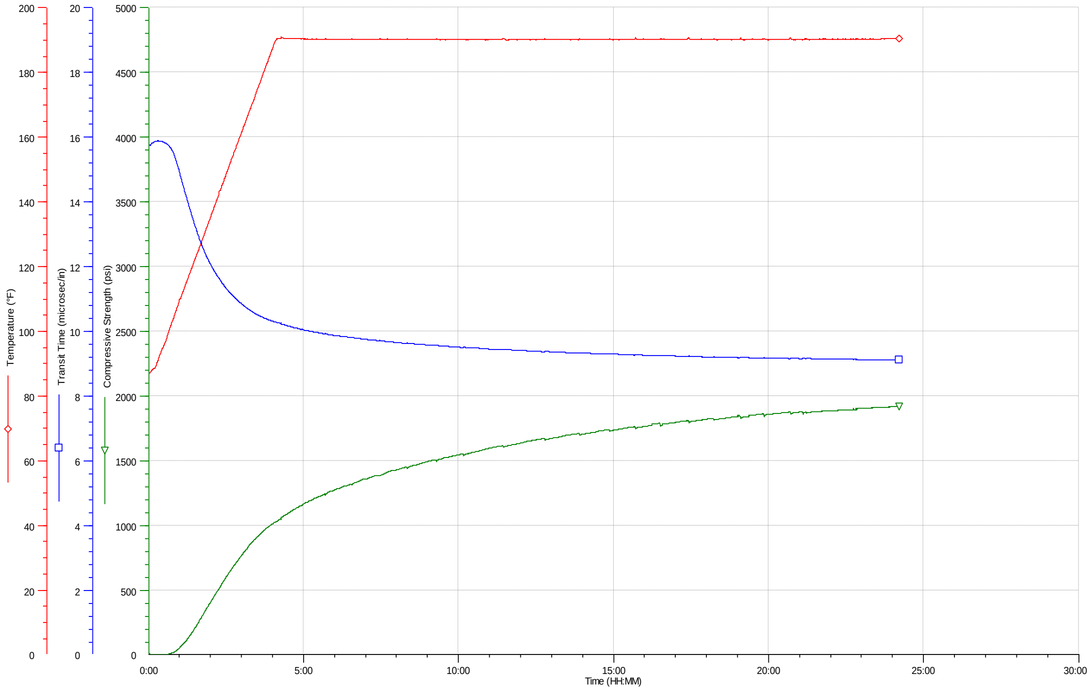

Figure A.16. Cement + 44% Water + 10% $CaCl_2$

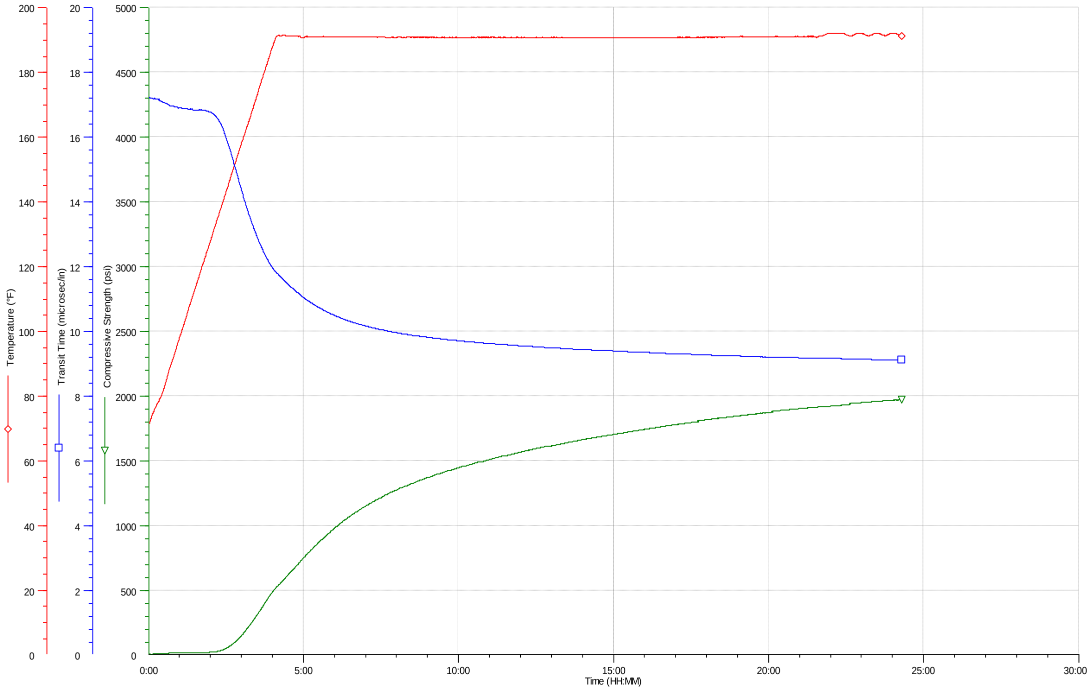

Figure A.17. Cement* + 44% Water

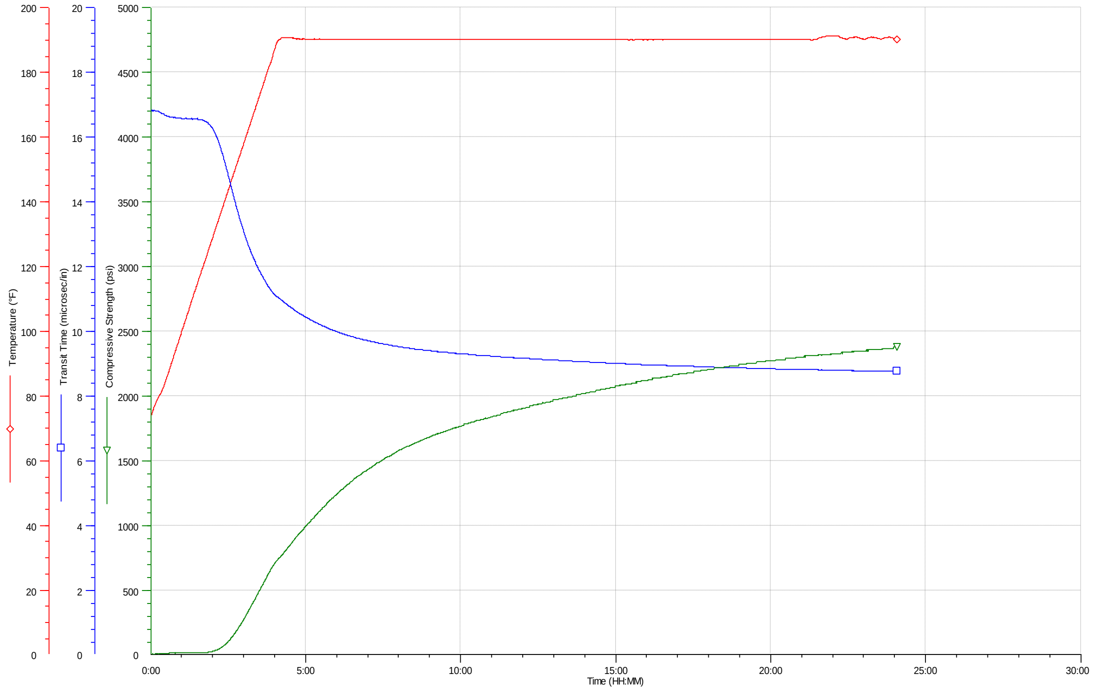

Figure A.18. Cement* + 44% Water + 1% NaCl

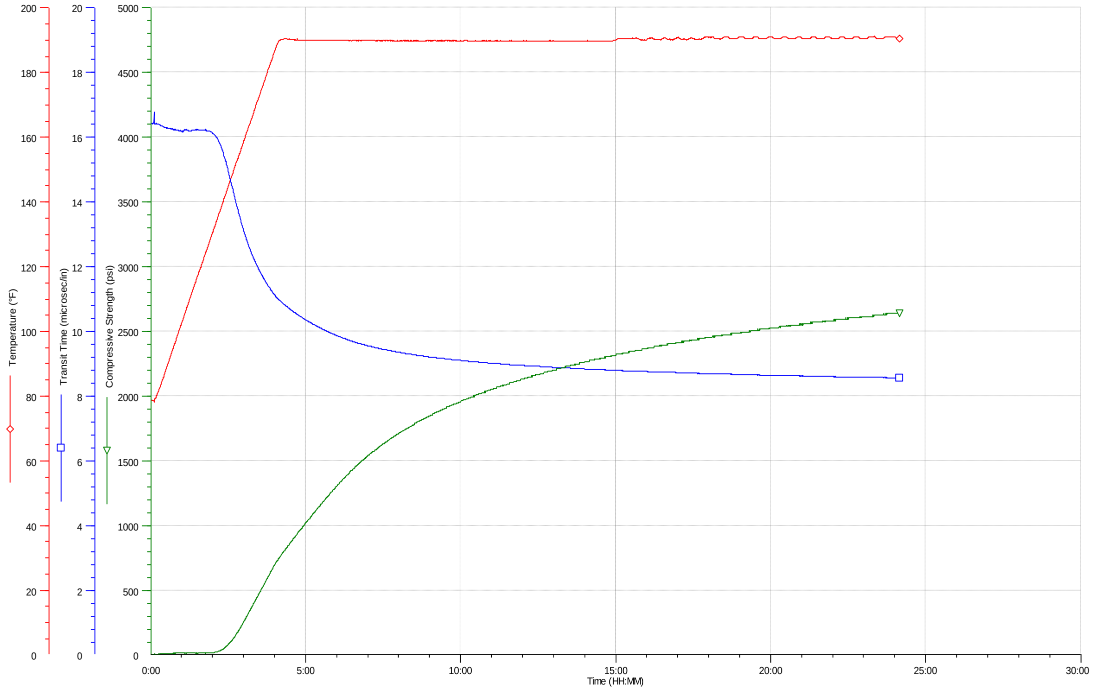

Figure A.19. Cement* + 44% Water + 3% NaCl

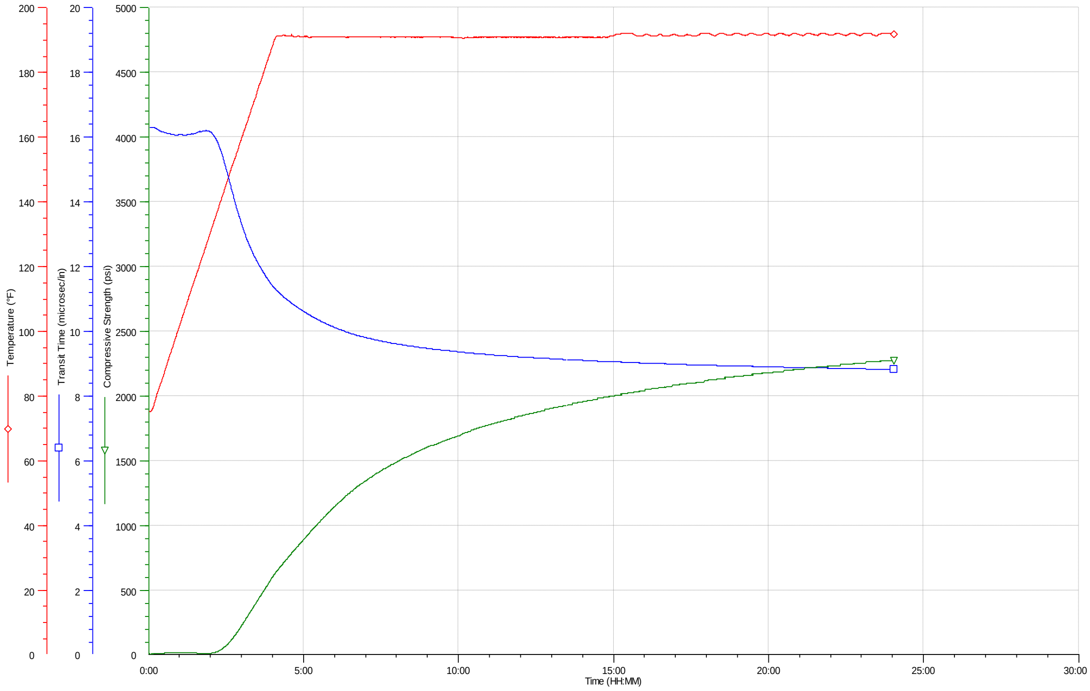

Figure A.20. Cement* + 44% Water + 5% NaCl

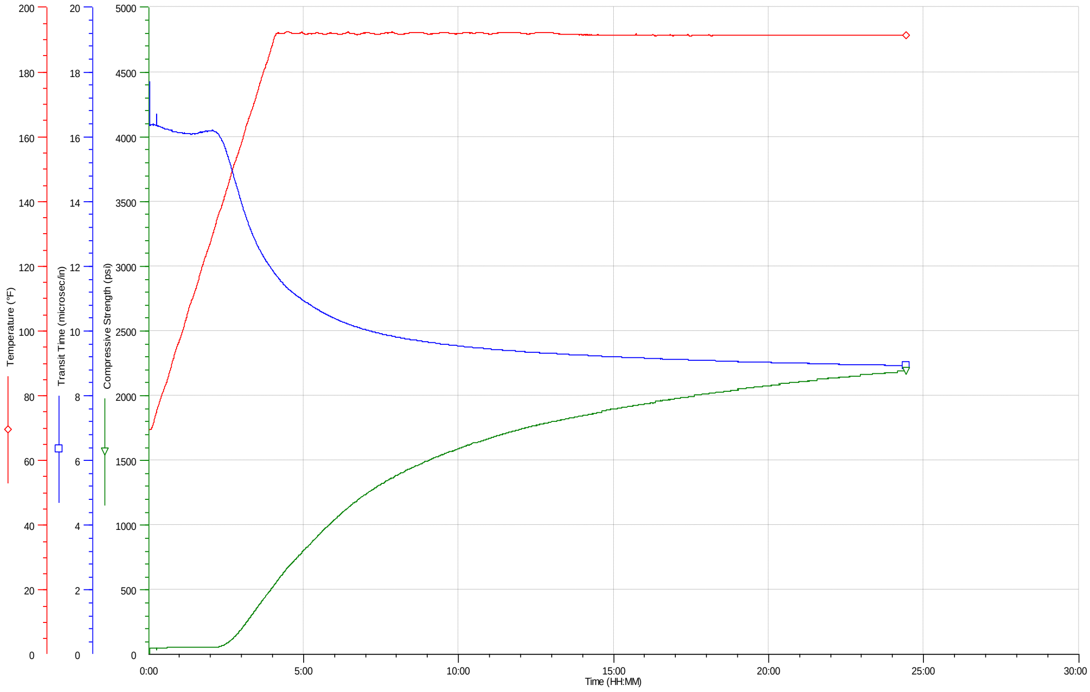

Figure A.21. Cement* + 44% Water + 7% NaCl

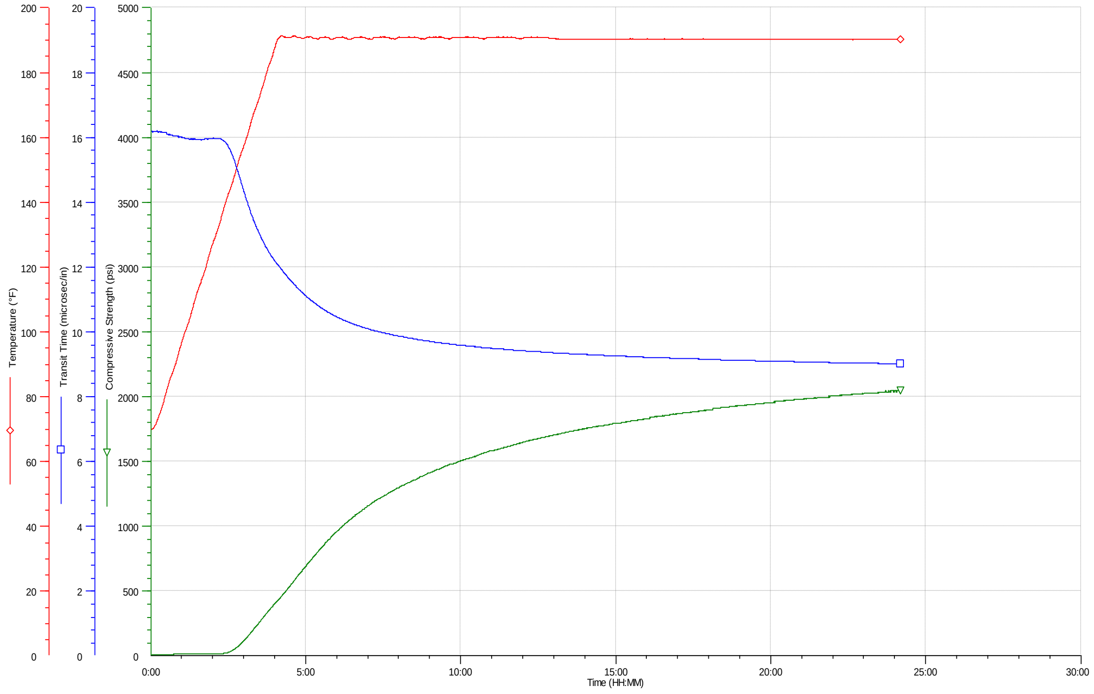

Figure A.22. Cement* + 44% Water + 10% NaCl

B. THICKENING TIME OF CEMENT SLURIES BY HPHT CONSISTOMETER

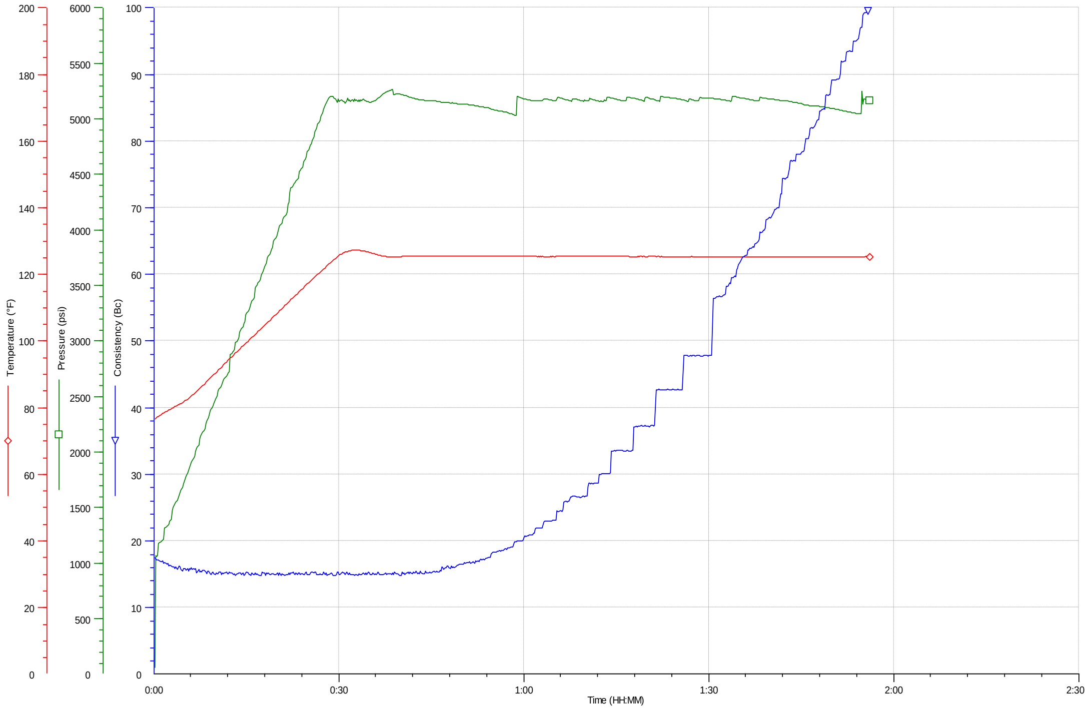

Figure B.1. Cement + 44% Water

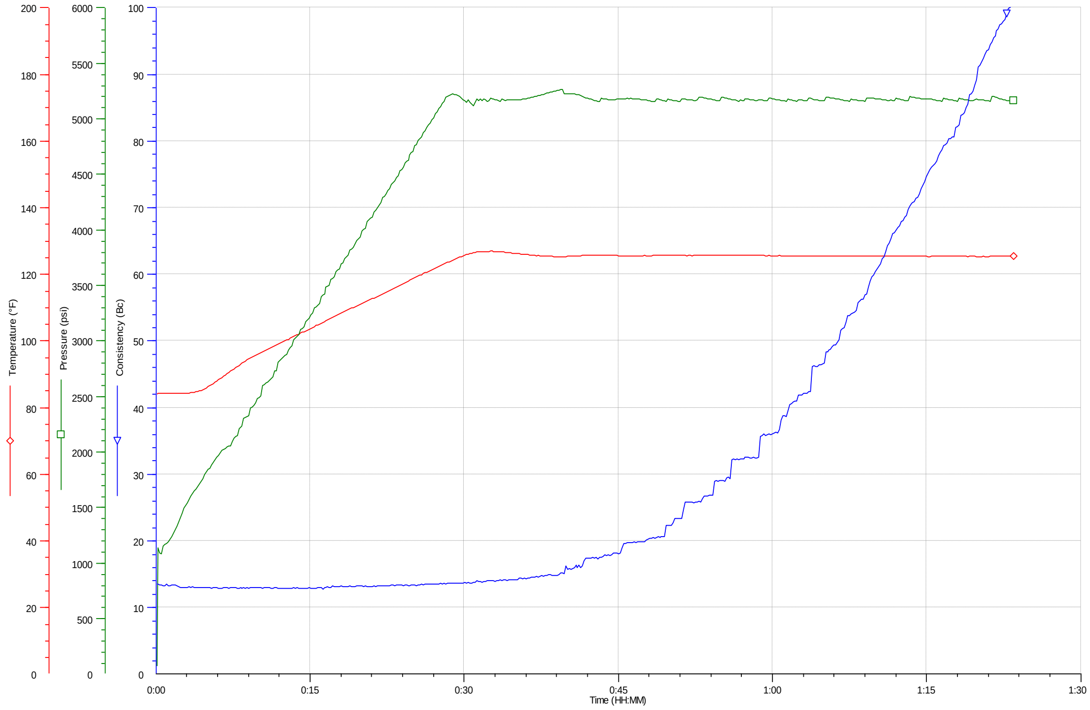

Figure B.2. Cement + 44% Water + 3% NaCl

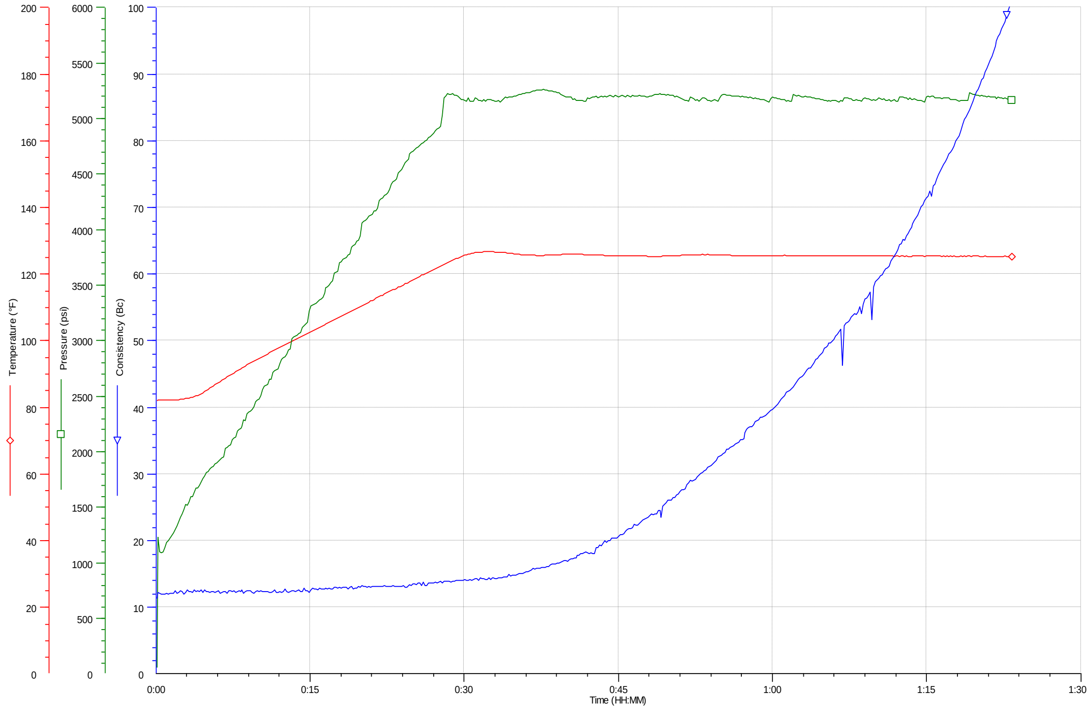

Figure B.3. Cement + 44% Water + 5% NaCl

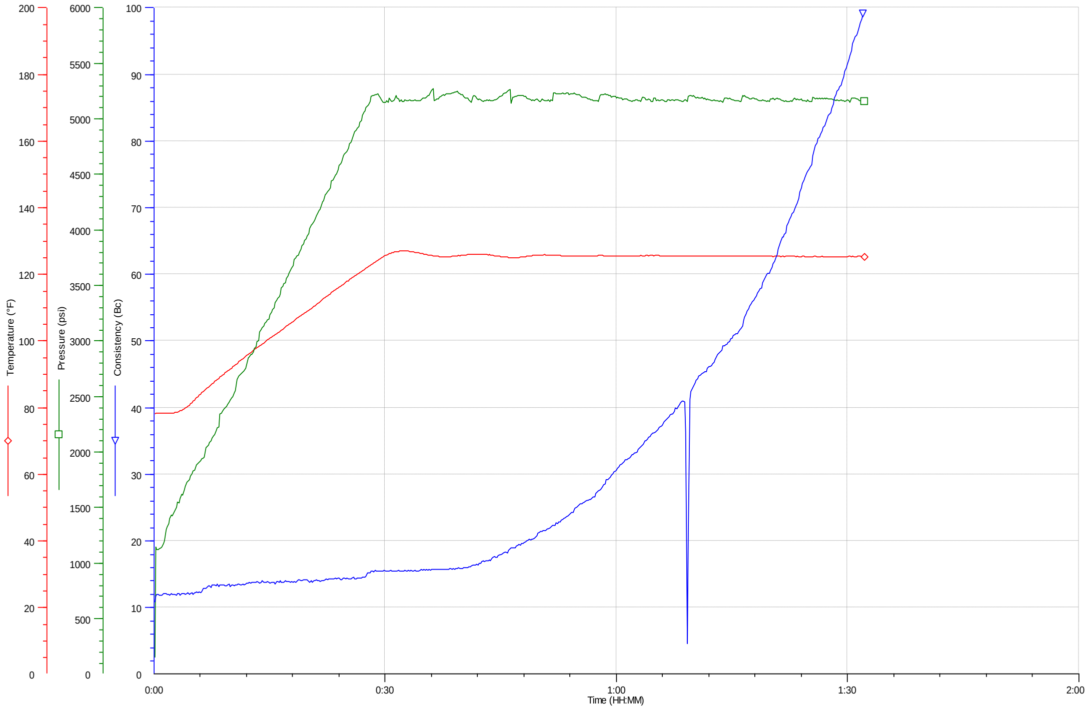

Figure B.4. Cement + 44% Water + 10% NaCl

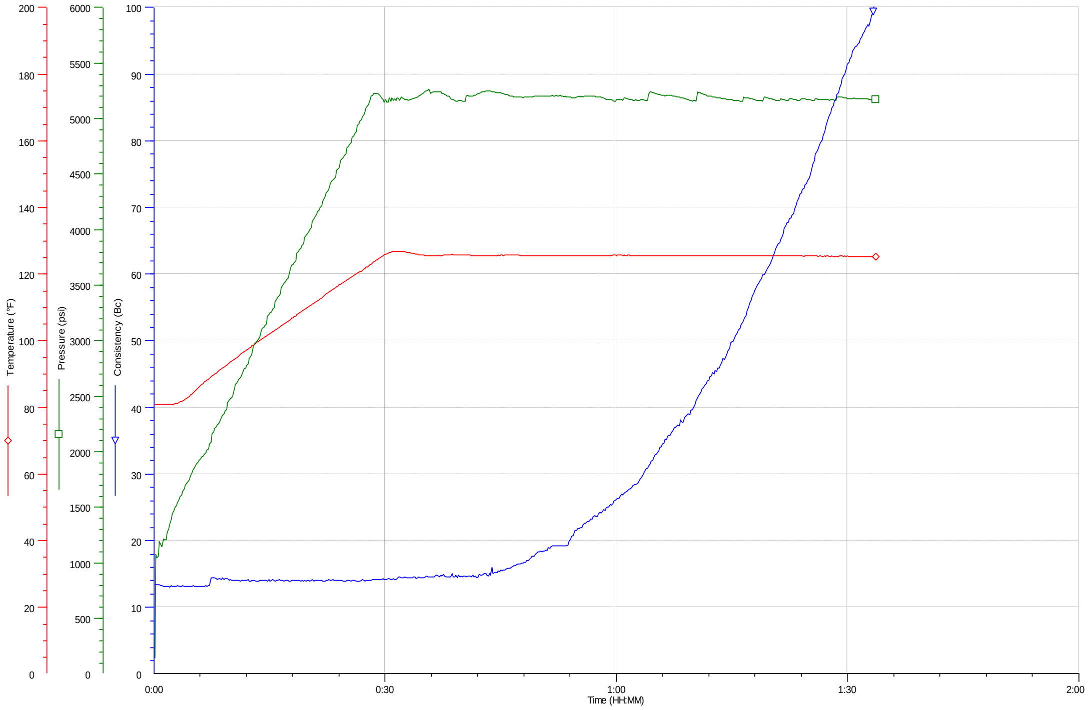

Figure B.5. Cement + 44% Water + 12% NaCl

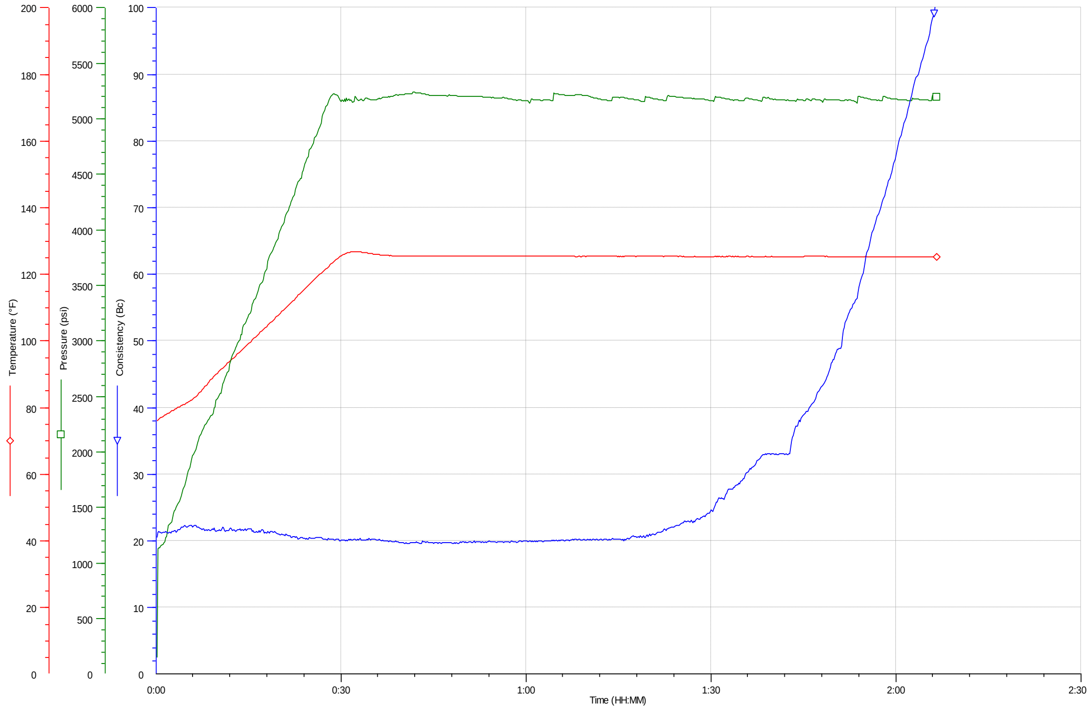

Figure B.6. Cement + 44% Water + 12% NaCl

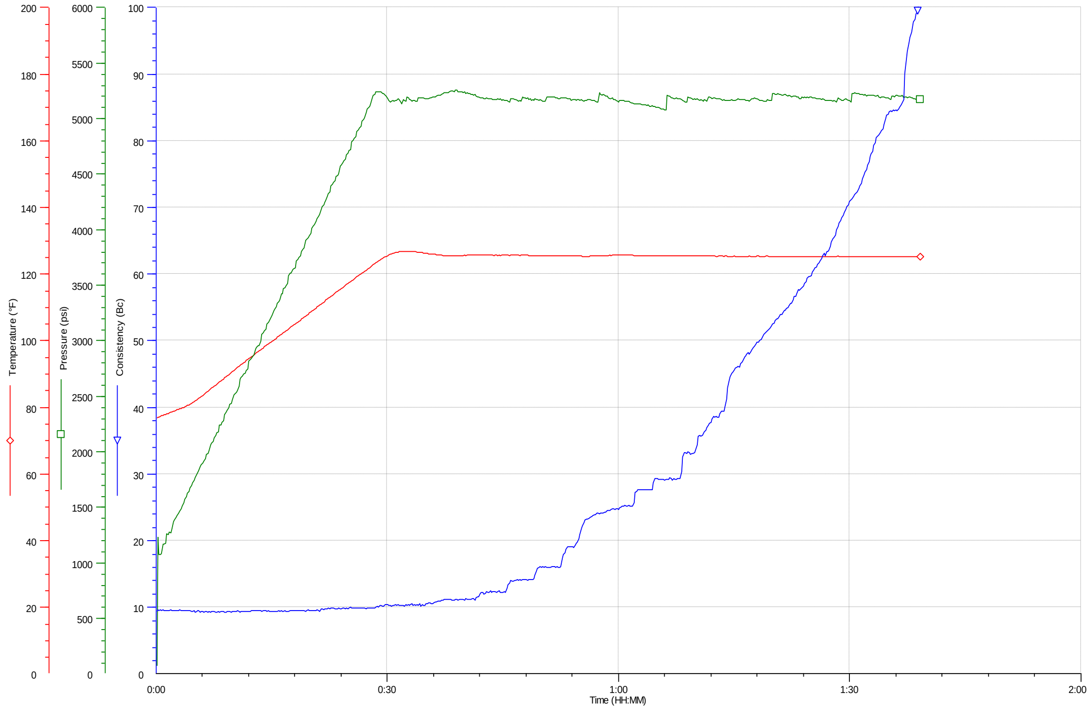

Figure B.7. Cement + 44% Water + 1% KCl

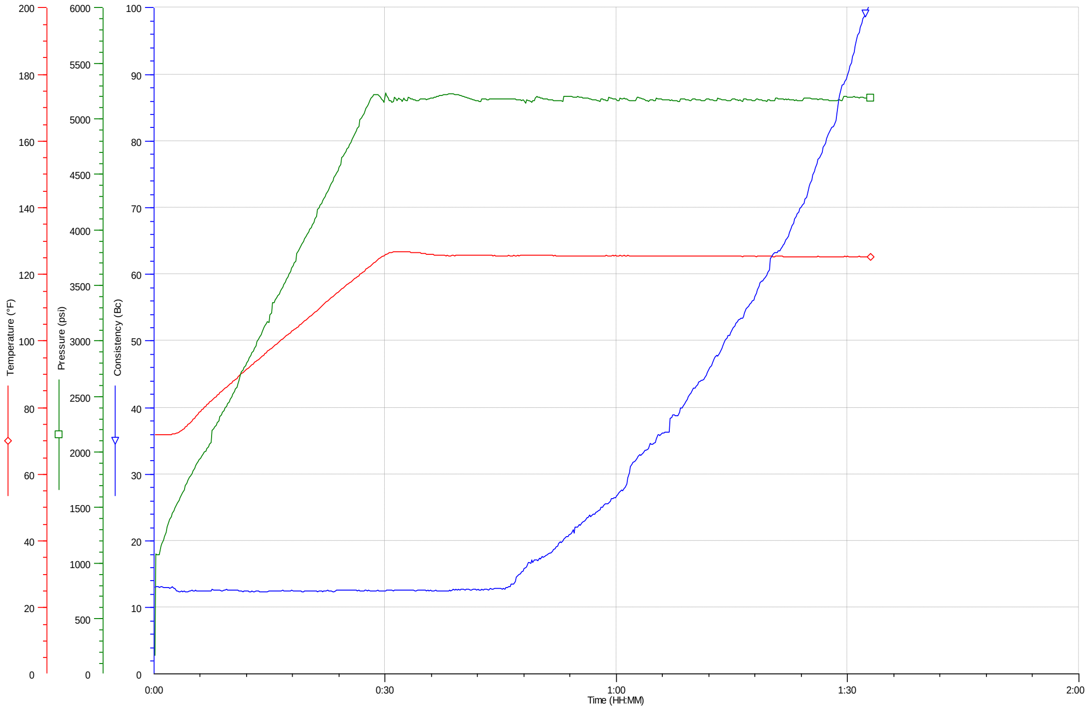

Figure B.8. Cement + 44% Water + 3% KCl

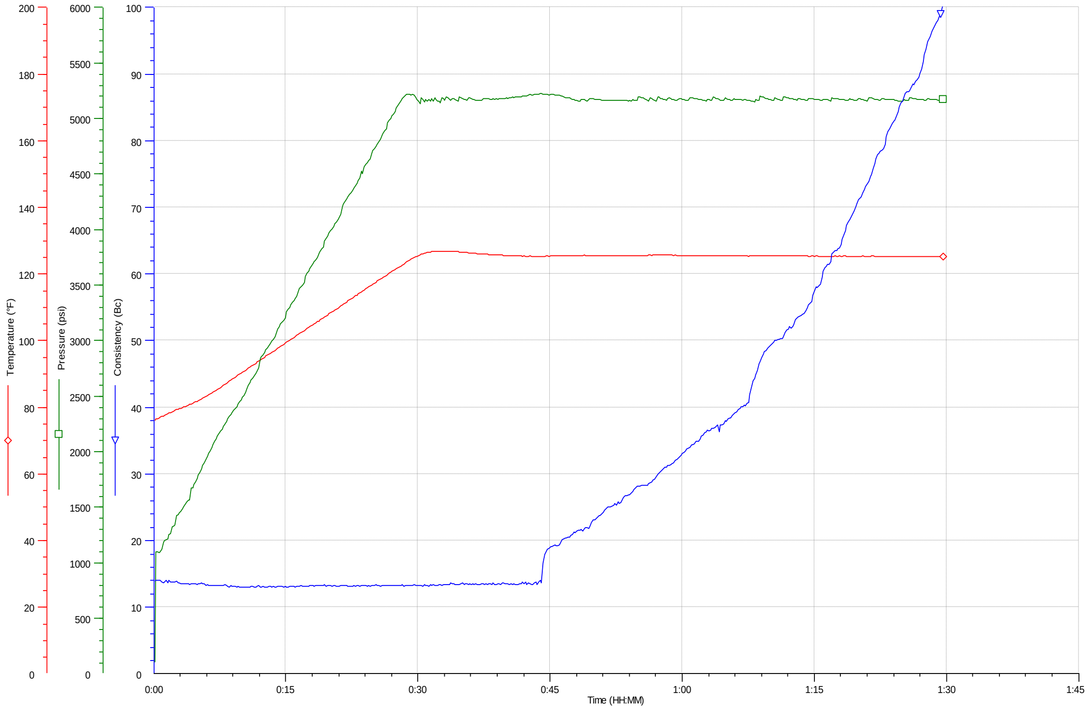

Figure B.9. Cement + 44% Water + 5% KCl

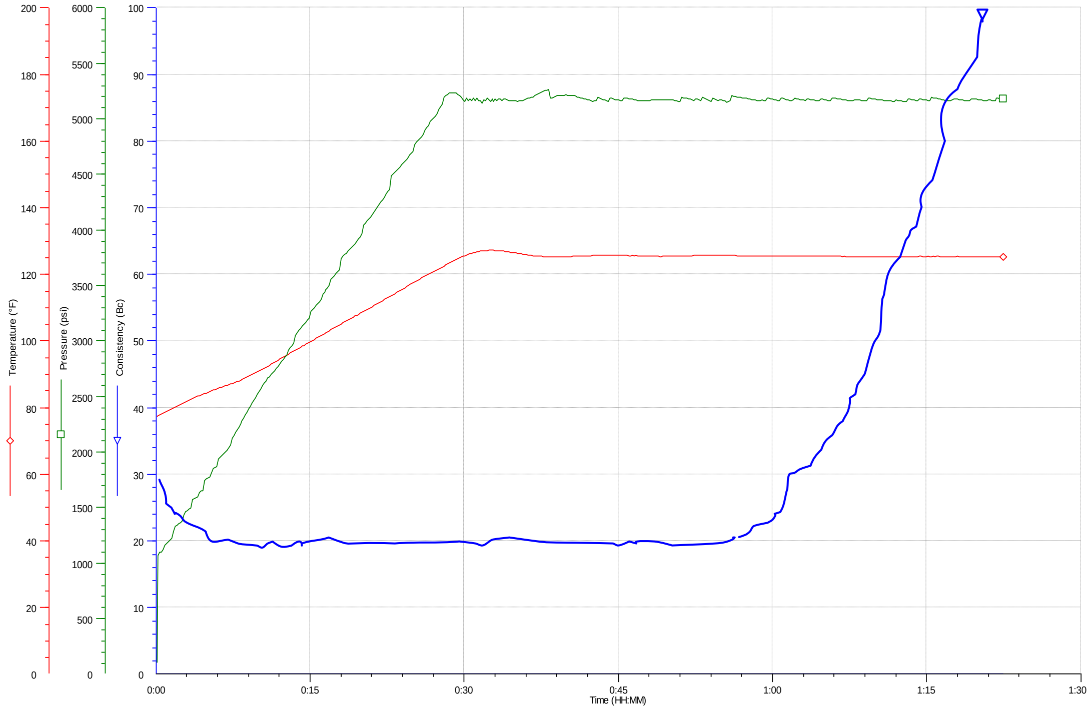

Figure B.10. Cement + 44% Water + 7% KCl

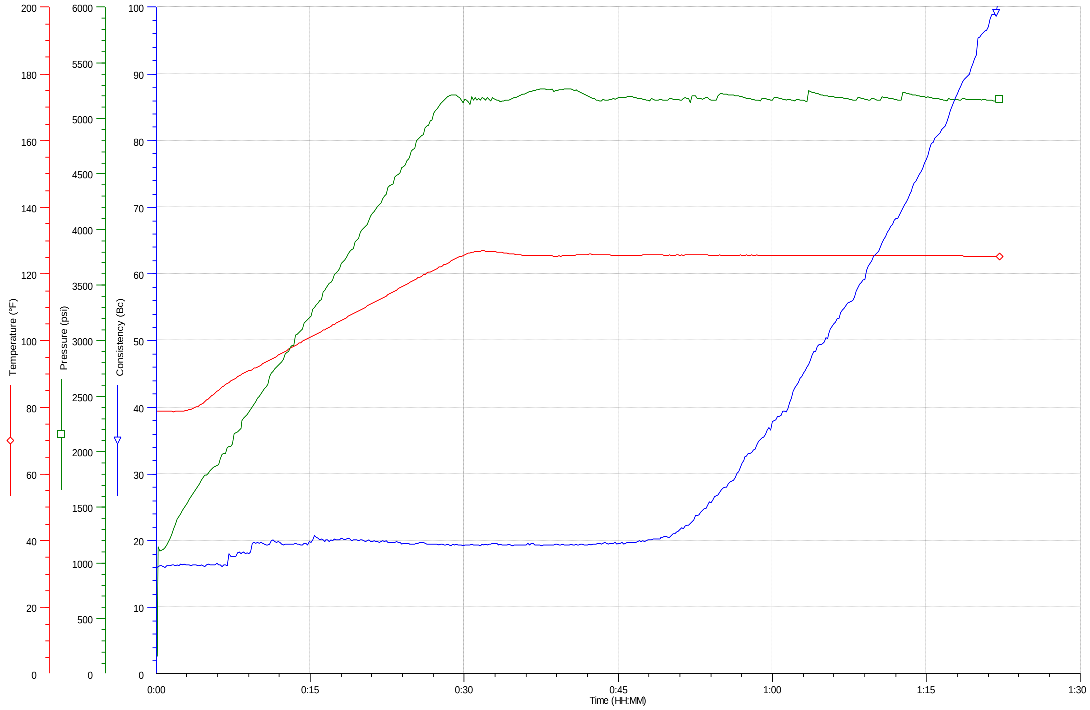

Figure B.11. Cement + 44% Water + 10% KCl

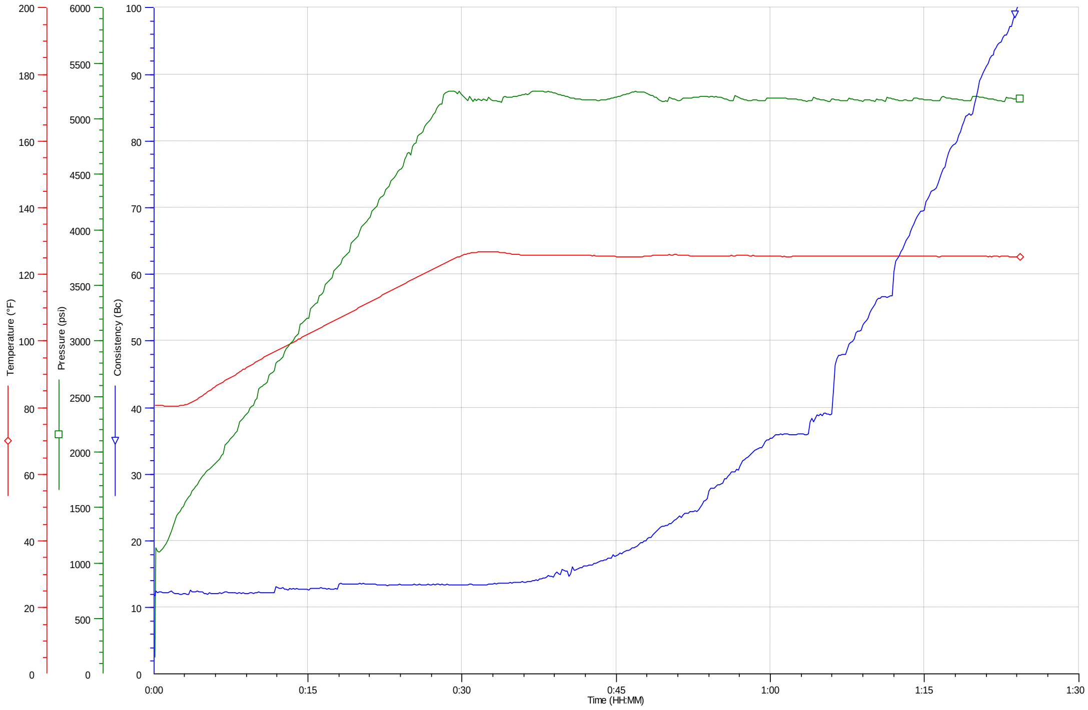

Figure B.12. Cement + 44% Water + 1% $CaCl_2$

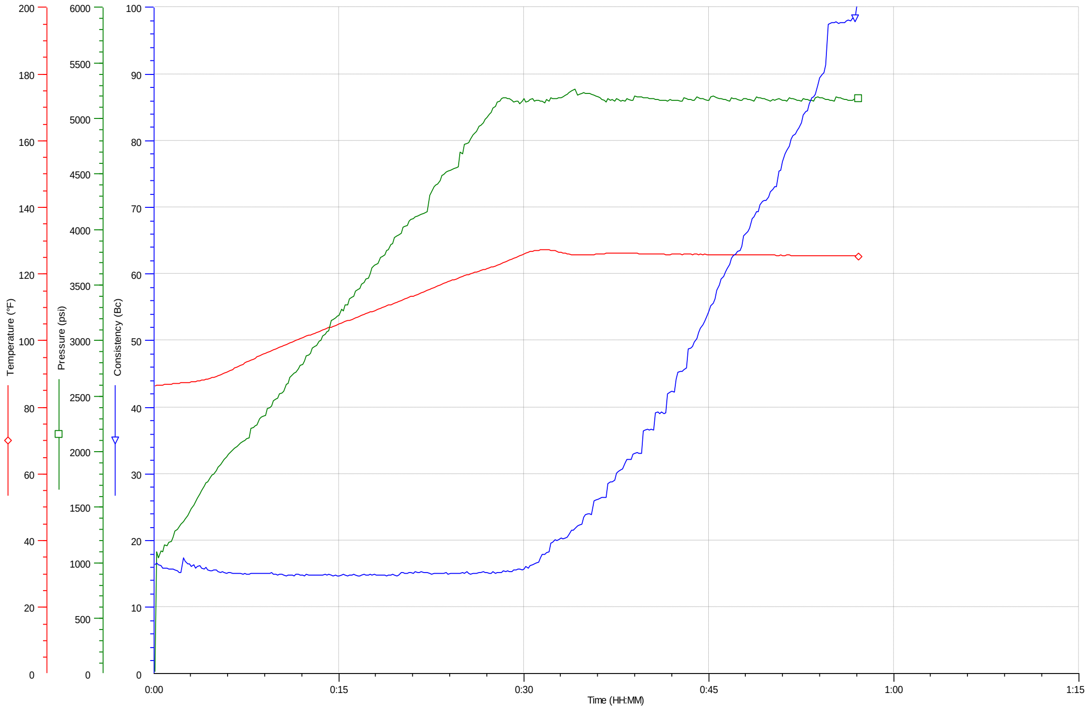

Figure B.13. Cement + 44% Water + 3% $CaCl_2$

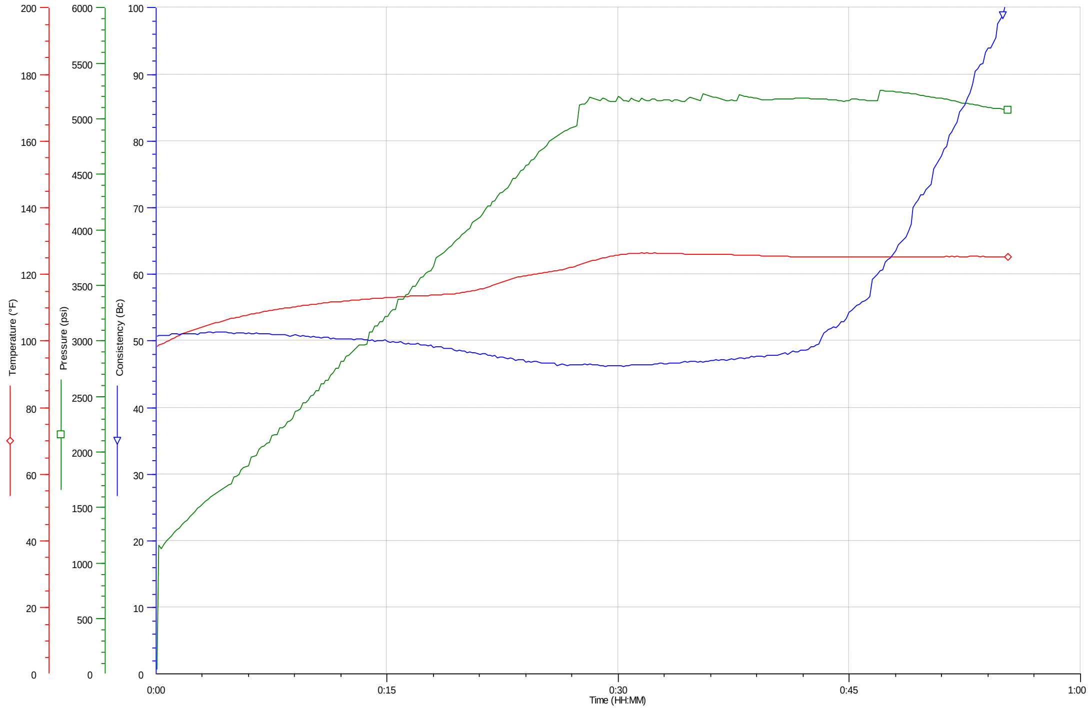

Figure B.14. Cement + 44% Water + 5% $CaCl_2$

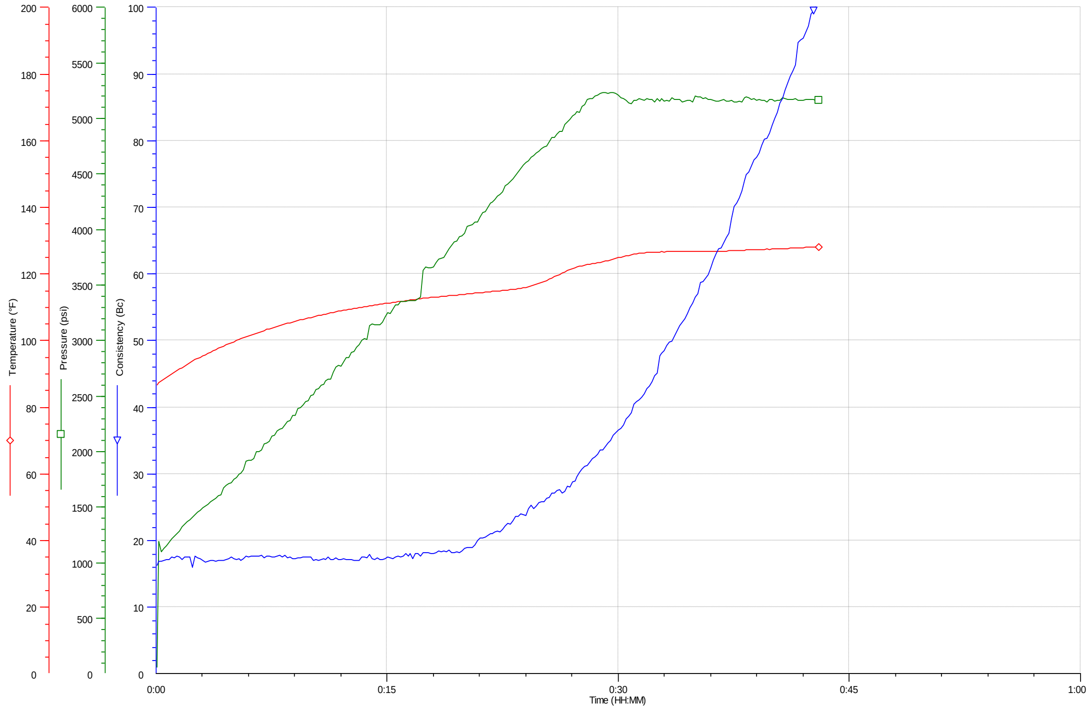

Figure B.15. Cement + 44% Water + 7% $CaCl_2$

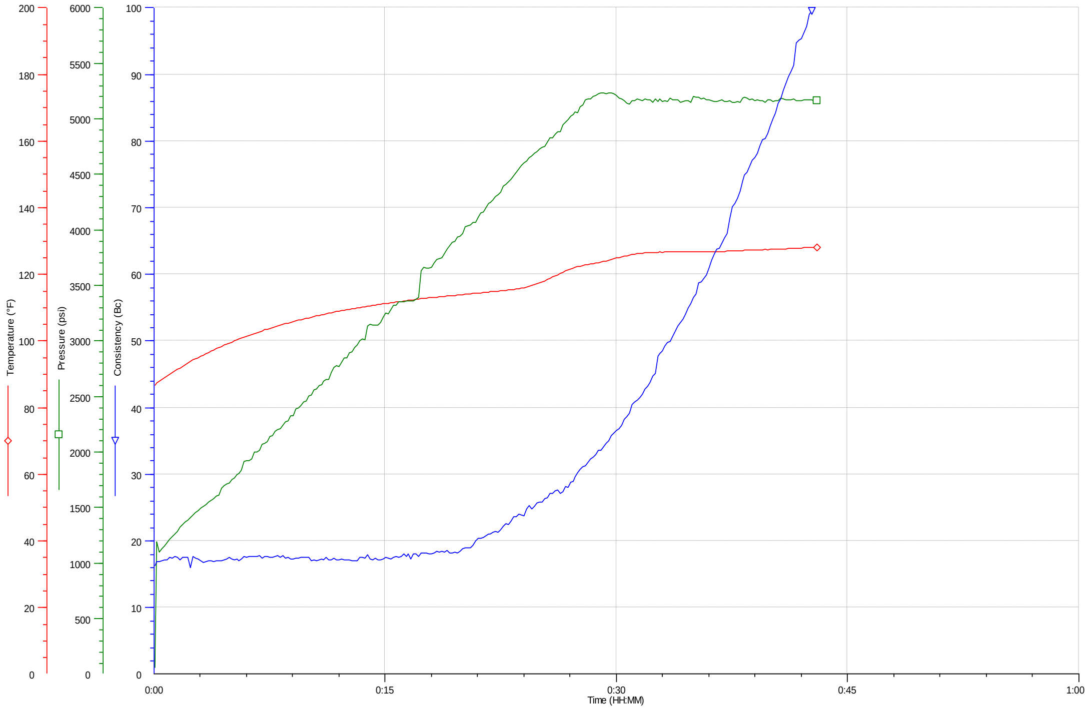

Figure B.16. Cement + 44% Water + 10% $CaCl_2$

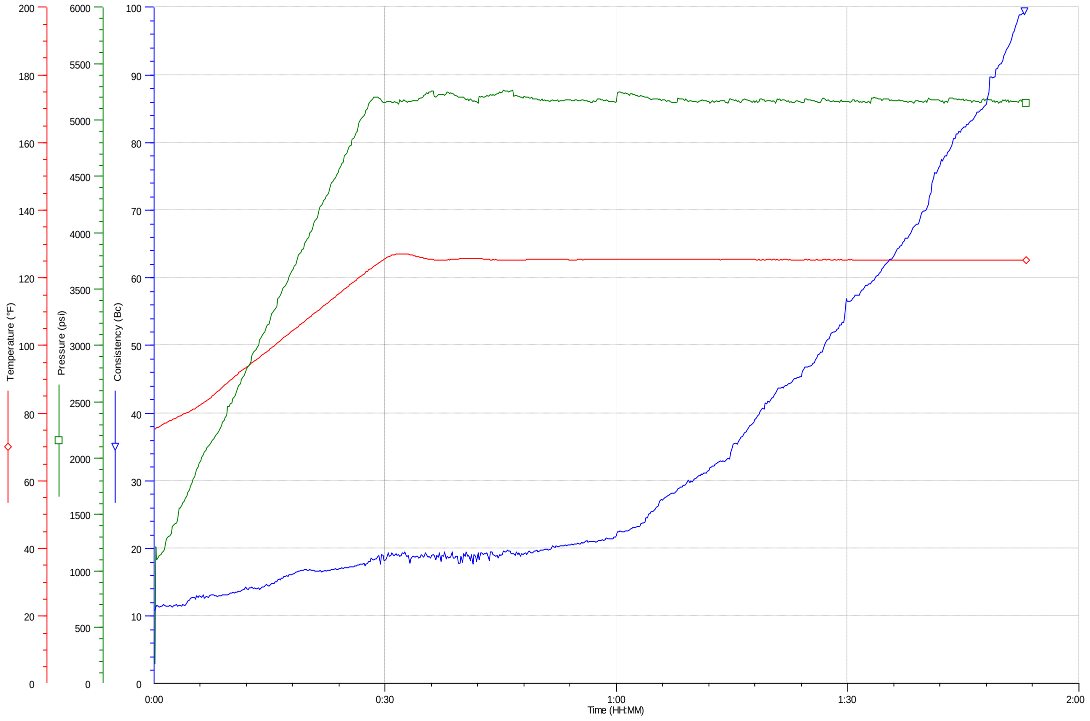

Figure B.17. Cement* + 44% Water

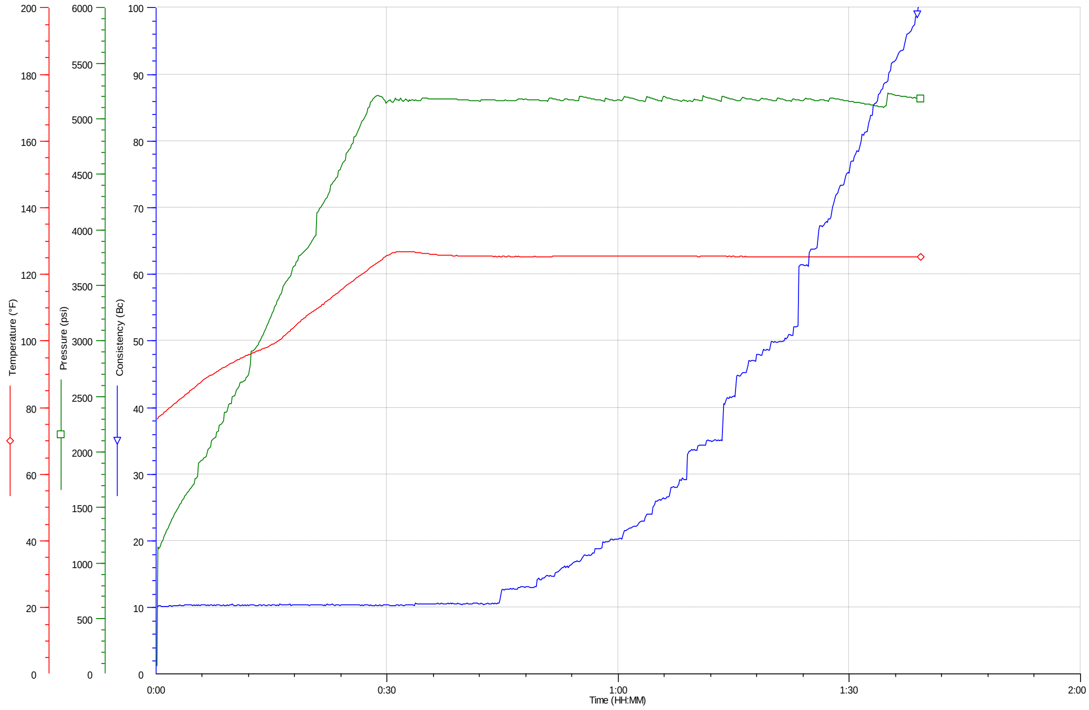

Figure B.18. Cement* + 44% Water + 1% NaCl

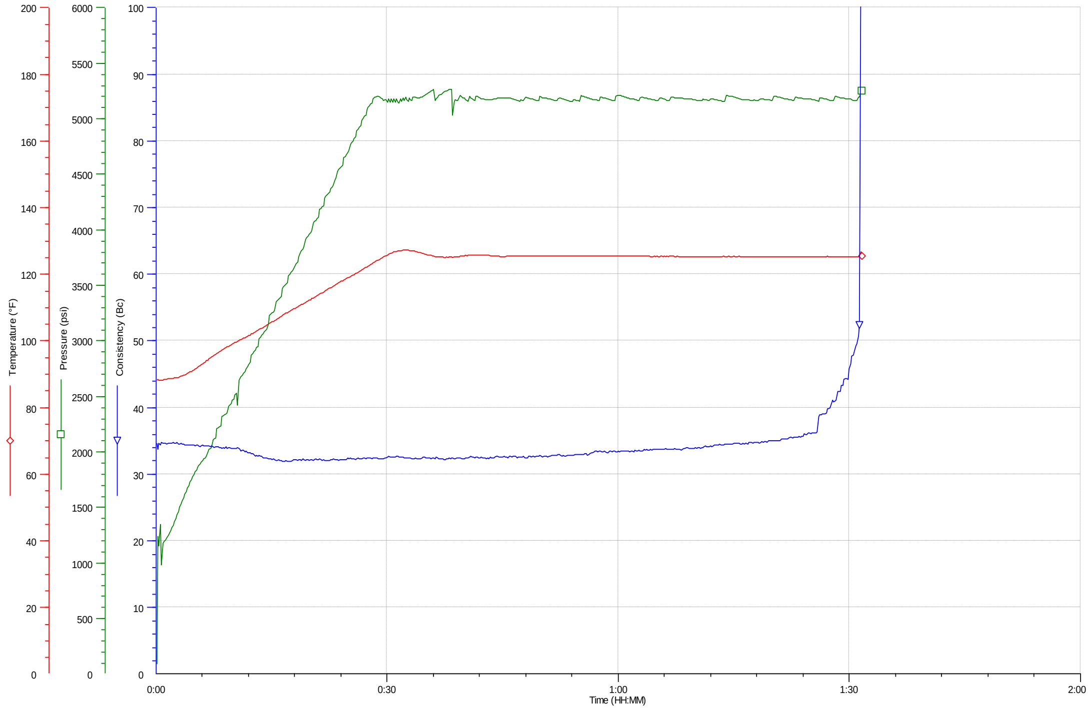

Figure B.19. Cement + 44% Water + 3% NaCl

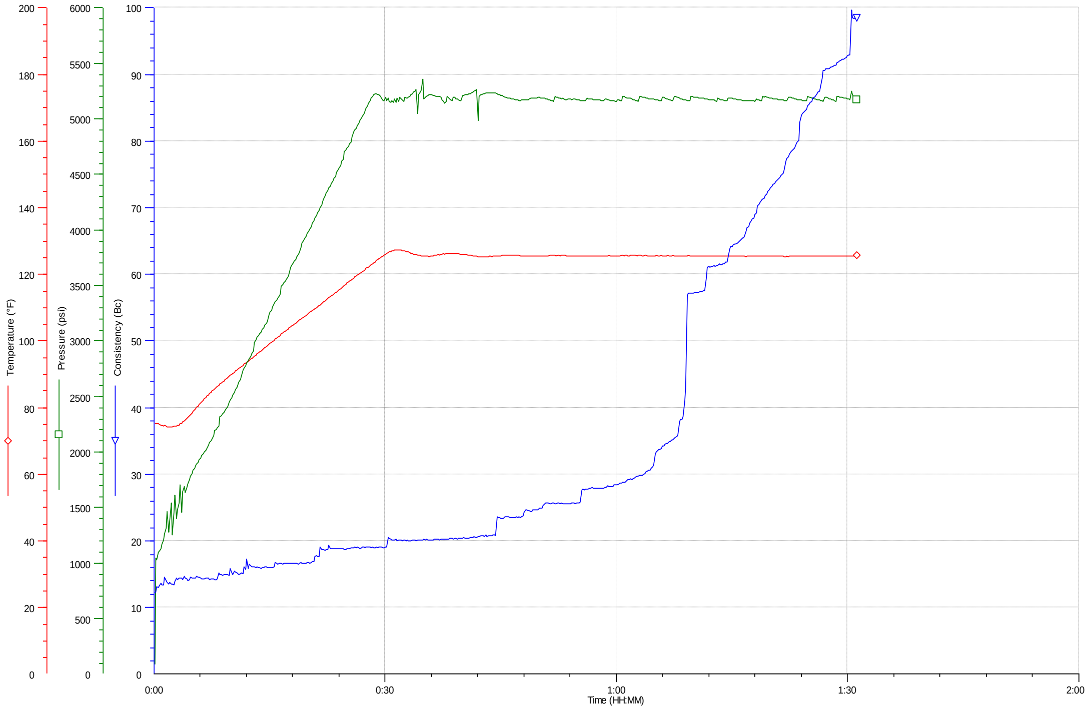

Figure B.20. Cement* + 44% Water + 5% NaCl

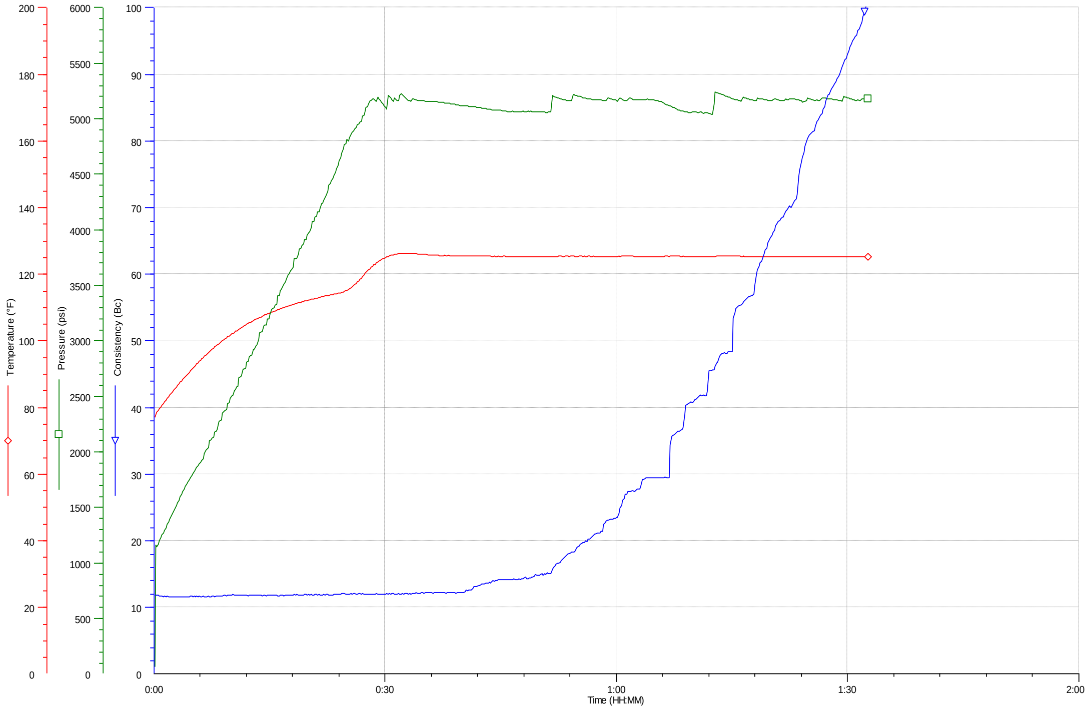

Figure B.21. Cement* + 44% Water + 7% NaCl

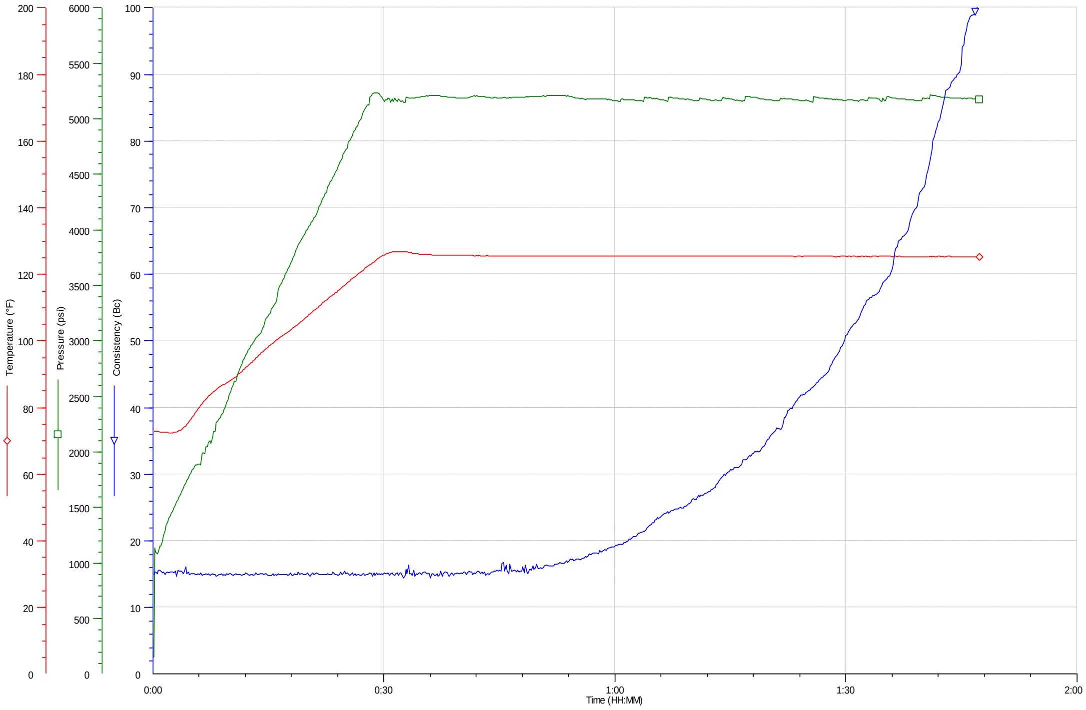

Figure B.22. Cement* + 44% Water + 10% NaCl

C. VISCOMETER READINGS OF CEMENT SLURRIES

Table C.1 Viscometer readings for NaCl containing slurries

Influence of NaCl Concentration (%bwow) on Rheology						
RPM	0%	3%	5%	10%	12%	15%
600	104	105	101	98	97	123
300	65	68	66	64	63	81
200	53	56	56	52	51	67
100	40	43	42	40	38	51
6	13	14	16	17	14	19
3	6	8	9	10	9	12

Table C.2 Viscometer readings for KCl containing slurries

Influence of KCl Concentration (%bwow) on Rheology						
RPM	0%	1%	3%	5%	7%	10%
600	104	103	95	93	96	135
300	65	65	60	58	60	95
200	53	54	51	48	56	87
100	40	43	39	37	44	73
6	13	14	13	13	16	24
3	6	8	6	8	9	14

Table C.3 Viscometer readings for $CaCl_2$ containing slurries

Influence of CaCl2 Concentration (%bwow) on Rheology						
RPM	0%	1%	3%	5%	7%	10%
600	104	106	113	126	173	300+
300	65	71	78	88	132	274
200	53	60	66	75	115	250
100	40	46	50	60	94	210
6	13	13	16	23	36	91
3	6	8	12	17	28	69

Table C.3 Viscometer readings for NCl containing slurries prepared with different G class cement

Influence of NaCl* Concentration (%bwow) on Rheology						
RPM	0%	1%	3%	5%	7%	10%
600	118	121	122	122	122	129
300	80	78	83	83	84	86
200	67	65	70	69	72	70
100	53	50	54	53	56	53
6	9	17	19	22	24	20
3	6	10	12	13	14	12