

EVALUATION OF LIMESTONE INCORPORATED CEMENT COMPOSITIONS
FOR CEMENTING GAS HYDRATE ZONES IN DEEPWATER
ENVIRONMENTS

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COMPOSITIONS FOR CEMENTING GAS HYDRATE ZONES IN
DEEPWATER ENVIRONMENTS**

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ABSTRACT

EVALUATION OF LIMESTONE INCORPORATED CEMENT COMPOSITIONS FOR CEMENTING GAS HYDRATE ZONES IN DEEPWATER ENVIRONMENTS

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One of the potential problems which must be overcome during oil or gas exploration in deepwater environments is to complete the drilling operations without decomposing the gas hydrates. Gas hydrates remain stable as long as the thermodynamic conditions are not changed. But, especially by increasing temperature during drilling operations, there is always a possibility of change in thermodynamic conditions, which will cause decomposition. Another factor which may disturb the thermodynamic conditions is the evolved heat during hydration of cement which is used to fill the annular space between the protective pipe, casing, and the wall of the well.

In this study, CEM-I cement, API Class G cement and limestone were mixed with different proportions and 8 different blended cement compositions were prepared. The cement pastes were cured for ages of 1-day, 7-days and 28-days at 15°C and in order to investigate the applicability of cement samples, compressive strength, heat of hydration, porosity and permeability tests were carried out.

The results showed that the presence of an adequate amount of limestone in the blend decreases the heat of hydration of cement blends. On the other hand, increasing the amount of limestone affects compressive strength development of cement blends adversely. Additionally, increasing amount of limestone also increases the porosity of cement blends while the effect of limestone amount on the permeability is not significant. Even if permeability values show a slight increase with the increasing amount of limestone, they are still very low. At the end of this study, results indicate that limestone blended CEM-I and API Class G cements show better performance than neat CEM-I or API Class G cements for cementing low temperature formations where gas hydrates exist.

Keywords: Natural gas hydrates, well cementing, heat of hydration, deepwater drilling, limestone blended Portland cement

ÖZ

KİREÇ TAŞI KATKILI ÇİMENTO KOMPOZİSYONLARININ DERİN DENİZLERDE GAZ HİDRATI İÇEREN KATMANLARIN ÇİMENTOLANMASI İÇİN KULLANILMASININ ARAŞTIRILMASI

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Derin denizlerde yapılmakta olan petrol veya doğal gaz aramacılıđının üstesinden gelinmesi gereken potansiyel problemlerinden birisi de sıđ sediman tabakalarında görülebilen doğal gaz hidrat oluşumlarının bozunmasına yol açmadan sondaj operasyonunun gerçekleştirilebilmesidir. Doğal gaz hidratlarının oluştuđu katmandaki termodinamik koşulları deđiştirmedikçe (basıncın düşürülmesi ve/veya sıcaklıđın yükseltilmesi) hidrat yapıları kararlı olabilmektedir. Ancak, ham petrol ve doğal gaz rezervlerinin tespiti amacıyla yapılan sondaj operasyonu sırasında hidrat tabakasının termodinamik koşullarının deđiştirilmesi, özellikle ortam sıcaklıđının arttırılmasıyla hidrat yapısının bozunması, olasılıđı her zaman mevcuttur. Hidrat yapısının bozunmasına yol açabilecek dış etkenlerden biri de sondaj operasyonu sırasında kuyuya indirilen muhafaza borularının dış çevresinin çimentolanması aşamasında ortaya çıkacak çimento hidratasyon ısısidir.

Bu çalışmada, yapı sektöründe kullanılan Portland çimentosu ve Amerikan Petrol Enstitüsü'nün (API) G-tipi kuyu çimentosu deđişik oranlarda kalker ile karıştırılarak 8 farklı kompozisyon elde edilmiştir. Elde edilen bu kompozisyonlar, düşük ortam sıcaklıđındaki kuyuların çimentolanmasındaki uygunluklarının araştırılması için

15°C sıcaklıkta, 1, 7 ve 28 gün süreyle krlenmiřler ve basınç dayanımı, hidrasyon ısısı, gzeneklilik ve geirgenlik testleri yapılmıřtır.

Yapılan deneyler sonucunda, imento karıřımında uygun miktarlarda kalker bulunması imento hamurunun hidrasyon ısısını dřrmekte ancak yksek oranlarda kalker ieren imento kompozisyonlarının basınç dayanımlarında artan kayıplar olduėu grlmřtir. Buna ek olarak artan kalker miktarı gzenekliliėi arttırmasına raėmen, geirgenlik zerinde olumsuz bir etki yapmamıř; geirgenlik deėerleri artıř gstermesine raėmen ok dřk seviyelerde kalmıřtır. Bu alıřmanın sonucunda kalker katkılı CEM-I ve API G tipi imentoların hidrat ieren formasyonlarda kuyu imentolamasında CEM-I ve API G tipi imentolardan daha iyi performans gsterdiėi saptanmıřtır.

Anahtar Kelimeler: Doėal gaz hidratları, kuyu imentolama, hidrasyon ısısı, derin deniz sondajı, kalker katkılı Portland imentosu

To all meritorious people who set their bodies on fire to strangle the darkness...

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NOMENCLETURE

ACI	American Concrete Institute
AFt	Alumina, ferric oxide, tri-sulfate
API	American Petroleum Institute
ASTM	American Society for Testing Materials
BHP	Bottom Hole Pressure
BSR	Bottom Simulating Reflector
BTU	British Thermal Unit
CT	Computerized Tomography
CV	Coefficient of Variation
EN	European Norm
GHSZ	Gas Hydrate Stability Zone
HOH	Heat of Hydration
NGH	Natural Gas Hydrates
Psi	Pound per Square inch
US DOE	United States Department of Energy
WOC	Wait on Cement
W/C	Water to Cement Ratio

CHAPTER 1

INTRODUCTION

1.1 Purpose of Oil-Well Cementing

Well cementing is one of the most critical steps in the drilling and completion of oil/gas wells. There are two types of cementing operations which are primary cementing and remedial cementing. The objectives of primary cementing are to provide hydraulic seal, create zonal isolation, protect usable water, and provide structural support for casing. It is important and needs to be achieved effectively to increase the life of the well. Remedial cementing operations are usually done to repair problems related with primary cementing or enhance conditions emerging after wellbore has been constructed. Squeeze cementing and plug cementing are two main categories of remedial cementing.

1.2 Cementing of Deepwater Wells

Presence of hydrates is one of the problems encountered during construction and production of deepwater wells and presents many challenges during drilling, cementing and production operations. If gas hydrates decompose during well operations, gas can rise to surface and create catastrophic problems in worst cases. Therefore, destabilization of hydrates must be prevented from the beginning to the end of the well operations during the life of the well.

It is illustrated many times in the published literature (Hannegan et al., 2004; Collett and Dallimore, 2002; Reed, 2002; Ohara et al., 2000; Schofield et al., 1997), especially drilling operations can be problematic in the presence of hydrates. Cementing problems, casing failures, stuck drillpipes, gas releases, fires and blowouts are the encountered problems during drilling (Reddy, 2008).

1.3 Problems Associated with Conventional Cements

Hydration of cement is an exothermic reaction, in other words heat is released during slurry hydration. The diameter of surface casing is large. It also means that the annular volume between surface casing and formation is also large. Since the slurry that placed to set the surface casing is large, the amount of the heat released during slurry hydration is high.

Heat of hydration is not that important for conventional wells however it needs to be taken into consideration for wells drilled in low temperature formations. Heat of hydration is important for cementing gas hydrate zones because gas may start to release from gas hydrates and create problems if gas hydrates start to decompose during hydration of cement (Reddy, 2008).

High heat of hydration of conventional cements may disturb gas hydrate stability and gas flow may occur after a cement job in deepwater environments that contain major hydrate zones. Gas flow slows down in hours to days if it is not a serious decomposition. However, the consequences could be more severe in some cases. Additionally, poor bonding between cement and formation and formation of gas channels in the cement column may be the long-term problems if hydrates decompose during cementing operations. Therefore, it is important to understand the factors contributing to the hydrates' destabilization and to implement a solution (Ravi, Iverson, & Moore, 2008). Any factor which can change thermodynamic conditions in gas hydrate zone can cause decomposition. Hence, it is important to reduce heat of hydration of cement as much as possible without affecting negatively the other required properties of cement.

1.4 Ideal Deepwater Well Cement Properties

Low temperature formations such as permafrost zones, require special cement compositions for cementing. These cement compositions can set and harden at low temperature and yet have low heat of hydration (HOH). This is also valid for deepwater environments where gas hydrate exists (Reddy, 2008).

It is obvious that many of the problems encountered because of hydrate dissociation during the drilling process are also the case for the cementing operation. In published literature, recommended slurry characteristics for cementing gas hydrate zones are similar to those for cementing permafrost zones. Some recommended slurry characteristics involve (Collett and Dallimore, 2002, Halliburton; Schlumberger, Bengtson et al., 1982):

- Low heat of hydration
- High strength
- Good bond
- Short wait on cement (WOC) time
- Low thermal conductivity
- Superior anti-gas migration performance

Designed cement slurries for low temperature formations to lower the heat of hydration while meeting or exceeding the other requirements are needed for successful deepwater cementing. Heat of hydration is reduced by a factor of more than two when compared to the conventional cement slurries. The cement slurries achieve low heat-of hydration by using a variety of blends (Ravi et al., 2008). Portland cement and gypsum combinations are one of the earliest compositions used to lower the HOH (Shryock et al. 1975). Portland cement and aluminosilicate, calcium aluminate and calcium sulfate, and zeolite or zeolite and fly ash-based combinations are the other composition used to lower the HOH (Go Boncan, 2000; Boncan, et al. 1997; Wilson 1979; Luke et al. 2004).

The set cement must develop adequate mechanical strength to support the casing. In order to reduce weight on cement time (WOC) and cost associated with cement operations, it is important to accelerate strength gaining process. Usually, 500 psi compressive strength in 24 hours is considered as acceptable for casing support (Romero & Loizzo, 2000). Low temperature also affects compressive strength development. In order to accelerate hardening process, accelerators can be used.

In order to increase anti-gas migration performance of cement, thixotropic additives can be used. Thixotropy is a term used to describe the property exhibited by a system that is fluid under shear, but develops a gel structure and becomes self-supporting when at rest (Shaw, 1970).

1.5 Objective

The objective of this study is to evaluate the applicability of limestone incorporated cement slurries for cementing gas hydrate containing environments in deepwater. 8 different blended cement pastes were prepared for this study by using CEM-I, API Class G cement and limestone. Two of them are neat CEM-I and API Class G cement; and the other 6 cement compositions are the blends of limestone and CEM I/API Class G cement with different proportions. The prepared cement samples were tested in terms of compressive strength, heat of hydration, porosity and permeability. All cement slurries were tested in accordance with ASTM, API and EN standards under their requirements.

1.6 Scope

This thesis consists of six chapters,

Chapter 1 presents the brief explanation of oil well cementing, properties of cement for deepwater operations, objective and scope of this thesis.

Chapter 2 presents a review of literature on natural gas hydrates.

Chapter 3 presents a review of literature on cements.

Chapter 4 presents a statement of problem.

Chapter 5 presents the experimental set-ups and procedures used in this study.

Chapter 6 presents the results of the experiments.

Chapter 7 presents the conclusion and recommendations.

CHAPTER 2

NATURAL GAS HYDRATES

2.1 Introduction

As the consumption of fossil fuels increases day by day in order to supply global energy demand, an alternative energy becomes necessary. According to the US DOE, it has been forecasted that global energy demand will rise from 524×10^{15} BTU in 2010 to 820×10^{15} BTU in 2040 (U.S. Energy Information Agency, 2013). After shale gas became a feasible producible energy source, recent researches have been focusing on natural gas hydrate (NGH) reservoirs. NGH reservoirs have great importance because gas potential of these reservoirs is larger than all conventional hydrocarbon reservoirs all around the world.

NGHs are considered as a promising energy source due to its high potential in all over the world. Black Sea, Bering Strait, Gulf of Mexico, India, Japan, Korea, South China Sea and Trinidad are some of marine locations where NGH exists. Siberia (Russia), Mackenzie Delta (Canada), Qinghai-Tibet plateau (China) and Alaska (USA) are some of the permafrost regions for gas hydrate potential (Paull et al., 2010). Figure 2-1 shows all recovered and inferred places for NGHs all around the world.

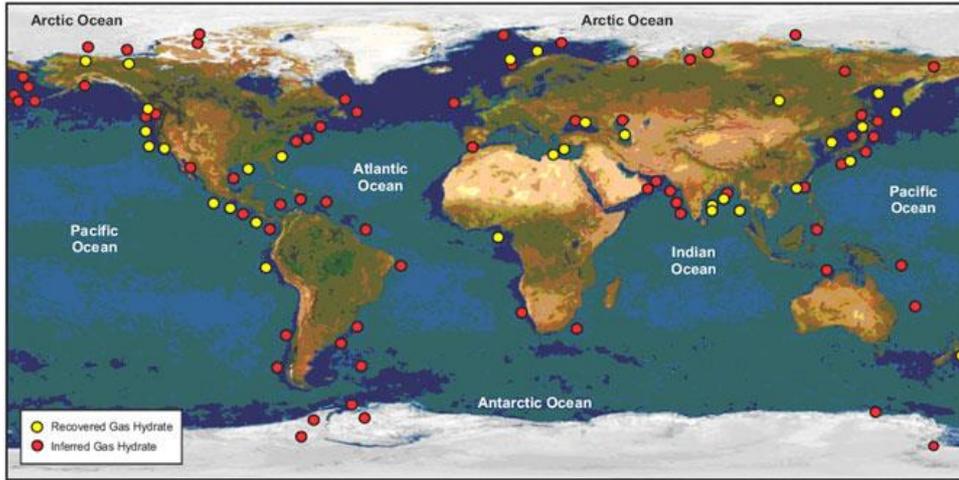


Figure 2-1: Gas hydrates around the world (Lu, 2015)

Boswell and Collett proposed NGH resource pyramid in 2006, Figure 2-2. The calculated size and favorability for production of the different natural gas hydrate reservoirs is displayed in the figure. According to the hydrate resource pyramid, because of low reservoir properties of shales and clays, only NGH in arctic, marine and non-marine sands with good reservoir properties are currently considered as targets for gas production (Xu & Li, 2015).

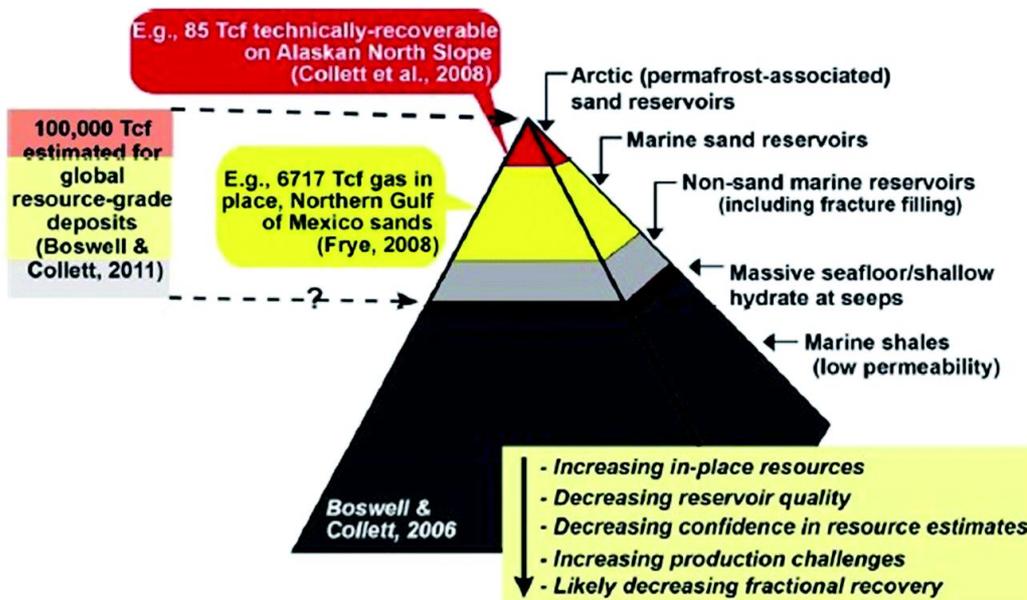


Figure 2-2: The hydrate resource pyramid (Xu & Li, 2015).

To dissociate NGHs and produce gas from reservoir, initial pressure and temperature conditions which are in the hydrate stability region should be shifted out of NGH equilibrium conditions (Kurihara, Ouchi, Narita, & Masuda, 2011). Possible production approaches applied in the industry during production tests involve depressurization, thermal stimulation, chemical inhibitor injection, combination of them and CO₂-CH₄ swapping. Among all, the depressurization method is considered as the most practical one, which is especially suitable for hydrate reservoirs overlying a free gas section and combination of depressurization and thermal stimulation method is considered as the practical one (Kurihara et al., 2011; Xu & Li, 2015).

Many countries including USA, Japan, India, China and Korea, have been working on NGH exploration projects. First production test in the world, was carried out Mallik site in the Mackenzie Delta in the Northwest Territories of Canada in 2002 by using a thermal stimulation method. In addition, the depressurization method was used for the tests in the same site in 2007 and 2008 (Yamamoto & Dallimore, 2008). In 2013, world's first offshore production test was accomplished by Japan and depressurization method was applied ("Japan Extract Gas," 2013).

2.2 Formation of Natural Gas Hydrates

Gas hydrates are non-stoichiometric crystalline solids which are formed through combination of gas molecules –guest molecule- in hydrogen bonded water molecule – host molecule- cages under low temperature and high pressure conditions. Natural gas hydrates in marine sediments and permafrost include methane (mostly) and other gases such as butane, ethane, propane, CO₂ and H₂S (Mazzini et al., 2004; Popescu et al., 2006).

NGH forms if gas and water coexist within gas hydrate stability zone (GHSZ) which is the region in between hydrate gas phase boundary and hydrothermal gradient in Figure 2-3. NGHs are stable under low temperature and high pressure conditions. NGH stability is disturbed at certain depths when going deeper in sediments because the temperature of sediments increases with depth and very high pressure conditions

are necessary to keep hydrate formations stable.

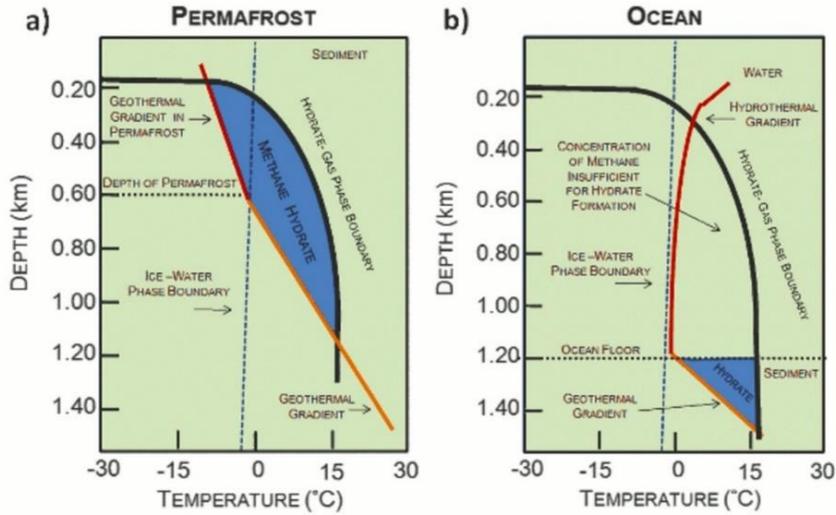


Figure 2-3: Methane hydrate stability conditions for both marine and permafrost settings (Harrison, 2010)

Due to the variety of sediment types in both marine and permafrost environment, the characteristics of NGH in sediments differ. As shown in Figure 2-4, NGH deposits in sediments can be formed in three types: Pore filling type, naturally fractured type, and massive/nodule type (Moridis and Collett, 2004; Xu & Li, 2015).

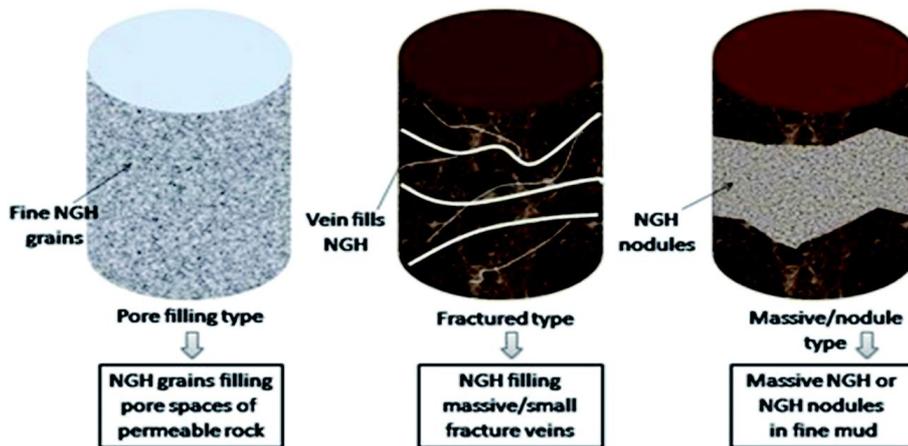


Figure 2-4: Type of NGH Reservoirs(Xu & Li, 2015).

In the first type, NGH is accumulated in pore spaces of porous media and mostly this type of filling is observed in coarse sands. NGH is accumulated in fractures or veins in second type. And finally, NGH is accumulated in the form of lump in fine grained muds in nodule type reservoirs (Xu & Li, 2015). Among all, the Mallik NGH reservoirs in Canada, Mt. Elbert NGH reservoirs in Alaska North Slope, and reservoirs located in the Eastern Nankai Trough offshore Japan were categorized as the pore filling type NGH reservoir (Boswell et al., 2008). Secondly, fracture type NGH reservoirs were found in offshore India and offshore Korea, and the third massive/nodule NGH reservoirs were confirmed in Gulf of Mexico and in Japan Sea.

2.3 Classification of Natural Gas Hydrates

NGH reservoirs are divided into four main classes according to conditions of the existing NGH, free water and free gas: Class-I, Class-II, Class-III, and Class-IV and they are shown in Figure 2-5 (Chong, Yang, Babu, Linga, & Li, 2016; Kurihara et al., 2011; Merey & Sinayuc, 2016; Xu & Li, 2015).

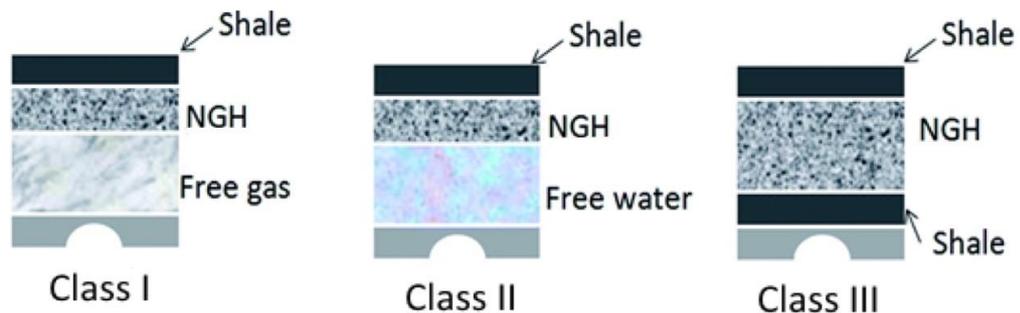


Figure 2-5: Classification of pore filling type NGH reservoirs (Kurihara and Narita, 2011).

Class I accumulations consist of two zones: the hydrate interval and underlying two phase fluid zone with free gas. In this class, effective permeability of the hydrate interval is low compared to free gas section due to the presence of large hydrate saturations in the pore space and bottom of GHSZ is usually consistent with the bottom of the hydrate interval. Class-I is the most desirable class for methane production.

Because very small changes in pressure and temperature are adequate to initiate NGH dissociation. Messoyakha Field in Russia and Sagavanirktok Formation in Alaska are typical examples of Class I deposits (Xu & Li, 2015).

Class II accumulations consist of two zones: the hydrate interval and mobile water zone with no free gas. In contrast to Class I, the entire hydrate interval might be well within the hydrate stability zone in Class II, i.e. the bottom of the hydrate interval does not mark the bottom of the hydrate stability zone. A part of reservoirs in the Eastern Nankai Trough and the Mallik site are Class II deposits (Xu & Li, 2015).

Class III accumulations consist of only a single zone of hydrate interval without an underlying zone of mobile fluids. Some other parts of reservoirs in the Eastern Nankai Trough and Mallik site are also categorized into Class III deposits (Xu & Li, 2015).

Different from other three types of accumulations Class IV accumulations are widely distributed and not bounded by confining strata. Class IV accumulations mainly appear as nodules with low saturation over large areas. However, presently, they are not accepted as potential accumulations for production (Moridis et al., 2004; Xu & Li, 2015).

As gas production targets, desirability of Class I is well defined but for Classes II and III, it has not been well defined yet and it may be affected by many factors like initial pressure and temperature, boundary conditions, environmental concerns, economic considerations (Moridis and Collett, 2003).

For all classes of NGH deposits, decomposition and gas production are highly associated with the properties of the porous media, temperature and pressure conditions. In order to evaluate the gas production possibility from the reservoir, many parameters are essential, such as depth, thickness, porosity, permeability, thermal conductivity, initial pressure and temperature. In addition to these parameters, heterogeneities of the reservoir such as spatial variation of permeability, NGH saturation, distribution of impermeable layer, are also quite important (Xu & Li, 2015).

2.4 Natural Gas Hydrates Detection Technology

Although there is a controversy about the amount of NGH in the world, it is obvious that there is huge NGH potential and trapped gas in these reservoirs might supply the world's natural gas needs for a few centuries (Kvenvolden 1988; Kvenvolden & Lorenson 2001; Boswell & Collett 2006). Even though NGHs occur in permafrost regions, it was estimated that more than 95 % of NGH are found in marine sediments (Max & Johnson, 2014). Therefore, the following methods in this sub-section are specifically related with oceanic environments.

Geophysical methods, like reflection seismology, ocean bottom seismometer, submarine ground resistance etc. are used for the detection of marine gas hydrates as illustrated in Figure 2-6. (Chen & Wang, 2007).

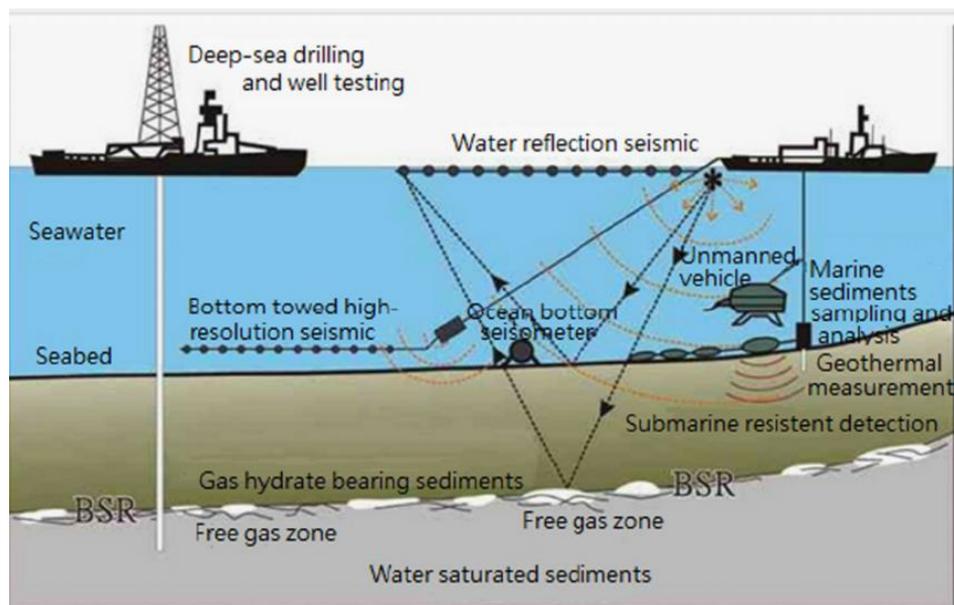


Figure 2-6: Different methods for the detection of gas hydrates (Lu, 2015)

Presently, one of the most commonly used techniques for marine gas hydrate reservoirs is the seismic reflection characteristics by Bottom Simulating Reflector (BSR) (Lu, 2015). BSR is simply a reflection which parallels to the sea floor reflection. It is caused by the contrast between an overlying gas hydrate and

underlying gas-saturated sediments and BSR is one of the indicators of NGH at GHSZ with free gas subsection but the absence of BSR does not mean that there is no NGH in the sediments. When NGH with free gas section exists, it creates anomaly in seismic signals because NGH is in solid form. Signals propagate neatly without significant reflection which is called anti-white phenomenon, in hydrate layer. However, shock propagation speed becomes faster in the layer which separates gas hydrate and free gas. As seen in Figure 2-7, it looks like thick line on the BSR cross sectional view.

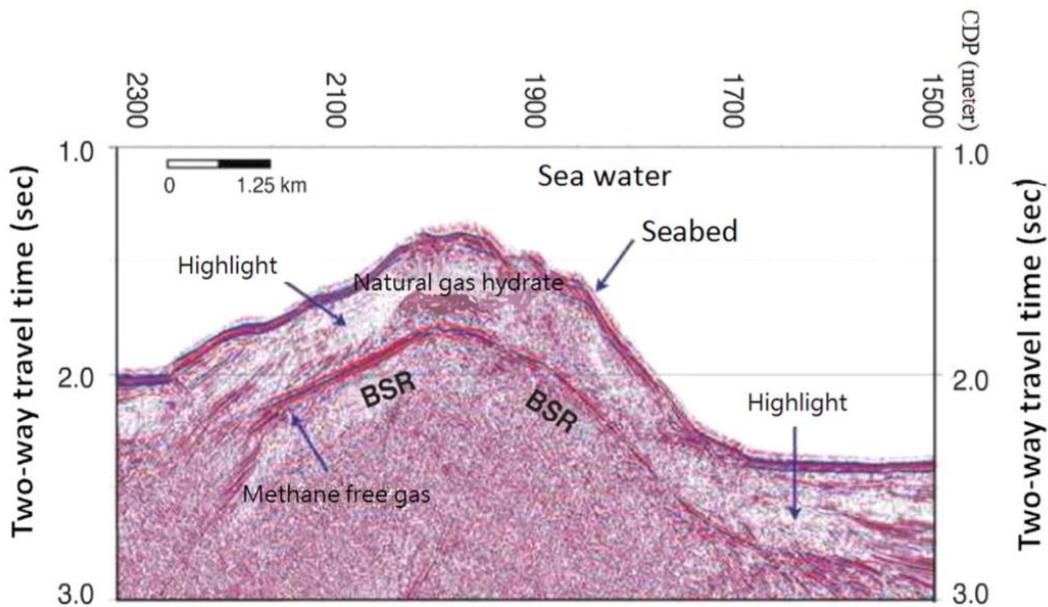


Figure 2-7: BSR Cross Sectional View (Chen & Wang, 2007).

Then the propagation speed becomes slower and the interface high impedance contrast is formed on the bottom of the hydrate stability zone, resulting in a strong reflection phenomenon (Lu, 2015). Strong BSRs means that there is a high possibility of gas hydrate existence. The maximum depth of gas hydrates, i.e. GHSZ, mainly depends on pressure and temperature of sediments. Up to a point, sea depth is an important parameter for marine sediment temperatures. For example, in the past, sea level changes caused sudden gas hydrate dissociations or gas hydrate formations. If sea depth increases, the temperature of marine sediments also decreases and overburden pressure increases. Hence, the thickness of GHSZ also increases with sea depth. It is

generally stated that, BSRs are commonly detected in GHSZ where gas hydrate is likely to exist with free gas subsection (Chen & Wang, 2007; Lu, 2015).

2.5 Production Methods

Currently, 3 methods, depressurization, thermal stimulation and inhibitor injection, are being tested by the industry for the dissociating NGH. Depressurization and thermal methods change initial pressure and temperature conditions and therefore NGH starts to dissociate. Chemical inhibitor injection method shifts equilibrium conditions of the system to the low temperature and high pressure side and hence NGH dissociates at the in-situ conditions (Chong et al., 2016; Kurihara et al., 2011). In addition to these methods, several other methods such as CO₂ injection, electrical heating, and irradiation of ultrasonic wave are also examined specifically for the NGH dissociation (Xu & Li, 2015). Figure 2-10 shows the schematic of the three production methods and pressure-temperature diagram. Details of these methods are described in the following sections.

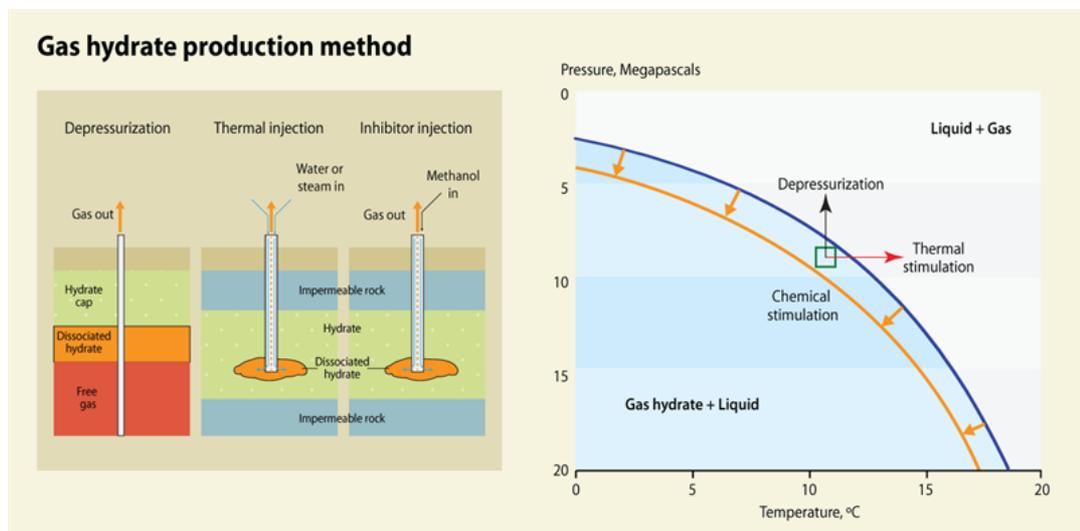


Figure 2-8: NGH production methods (GRID, 2009).

2.5.1 Depressurization Method

In the depressurization method, as depicted in Figure 2-9, the bottomhole pressure is reduced by producing gas from the near wellbore area. When the bottomhole pressure

is lower than the equilibrium pressure, NGH dissociates and natural gas and water start to release. Dissociation starts from near wellbore area. In this area, with NGH dissociation, permeability of sediments increases. And effect of depressurization method extends from near wellbore through interior part of gas hydrate sediments and the gas production increase with time but the effect of depressurization method decreases with time because the dissociation of NGH is an endothermic reaction, in other words the reservoir temperature decreases along with the dissociation. Therefore, when the reservoir temperature is lower than or equal to the equilibrium temperature corresponding to the reservoir pressure, the NGH dissociation stops and external heat might be necessary. The sustainability of gas production depends on not only pressure but also temperature in the depressurization method (Xu & Li, 2015; Kurihara et al., 2011).

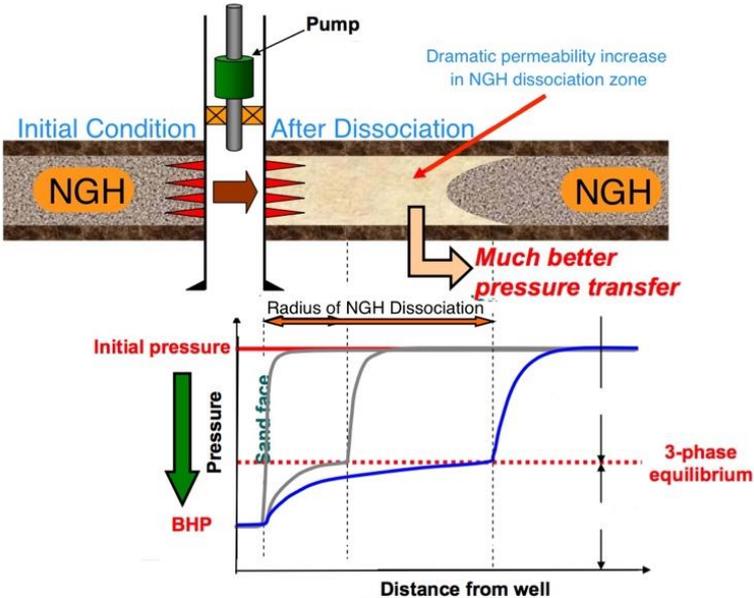


Figure 2-9: Schematic view of pressure reduction and (Kurihara et al., 2011)

The world’s first successful production tests were conducted using the depressurization method in the Mallik production program in April 2007 and March 2008 (Kurihara et al., 2011).

2.5.2 Thermal Method

The general term, thermal method, is used for the methods promoting the dissociation of NGH by increasing the reservoir temperature. As shown in Figure 2-10, thermal methods include thermal stimulation methods and thermal flooding methods. The aim of the thermal stimulation methods is increasing the temperature of the near wellbore area. Thermal stimulation methods include hot water circulation method, wellbore heating method and hot water huff and puff method. In the first method, hot water is circulated in the wellbore to increase bottomhole temperature. In wellbore heating method, wellbore is heated by using one or more heater installed in the downhole. In last method, hot water or steam is injected into the reservoir (huff), then well is shut-in for a certain time to transfer the heat from the injected fluid to a reservoir (soak), and finally gas and water are produced from the same well (puff). Different from thermal stimulation methods, in thermal flooding methods, the heat supply such as hot water is injected into the reservoir from a well, which creates a hot water flood toward other wells and meanwhile increases the reservoir temperature. Therefore, NGH located in between wells dissociates and gas is produced from production wells (Xu & Li, 2015; Kurihara et al., 2011).

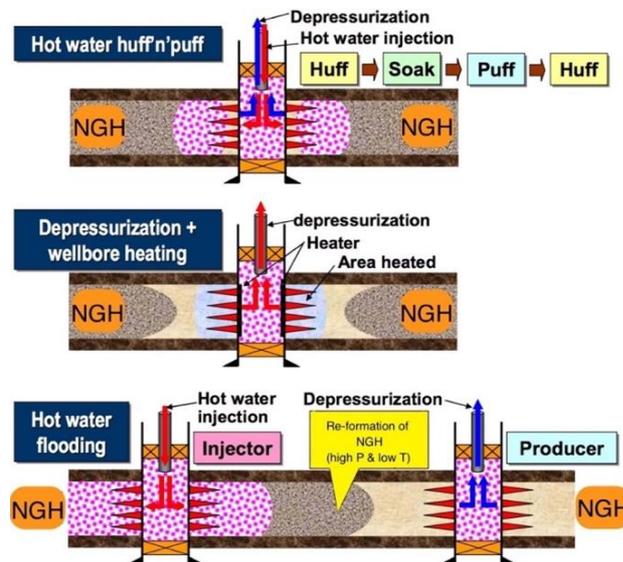


Figure 2-10: Various types of thermal methods (Kurihara et al., 2011)

The world's first successful production test was conducted at the Mallik site in Canada by applying hot water circulation method in 2002 (Xu & Li, 2015).

2.5.3 Inhibitor Injection Method

In this method, inhibitors of hydration such as brine, electrolyte solutions, ethanol, methanol, salt and alcohol are injected into the reservoir to shift the equilibrium conditions to the high pressure low temperature side. This shift causes dissociation of NGH automatically. Because the magnitude of this shift is small, higher amount of NGH dissociation cannot be achieved in the sole inhibitor injection method. Additionally, as in hot water injection, it is difficult to inject an inhibitor smoothly into the reservoir because of very low effective permeability to water at initial state. Hence, it is better to inject an inhibitor together with hot water in applying hot water huff and puff or hot water flooding method to increase the efficiency of thermal methods. However, because the inhibitors are expensive, harmful to environment, the use of the inhibitor injection method is still under question (Kurihara et al., 2011).

CHAPTER 3

WELL CEMENTS

3.1 Portland Cement

3.1.1 Raw Materials and Manufacture of Portland Cement

Limestone, clay or shale are the basic raw materials for manufacturing of Portland cements. If iron and alumina are not present in sufficient amount in the clay or shale, they can be added to the raw mixture (ACI, 2001).

The proportioning of the raw materials is important to obtain cement with required properties. Raw materials are powdered and mixed with specific proportions. The process used for mixing materials can be either dry or wet process. The mixture is heated in a rotary kiln without addition of any water in the dry process. While, in the wet process, water is added to the mixture, in order to make the mixture more homogeneous. But the required energy for heating is higher in the wet process due to this addition. After blending, resulting mixed material is fed into the kiln and burned in rotary kiln at about 1500°C. Excess water and gases like CO₂ are removed by the effect of temperature. The raw materials decompose into their oxides with the effect of heat in rotary kiln (ACI, 2001; Kuleli, 2009).

The main process occurred in the kiln is called “clinkering”. At the end of the process, after certain chemical reactions, the product called “clinker” is obtained. (Kuleli, 2009). When the clinker is cooled, 3% to 5% of gypsum is added and the mixture is pulverized. The final, pulverized, product is ordinary Portland cement (Labahn, 1983).

3.1.2 Oxides and Their Notations

Portland cement clinker consists of oxides of calcium, silicon, aluminum and iron. Limestone is the source of calcium oxide and clay is the source of silicon oxide,

aluminum oxide and iron oxide. Typical composition of Portland cement is given in Table 3-1.

Table 3-1: Typical composition of Portland cement (Neville, 2003)

Oxides	Cement Chemistry Notation	Average Amount (Weight %)
CaO	C	60 – 67
SiO ₂	S	17 – 25
Al ₂ O ₃	A	3 – 8
Fe ₂ O ₃	F	0.5 – 6.0
SO ₃	\bar{S}	2.0 – 3.5
MgO	M	0.5 – 4.0

Portland cement clinker consists of four crystalline phases. The names, chemical notations and cement chemistry notations of these crystalline compounds are given in Table 3-2.

Table 3-2: Clinker Compounds (Labahn, 1983; Odler, 2004; Domone and Illstone, 2010)

Clinker Compound	Cement Chemistry Notation	Chemical Notation	Average Amount (Weight %)
Alite	C ₃ S	3CaO.SiO ₂	50-70
Belite	C ₂ S	2CaO. SiO ₂	15-20
Aluminate	C ₃ A	3CaO.Al ₂ O ₃	5-10
Ferrite	C ₄ AF	4CaO. Al ₂ O ₃ .Fe ₂ O ₃	10-15

3.1.3 Portland Cement Hydration

The compounds present in Portland cement are anhydrous. Due to the fact that the principal components of Portland cement (C₃S, C₂S, C₃A, and C₄AF) display different

hydration kinetics and form different hydration products, it is better to investigate hydration of the clinker phases separately.

3.1.3.1 Hydration of the Silicate Phases

The silicate phases in Portland cement are generally comprising more than 80% of the total material. C₃S is the principal component and its concentration can reach up to 70% of the total material, while the concentration of the C₂S is normally limited by 20%. (Nelson, 1990). The hydration products for C₃S and C₂S are calcium silicate hydrate and calcium hydroxide as shown below (Neville, 2003).



C₃S is generally responsible for the early strength development, hydration rate is high and high amount of heat generated. C₂S is responsible for the ultimate strength development. Although hydration of C₂S is similar to C₃S, hydration rate is slower and lower amount of heat generated. Due to the fact that the mechanism of the C₂S hydration is very similar to that of C₃S, the hydration of C₃S can be considered as a model for the hydration behavior of Portland cement (Nelson, 1990).

3.1.3.2 Hydration of the Aluminate Phases

The aluminate phases, especially C₃A, are the most reactive at short times. Although their abundance is considerably lower than the silicates, they have significant influence on the rheology of the cement slurry and early strength development and generates more heat than C₃S (Nelson, 1990).

The first step of hydration of C₃A is an interfacial reaction between the surface of the anhydrous solid and water and gel-like material on the surface of the C₃A is formed. The calcium aluminate hydrates are metastable and occur as hexagonal crystals (Nelson, 1990). The calcium aluminate hydrates are eventually transformed into the

more stable cubic form. But this reaction occurs within several days at ambient temperatures.

In order to avoid very rapid hydration, gypsum is usually added to Portland cement. In the presence of gypsum, ettringite which is a needle-shaped prismatic crystal structure present in hydrated cement paste, forms as a result of reaction of C_3A with gypsum. Formed ettringite precipitates onto the C_3A surfaces. As a consequence, C_3A solubility decreases and hydration slows down.

3.1.3.3 Hydration of the Ferrite Phases

The hydration process of ferrite phase is similar to that of the aluminate phase but the rate of hydration is much slower (Ramachandran and Beaudoin, 1980).

3.1.4 Mechanism of Portland Cement Hydration

The rate of heat evolution of Portland cement changes with time. Figure-3-1 shows the heat evolution curve for a typical Portland cement. Due to the fact that there are different stages where rate of heat of hydration accelerates and decelerates, Odler (2004) divided the graph into 4 stages.

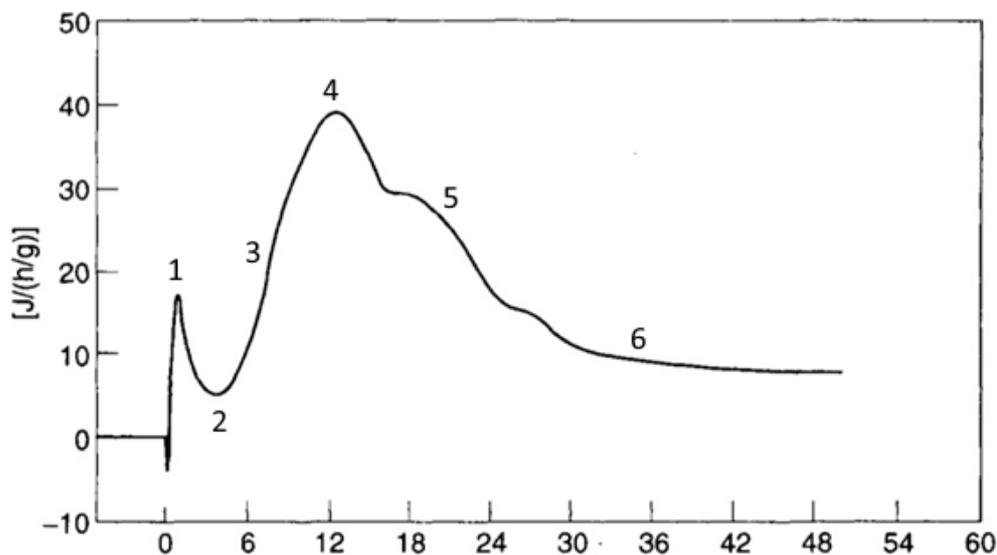


Figure 3-1: Rate of heat evolution during hydration of Portland cement adapted from (Odler, 2004). 1. Pre-induction period, 2. Induction period, 3. Acceleration stage, 4. C_3S hydration, 5. C_3A hydration, 6. Post-acceleration Stage

- **Pre-induction Period (first minutes)**

Immediately after mixing of cement and water, ionic species rapidly dissolves into liquid phase. Alkali sulfates dissolve completely within a few seconds and K^+ , Na^+ , SO_4^{-2} ions are released. Calcium sulfate dissolves until saturation and Ca^+ and additional SO_4^{-2} ions are released. In the pre-induction period, 2 to 10 % of C_3S , 5 to 25% C_3A are hydrated. Hydration rate of C_2S is very low in this period and only small amount of C_2S is hydrated. As the hydration products are deposited on the cement grains, the early fast hydration reactions slow down (Odler, 2004).

- **Induction (dormant) Period (first few hours)**

After pre-induction period, the overall hydration rate slows down significantly for a few hours. In induction period, the hydration of all the clinker minerals progresses very slowly. The concentration of calcium hydroxide reaches its maximum value and starts to precipitate in this period. The concentration of SO_4^{-2} remains constant because of the dissolution of additional amounts of calcium sulfate (Odler, 2004).

- **Acceleration Stage (3 – 12 hours after mixing)**

In this period, the rate of C_3S hydration accelerates, a noticeable amount of C_2S contribute the hydration and the *second stage calcium silicate hydrate* starts to be formed. Crystalline calcium hydroxide (portlandite) precipitates and simultaneously the concentration of Ca^{+2} in the liquid phase gradually declines. The concentration of SO_4^{-2} in the liquid phase starts to decline because of the formation of the ettringite phase (Odler, 2004).

- **Post- Acceleration Period**

In this period, the hydration rate slows down because the amount of the non-reacted materials declines and the rate of the hydration process becomes diffusion controlled. As a consequence of the hydration process, strength of hardened cement paste increases while porosity decreases. Water cement ratio is important for hydration

process and sufficient amount of water should be used because the reaction may stop in the presence of significant amounts of non-reacted material, due to the lack of sufficient amounts of water needed for the hydration process (Odler, 2004).

3.1.4.1 Heat of Hydration

Portland cement clinker is formed at high temperatures hence, it is in a high-energy state. When anhydrous cement grains react with water, compounds reach a low-energy state and energy which is in the form of heat, is liberated. This heat is called *heat of hydration*. The heat of hydration is a measure of amount of heat evolved for each unit mass of anhydrous compound which has reacted. The total amount of heat liberated increases with time while the rate of heat of hydration decreases.

3.1.4.2 Measurement of the Heat of Hydration of Cement

In the industry, different calorimetric methods are used to measure the heat of hydration. Solution method, semi-adiabatic method and isothermal calorimeter method are three of them. Solution method is recommended by EN 196-8 and ASTM C186. Semi-adiabatic method is proposed by EN 196-9 and finally isothermal calorimeter method is the test described in ASTM C1702. Any of these three tests can be used to measure heat of hydration of cement.

3.1.5 Types of Portland Cement

Portland cements are manufactured to meet certain physical and chemical requirements, which depend on application. Although there are several classification systems and specifications to promote consistency of performance among cement manufacturers, because of the content of this research, only EN and API systems will be given.

According to European norms, cement types are divided into 5 different groups with respect to the mineral admixture that they incorporate and its content. In Table 3-3, EN 197-1: “Composition, specifications and conformity criteria for common cements” is given.

Table 3-3: Classification of Portland cement according to EN 197-1

Main types	Notation of the 27 products (types of common cement)		Composition (percentage by mass ^a)											Minor additional constituents	
			Main constituents												
			Clinker	Blast-furnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone				
						natural	natural calcined	siliceous	calca-reous		L	LL			
K	S	D ^b	P	Q	V	W	T	L	LL						
CEM I	Portland cement	CEM I	95-100	-	-	-	-	-	-	-	-	-	-	-	0-5
CEM II	Portland-slag cement	CEM II/A-S	80-94	6-20	-	-	-	-	-	-	-	-	-	-	0-5
		CEM II/B-S	65-79	21-35	-	-	-	-	-	-	-	-	-	-	0-5
	Portland-silica fume cement	CEM II/A-D	90-94	-	6-10	-	-	-	-	-	-	-	-	-	0-5
	Portland-pozzolana cement	CEM II/A-P	80-94	-	-	6-20	-	-	-	-	-	-	-	-	0-5
		CEM II/B-P	65-79	-	-	21-35	-	-	-	-	-	-	-	-	0-5
		CEM II/A-Q	80-94	-	-	-	6-20	-	-	-	-	-	-	-	0-5
		CEM II/B-Q	65-79	-	-	-	21-35	-	-	-	-	-	-	-	0-5
		CEM II/A-V	80-94	-	-	-	-	6-20	-	-	-	-	-	-	0-5
		CEM II/B-V	65-79	-	-	-	-	21-35	-	-	-	-	-	-	0-5
	Portland-fly ash cement	CEM II/A-W	80-94	-	-	-	-	-	6-20	-	-	-	-	-	0-5
		CEM II/B-W	65-79	-	-	-	-	-	21-35	-	-	-	-	-	0-5
		Portland-burnt shale cement	CEM II/A-T	80-94	-	-	-	-	-	-	6-20	-	-	-	0-5
			CEM II/B-T	65-79	-	-	-	-	-	-	21-35	-	-	-	0-5
	Portland-limestone cement	CEM II/A-L	80-94	-	-	-	-	-	-	-	-	6-20	-	-	0-5
		CEM II/B-L	65-79	-	-	-	-	-	-	-	-	21-35	-	-	0-5
		CEM II/A-LL	80-94	-	-	-	-	-	-	-	-	-	6-20	-	0-5
		CEM II/B-LL	65-79	-	-	-	-	-	-	-	-	-	21-35	-	0-5
	Portland-composite cement ^c	CEM II/A-M	80-88	<----- 12-20 ----->								-	-	0-5	
CEM II/B-M		65-79	<----- 21-35 ----->								-	-	0-5		
CEM III	Blastfurnace cement	CEM III/A	35-64	36-65	-	-	-	-	-	-	-	-	-	-	0-5
		CEM III/B	20-34	66-80	-	-	-	-	-	-	-	-	-	-	0-5
		CEM III/C	5-19	81-95	-	-	-	-	-	-	-	-	-	-	0-5
CEM IV	Pozzolanic cement ^c	CEM IV/A	65-89	-	<----- 11-35 ----->					-	-	-	0-5		
		CEM IV/B	45-64	-	<----- 36-55 ----->					-	-	-	0-5		
CEM V	Composite cement ^c	CEM V/A	40-64	18-30	-	<----- 18-30 ----->			-	-	-	-	0-5		
		CEM V/B	20-38	31-49	-	<----- 31-49 ----->			-	-	-	-	0-5		

^a The values in the table refer to the sum of the main and minor additional constituents.
^b The proportion of silica fume is limited to 10 %.
^c In Portland-composite cements CEM II/A-M and CEM II/B-M, in pozzolanic cements CEM IV/A and CEM IV/B and in composite cements CEM V/A and CEM V/B the main constituents other than clinker shall be declared by designation of the cement (for examples, see Clause 8).

3.1.6 Blended Cements

In order to decrease the amount of the greenhouse gases in the atmosphere and to slow down the global warming, many countries trying to find ways to curb the CO₂ emissions. The cement manufacturing process consumes energy at high levels, and this new era force the industry to decrease the CO₂ emissions. As a consequence of this force, blended cements are increasingly being used by the industry all over the world. The philosophy of blended cements is to replace a certain amount of clinker with cement replacement materials, such as limestone, fly ash, slag. These materials

may aid both initial and final strength, workability characteristics, durability performance or simply can be used as filler (Tokyay et al, 1999).

Menendez, Bonavetti and Irassar (2003), studied the benefits of limestone as a partial replacement material and they found that limestone replacement increases hydration at early ages however because of dilution effect limestone addition decreases the later age strength.

Heikal, El-Didamony and Morsy (2000) studied the effects of addition of limestone. They found that because of formation of carboaluminate, limestone fills the pores between cement particles. According to Heikal et al. (2000) this may cause increase on the rate of hydration of cement and decrease setting time.

3.2 Oil Well Cements

3.2.1 Types of Oil Well Cements

Specifications for oil well cements are different than that of the Portland cement types applied in construction industry. In the well conditions, cement slurries are exposed to high pressure, high temperature and corrosive underground fluids. API designates the specifications for cement types according to those well conditions. There are 8 types of API Portland cements defined according to depth of the well and degrees of sulfate resistance. Although API specifications do not cover all the well conditions for cementing including extremely hot and cold well conditions, these eight types of cements fulfil most of the well conditions. Descriptions of API cement types are given below.

Table 3-4: Brief description of API cement types

API Class	Intended for Use	Sulfate Resistance
A	Up to 1830m	Ordinary
B	Up to 1830m	Moderate and high
C	Up to 1830m	Ordinary, moderate and high
D	From 1830m to 3050m	Moderate and high
E	From 1830m to 4270m	Moderate and high
F	From 1830m to 4880m	Moderate and high
G	Applicable to wide range	Moderate and high
H		

The typical compositions of API cement types are listed in Table 3-5.

Table 3-5: Typical composition and fineness of oil well cements (Nelson, 1983)

API Class	Typical Potential Phase Composition (%)				Typical Fineness (cm ² /gr)
	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	
A	45	27	11	8	1600
B	44	31	5	13	1600
C	53	19	11	9	2200
D	28	49	4	12	1500
E	38	43	4	9	1500
G	50	30	5	12	1800
H	50	30	5	12	1600

3.2.2 Oil Well Cement Additives

In well cementing, cement slurries are exposed to temperatures ranging from below freezing in permafrost zones to 350°C in geothermal wells; pressures ranging from near ambient in shallow wells to more than tens of thousands psi in ultra-deep wells. In addition to severe temperature and pressure conditions, cement slurries also contend with weak or porous formations, corrosive fluids, over-pressured formations, etc. API

specifications fulfill most of the well conditions mentioned above. But in order to accommodate such a wide range of conditions, cement additives are often used.

Although lots of well cementing additives are available in the market either solid or liquid, seven categories of additives are generally recognized. Their actions and mechanism is given in Table 3-6.

Table 3-6: Summary of additives and mechanisms of action (Nelson, 1983)

		Accelerator	Extenders	Weighting Agents	Retarders	Friction Reducers	Filtration Additives	Lost Circulation Additives
Water Requirements	<i>Increases</i>		XX				X	X
	<i>Decreases</i>					X		
Density	<i>Increases</i>			XX				
	<i>Decreases</i>		XX			XX		XX
Viscosity	<i>Increases</i>		X	X			X	
	<i>Decreases</i>	X			X	XX		
Thickening Time	<i>Increases</i>	XX						
	<i>Decreases</i>		X		XX	X	X	
Fluid Loss of Slurry	<i>Increases</i>							
	<i>Decreases</i>		X			X	XX	
Early Strength	<i>Increases</i>	XX				X		
	<i>Decreases</i>		X	X	XX		X	
Final Strength	<i>Increases</i>					X		
	<i>Decreases</i>		X					
Durability	<i>Increases</i>					X		
	<i>Decreases</i>		X					

XX: Major Effects

X: Minor Effects

CHAPTER 4

STATEMENT OF PROBLEM

Hydration of cement is an exothermic reaction, i.e. heat is evolved during hardening of cement paste. The amount of evolved heat is not an important parameter for most of the cementing operations conducted during oil, gas or geothermal well drilling. However, it became important after the industry gravitated to low temperature environments for exploring resources.

Natural gas hydrates form under low temperature and high pressure conditions if the gas and water exist and they are stable as long as temperature and pressure conditions are not changed. But high heat of hydration of conventional cements may disturb the gas hydrate stability and cause problems during cementing operations. Hence, it is important to lower the heat of hydration of cement slurries while meeting or exceeding other requirements for good cement jobs.

In this study, effects of changing limestone amount on the properties of CEM-I and API Class G cements was studied. The heat of hydration of cement slurries were the main parameter while monitoring compressive strength, porosity and permeability of hardened cement pastes. This study also aims to promote the use of cement replacement materials to decrease the greenhouse gases in the atmosphere.

CHAPTER 5

EXPERIMENTAL SET-UP AND PROCEDURE

5.1 Introduction

Several laboratory tests were carried out during this study to predict and evaluate the performance of the limestone incorporated cement slurries for their effective use in deepwater cementing operations where gas hydrates exist. All tests were done in accordance with the API standards, however only water to cement ratio (W/C) was selected differently which is 40% as described in EN 196-8.

5.2 Materials

CEM-I 42,5R Portland cement, API Class G Cement, and limestone are used as raw materials in this study. All materials are obtained from Oyak Bolu Cement Plant. Chemical analysis, physical properties and mineralogical compositions of these materials as provided by their manufacturer are given in the Table 5-1, Table 5-2, and Table 5-3 respectively. Water used in this study for preparing cement slurries is distilled water.

Table 5-1: Chemical Analysis of Materials

Composition (%)	Materials		
	CEM I 42.5 R	Class G	Limestone
CaO	63.04	63.11	55.31
SiO ₂	20.10	19.54	0.52
Al ₂ O ₃	5.01	4.36	0.13
Fe ₂ O ₃	4.32	5.93	0.10
MgO	1.64	2.05	0.28
SO ₃	3.28	2.58	0.04
Na ₂ O	0.23	0.23	0.02
K ₂ O	0.53	0.49	0.04
Cl-	0.0267	0.018	-
TiO ₂	-	-	-
Mn ₂ O ₃	-	-	-
Loss on Ignition	1.33	1.42	43.56
Free CaO	0.73	-	-

Table 5-2: Physical Analysis of Materials

Physical Properties	Materials	
	CEM I 42.5 R	Class G
Specific Gravity	3.18	3.21
Initial setting time, min	105	115
Specific Surface, cm ² /gr	4400	3200
Compressive Strength (2 days), MPa	33.0	18.1
Compressive Strength (28 days), MPa	55.3	45.3

Table 5-3: Mineralogical composition of the Portland cement and Class G cement clinker

Minerals	Materials	
	CEM I	Class G
C3S	54.62	63.22
C2S	16.50	8.40
C3A	6.00	1.55
C4AF	13.20	18.10

Eight cement slurry compositions were prepared. First two compositions were prepared with neat CEM-I cement (C100) and API Class G (G100). The remaining ones were prepared with the blends of CEM I, Class G and limestone. The ratios of CEM I, Class G and limestone in the blends by mass are given in the following table.

Table 5-4: Prepared Cement Samples

		CEMENT TYPE							
		C0	C15	C30	C45	G0	G15	G30	G45
CONTITUENTS	CEM-I (g)	100	87	77	69	0	0	0	0
	API G-TYPE (g)	0	0	0	0	100	87	77	69
	LIMESTONE (%bwoc)	0	15	30	45	0	15	30	45
	WATER (ml)	40	40	40	40	40	40	40	40

5.3 Slurry Preparation

Cement slurries were prepared according to the specifications in API Spec. 10A (API, 2010). The mixing device is 1 liter, two speed, bottom drive, blade type mixer from Chandler Engineering.

Slurry Preparation for Heat of Hydration Determination

Cement slurries are prepared by mixing manually 10 g of anhydrous cement with 4 g of distilled water for 3 minutes at ambient temperature, Figure 5-1a and 5-1b. Because of given W/C is 0.40 in EN 196-8, in order to standardize all tests with each other, W/C is determined as 0.40 for all tests. The resulting pastes are put into the plastic cylindrical vials and sealed to prevent evaporation of water, Figure 5-1c.

Slurry Preparation for Other Tests

Distilled water is used for testing. Mixing quantities are determined by using selected W/C of %40. Water is put into the mixing container. Then the motor is turned on and maintained at 4000 rpm, Figure 5-2a. Cement and other materials are added to water in no more than 15 seconds. Finally, cover is placed on the container and mixing is continued at 12000 RPM for 35 seconds, Figure 5-2b.



Figure 5-1: Slurry Preparation for Heat of Hydration Determination



Figure 5-2: Slurry Preparation for Other Tests

5.4 Heat of Hydration Determination

Heat of hydration measurement is important for assessing the cement hydration rate as well as assessing the potential temperature rise/fall in concrete elements. Temperature rise that occurs due to mixing of cement with water is caused by the exothermic nature of the interaction of anhydrous cement with water.

In order to determine the heat of hydration value of each slurry and rate of heat release during hydration, all slurries were tested at 1st, 7th, and 28th day. Tests were carried out as described in EN 196-8 and ASTM C1702. Briefly, EN 196-8 measures the heat of solution of anhydrous cement in an acid mixture and that of hydrated cement in the same acid mixture under predetermined conditions and time intervals. The heat of hydration for each period is found by subtracting the heat of solution of hydrated cement from that of anhydrous cement. On the other hand, ASTM C1702 uses an isothermal conduction calorimeter. Energy produced by chemical reactions is measured by calorimeter and visualized by software. The advantage of ASTM C1702 is that highly detailed data can be collected during HOH measurements from the beginning of the experiment to the end.

Figure 5-3 shows the calorimeter used during tests. It was manufactured in this study according to EN 196-8. All spare parts, including data logger, acid resistant Pt-100 thermometer, high speed mixer, propeller, Dewar flask, insulating container, foam and plug, were purchased or fabricated according to EN 196-8. Then they were all put together for the tests. The details of the design phase of the calorimeter is given in Appendix E.

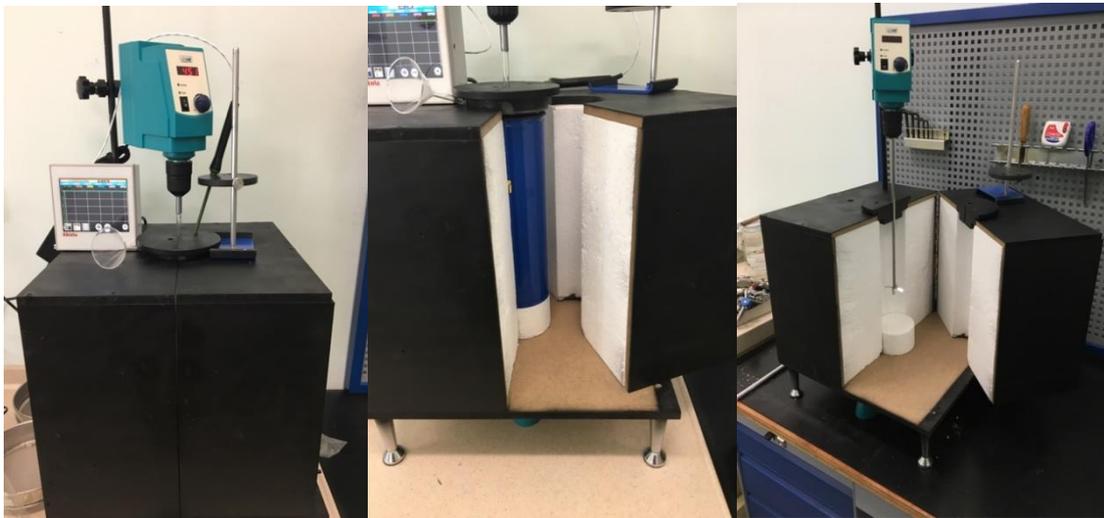


Figure 5-3: Designed Calorimeter

5.5 Compressive Strength

The cement slurries are prepared according to API Specification 10A, except W/C, and placed into cylindrical vials with a diameter and length of 36 mm and 55 mm, respectively, Figure 5-4a. The vials are then cured in a temperature-controlled room at 15 °C for 1, 7, and 28 days respectively. The compressive strengths of the specimens are tested at a loading rate of 1.5 kN/s by UTEST in the Materials of Construction laboratory of METU Civil Engineering Department, Figure 5-4b and 5-4c.



Figure 5-4: Compressive strength tests

5.6 Porosity

Cement slurries are prepared and put into the cylindrical vials. As for compressive strength test, vials are cured in a temperature-controlled room at 15 °C for 1, 7, and 28 day respectively. Before porosity measurements, the core specimens are put into temperature-controlled vacuum oven to remove moisture to stop further hydration of hardened cement pastes (Figure 5-5). The conditioning program of the core samples in the oven is given in Table 5-5.

Table 5-5: Conditioning program of the core samples for porosity measurements

Step	Temperature (°C)	Time (hour)
1	60	4
2	80	4
3	110	12
4	40	4



Figure 5-5 : Removing moisture inside the core specimens by using vacuum oven

Helium Porosimeter, based on Boyle's Law, was used to determine porosity of the hardened cement pastes as shown in Figure 5-6.



Figure 5-6: Helium Porosimeter

Apparatus basically measures final pressure and using Boyle's law, solid volume can be calculated easily. Cores are tested with helium under the pressure of around 7 bar. The test method is performed according to the specifications described in API RP 40 (API, 1998). After measuring solid and pore volume, porosity is calculated with the following equations.

$$\text{Pore Volume} = \text{Bulk Volume} - \text{Solid volume} \quad (5.1)$$

$$\text{Porosity} = \text{Pore Volume} / \text{Bulk Volume} \quad (5.2)$$

5.7 Permeability

After measuring porosity, permeability of hardened cement pastes was measured by using Gas Permeameter in METU Petroleum & Natural Gas Engineering Department (Figure 5-7). Because of the fact that hardened cement pastes have lower permeability, helium gas is used instead of water to measure permeability.



Figure 5-7: Steady state gas permeameter

Apparatus basically measures flow rates at different pressure values. Then the calculation of permeability is derived by using Klinkenberg Effect. The permeability of a sample to a gas changes with the molecular weight of the gas and the applied pressure, as a result of gas slippage at the pore wall. Klinkenberg (1941) determined that,

$$k_L = k_g / \left(1 + \frac{b}{p} \right) \quad (5.3)$$

Where:

k_L is the liquid permeability, mD

k_g is the gas permeability, mD

p is the mean flowing pressure, bar

b is a constant for a particular gas in a given rock type

CHAPTER 6

EXPERIMENTAL RESULTS AND DISCUSSION

6.1 Compressive Strength

Compressive strength development is highly dependent on the temperature. Cement slurries are exposed to low temperatures during deepwater drilling operations. The sediment depths where gas hydrates reside are the top 200-300m where the temperature is expected in the range of 15-20°C. In that respect, the curing temperature of cement slurries is taken as 15°C.

Table 6-1 shows the mean values of the results – details are given in Appendix A – of the compressive strength tests of hardened cement pastes at ages of 1-day, 7-days and 28-days, respectively. During compressive strength tests 4 hardened cement specimens were tested for each cement composition. Outliers are eliminated with a confidence level of 90%.

Table 6-1: Compressive strength and coefficient of variation (CV) of hardened cement pastes

<i>Cement Type</i>	<i>1-day (MPa)</i>	<i>CV</i>	<i>7-days (MPa)</i>	<i>CV</i>	<i>28-days (MPa)</i>	<i>CV</i>
<i>C0</i>	27.7	0.0348	41.4	0.0193	63.3	0.0260
<i>C15</i>	23.2	0.0428	38.3	0.0373	53.4	0.0126
<i>C30</i>	20.7	0.0159	30.7	0.0154	47.8	0.0149
<i>C45</i>	14.3	0.0579	22.4	0.0297	44.0	0.0274
<i>G0</i>	11.3	0.0643	23.2	0.0563	37.8	0.0242
<i>G15</i>	10.2	0.1025	16.7	0.0718	33.5	0.1138
<i>G30</i>	8.6	0.0319	16.3	0.0503	26.2	0.0889
<i>G45</i>	5.1	0.0465	7.8	0.0702	11.3	0.0570

According to Table 6-1, almost half of the hydration of C0 cement has been achieved in the first day and relatively lower strength gain is observed at later ages. On the contrary to C0 cement, compressive strength development of G0 cement is much slower. This can be explained by higher fineness value of C-cements. The API Class G cement used in this study has a higher C₃S content than CEM-I type cement, while fineness of the API Class G cement (3200 cm²/g) is lower than that of CEM-I type cement (4500 cm²/g). Although C₃S promotes early hydration in general and early strength of cement pastes expected to be higher as a result of early hydration, the API Class G cement has lower strength values than CEM-I type cement because API Class G cement is coarsely grounded which reduces hydration rate and compressive strength development.

The increasing amount of limestone decreases the compressive strength of cement pastes. C45 and G45 contain highest amount of limestone and show the lowest compressive strength at all ages. The percent reduction of compressive strength of cement pastes according to amount of limestone added is given in Figure 6-1 and 6-2. C0 and G0 are selected as a control samples for all ages, i.e. their compressive strength values assumed to be a 100%. As seen from the figures, incorporation of 45% limestone causes a strength reduction of 30% for CEM-I but 70% for Class-G cement at 28 days.

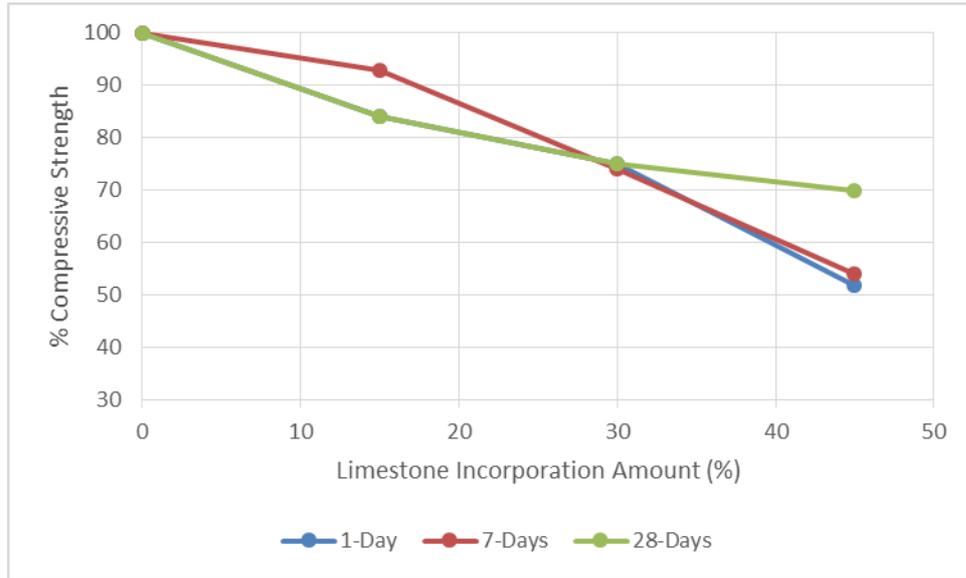


Figure 6-1: Percent reduction of compressive strength values of C-cements

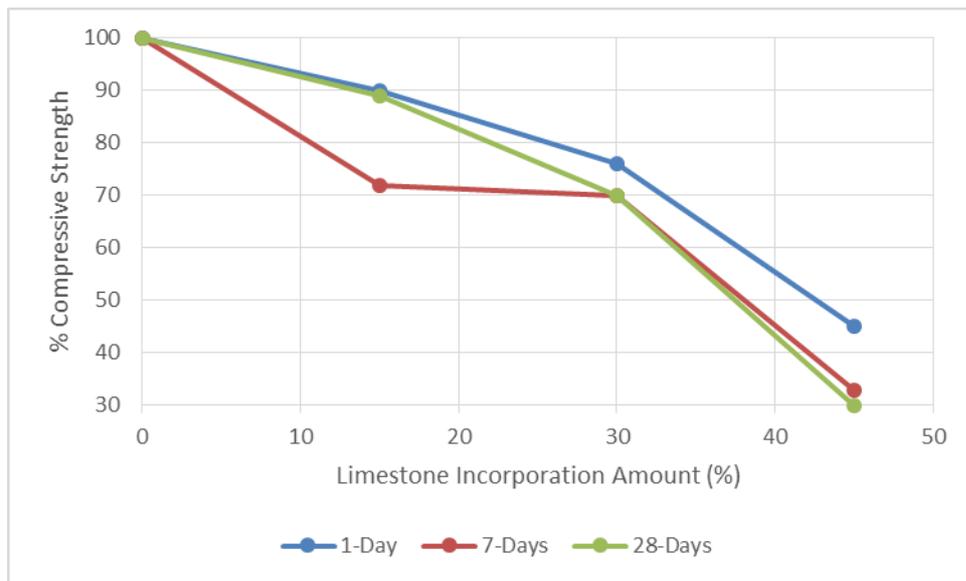


Figure 6-2: Compressive strength reduction of G-cements

6.3 Heat of Hydration of Cement Slurries

HOH of all samples were measured with isothermal conduction calorimetry and solution method according to ASTM C1702 and EN 196-8, respectively. For each measurement 3.5 g cement and limestone (if included) was mixed with 1.4 g of distilled water. Water cement ratio was 0.40 and channel temperature was chosen to be 23 °C for isothermal conduction calorimetry; and ambient temperature was chosen to be 20 °C for solution method during measurements of all samples. Heat of hydration tests applied to all of the cement pastes in this study in terms of 1 day, 7 days and 28 days. The test results are analyzed in terms of the amount of the limestone addition.

6.3.1 Isothermal Conduction Calorimetry (ASTM C1702)

The cumulative heat of hydration of all cement samples for 28 days is given in Figure 6-3 and the rate of heat liberation values obtained are given in Figure 6-4 and 6-5 for the first 3 days.

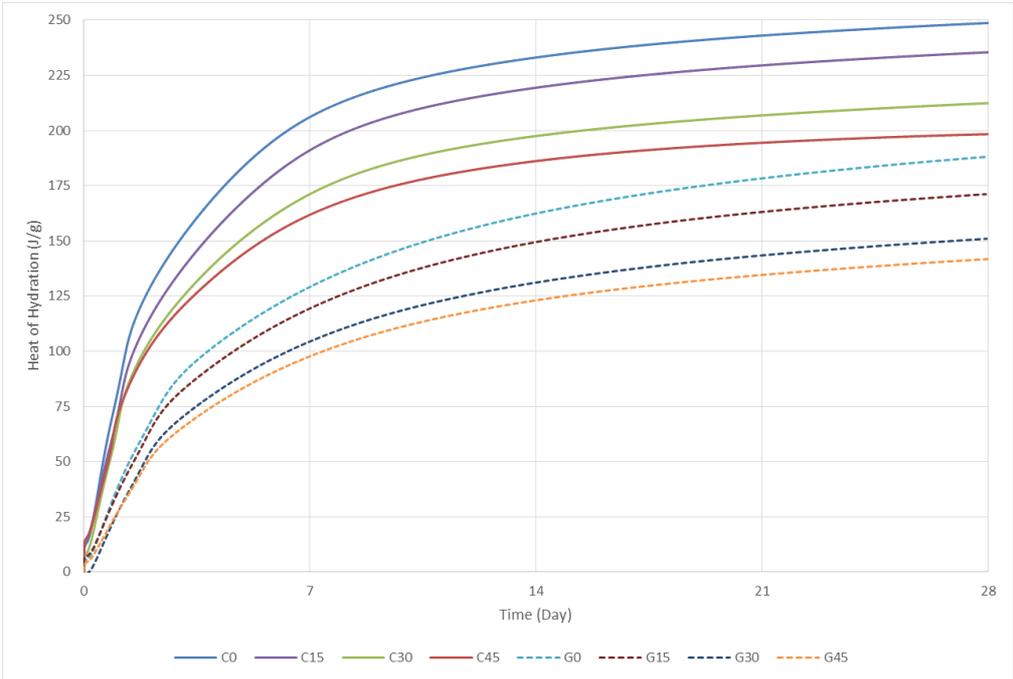


Figure 6-3: Cumulative HOH of all cement samples at 28 days

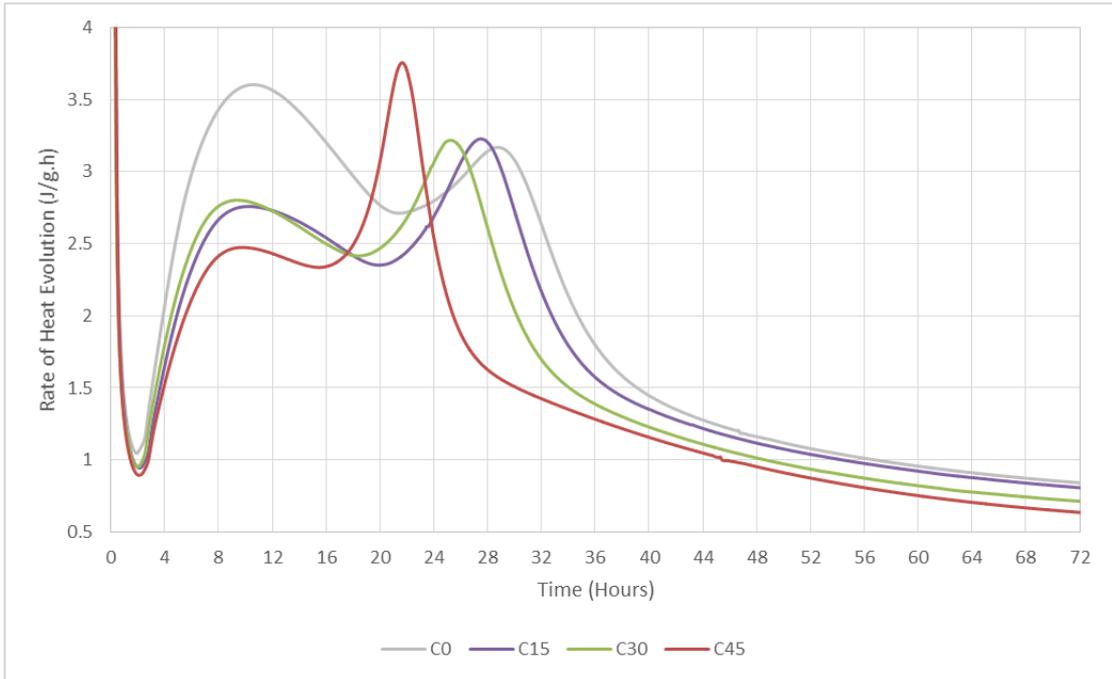


Figure 6-4: 72-h rate of heat liberation of C-cements

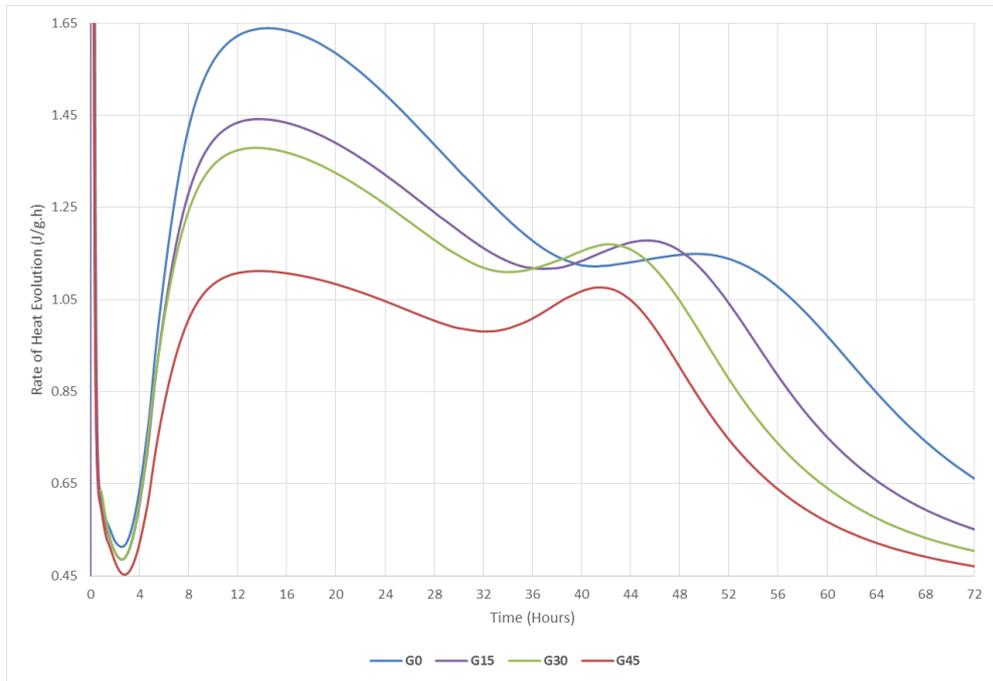


Figure 6-5: 72-h rate of heat liberation of G-cements

The heat of hydration of slurries containing CEM-I cement are higher than API Class G containing ones. Because of higher fineness value of CEM-I cement, more clinker particles react chemically with water and produce more heat when they are introduced to water.

The first peak seen in the figures is related with C₃S amount. Although C₃S content of API Class G Cement is higher than CEM-I cement, peak values of CEM-I containing pastes are higher because of its higher fineness value. Fineness also affects the rate of heat evolution of cement pastes. The required time to reach the peak value decreases with increasing fineness and amount of limestone added. Table 6-2 shows the required time to reach the peak value for each cement paste.

Table 6-2: Required time to reach the peak value

<i>Cement Type</i>	<i>C0</i>	<i>C15</i>	<i>C30</i>	<i>C45</i>
<i>Time (Hour)</i>	10.80	10.25	9.50	9.70
<i>Cement Type</i>	<i>G0</i>	<i>G15</i>	<i>G30</i>	<i>G45</i>
<i>Time (Hour)</i>	15.3	14.8	14.1	14.6

Generally, the end of the acceleration stage is seen in first 12 hours but for API Class G cement containing slurries the time is little bit higher. As seen in Table 6-2, the time is decreasing with increasing limestone amount and with increasing fineness value.

In most but not all cements, a small peak may be observed after the first (main) peak, which is probably due to renewed AFt (ettringite) formation (Lea, 1971). As shown in Figure 6-4 and 6-5, second peak is more significant for CEM-I cement containing slurries because of its higher C₃A content. Increasing amount of limestone content also decreases both peak value and the time required to reach that peak.

As a consequence, limestone decreases the amount of heat liberated during hydration and hence, decreases the cumulative heat of hydration. Limestone increases the rate of heat of hydration of cement samples which also means that because of its acceleration effect, limestone decreases the setting time of cement pastes. C_3S content of cement contributes heat of hydration directly however, the effect of fineness on the heat of hydration is more significant for this study than C_3S content. C_3A content affects both the rate of heat of hydration and cumulative heat of hydration of cement. Second peak after the main one may also take place if all soluble sulfate is consumed before the C_3A completely reacted and this may cause the rate of heat of hydration increase, which can be slightly or significantly according to cement's C_3A content.

6.3.2 Heat of Solution Calorimetry (EN 196-8)

The following table shows the mean values of the heat of hydration calculated for the eight different cement samples. During HOH tests, 2 consistent results were taken. Detail of the HOH data is given in Appendix B.

Table 6-3: Heat of hydration and coefficient of variation (CV) of cement pastes

<i>Cement Type</i>	<i>1-day HOH (J/g)</i>	<i>CV</i>	<i>7-days HOH (J/g)</i>	<i>CV</i>	<i>28-days HOH (J/g)</i>	<i>CV</i>
<i>C0</i>	76.46	0.0221	200.65	0.0186	224.00	0.0378
<i>C15</i>	69.00	0.0542	188.15	0.0394	202.20	0.0311
<i>C30</i>	64.35	0.0868	165.30	0.0239	183.00	0.003
<i>C45</i>	61.30	0.1323	160.20	0.022	175.80	0.0365
<i>G0</i>	47.00	0.0976	129.36	0.036	167.00	0.0381
<i>G15</i>	41.30	0.065	115.13	0.0067	141.00	0.0265
<i>G30</i>	36.25	0.0292	101.10	0.0587	122.40	0.0265
<i>G45</i>	33.20	0.2044	97.00	0.0619	115.00	0.0227

The results of the analysis showed that the cumulative heat of hydration decreases with increasing amount of limestone added. Figure 6-6 and 6-7 show effect of limestone amount on the heat of hydration of cement pastes. C0 and G0 were selected as a control samples, in other words heat of hydration of C0 and G0 were accepted 100%. As seen

from the figures, increasing amount of limestone in the cement pastes decreases the cumulative HOH at all ages. Incorporation of 45% limestone causes a HOH reduction of 20% for CEM-I cements while 32% for Class G cements at 28 days.

According to EN 196-8, the standard deviation of repeatability is 8 J/g. As shown in Table 6-4, standard deviation of samples is sometimes very close but always lower than reported value for this study. These results prove that calorimeter is properly designed in accordance with the EN 196-8.

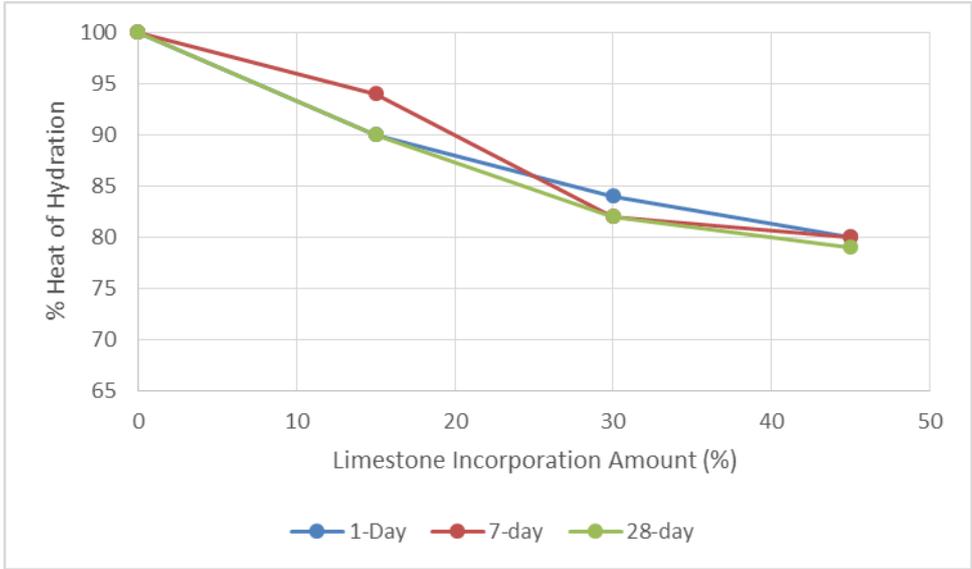


Figure 6-6: HOH reduction of C-cements

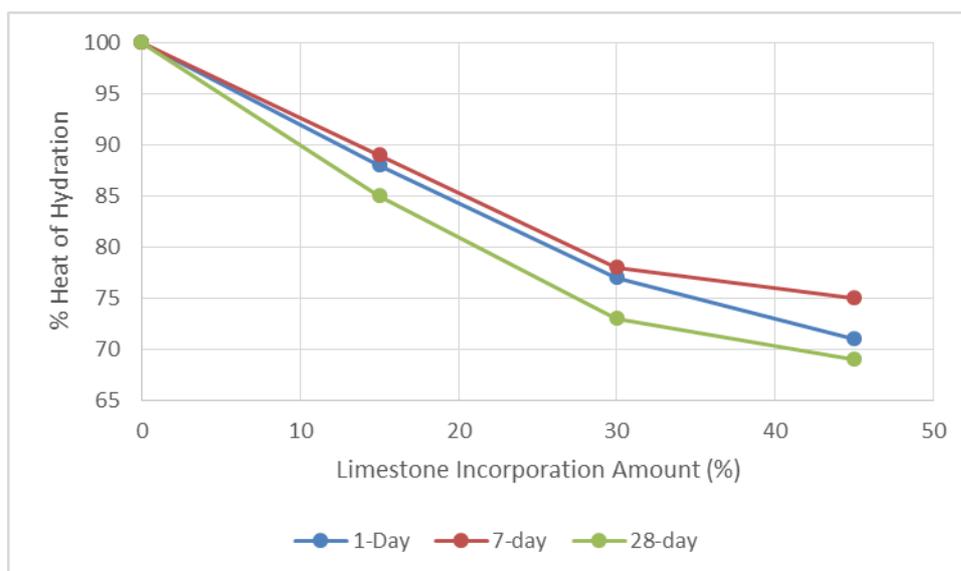


Figure 6-7: HOH reduction of G-cements

Table 6-4: Sample standard deviation of cement samples

	<i>C0</i>	<i>C15</i>	<i>C30</i>	<i>C45</i>	<i>G0</i>	<i>G15</i>	<i>G30</i>	<i>G45</i>
Standard Deviation (J/g)								
1-Day	1.70	3.75	5.59	7.42	4.60	2.69	1.06	6.79
7-Days	3.75	7.42	3.96	3.54	4.67	0.78	5.94	6.01
28-Days	7.77	6.29	0.57	6.43	6.36	3.75	3.25	2.62

6.3.3 Comparison of HOH Results Obtained by Two Different Standards

EN196-8 and ASTM C1702 are two different methods for HOH measurements of hydraulic cements. Heat of solution method (EN 196-8) measures the temperature rise of the acidic solution resulting from the decomposition of the anhydrous and hydrated cement. The difference between the heat of solution of the anhydrous and hydrated cement can be calculated as the heat evolved during the hydration period. ASTM C1702 uses an isothermal conduction calorimeter which has two ampoules. One of them is used to hold sample ampule and the other one for the reference material. Energy produced by chemical reactions is measured by calorimeter and visualized by software.

The advantage of ASTM C1702 is that highly detailed data can be collected during HOH measurements from the beginning of the experiment to the end. Additionally, isothermal conduction calorimeter measures the HOH instantly from the time of mixing of cement with water. This method can also be executed with better precision when compared to the heat of solution method.

Isothermal conduction calorimeter was used to evaluate the effect of limestone amount on the rate of hydration of cement pastes at early ages (3 days) during this study. But experiment was not stopped at 3 days thanks to availability of instrument and hence cumulative heat of hydration of cement samples for 28 days has also been analysed. Table 6-5 shows the HOH of cement pastes measured via isothermal conduction calorimeter.

Table 6-5: Heat of hydration of all cement pastes at different ages

<i>Cement Type</i>	<i>1-Day Heat of Hydration (J/g)</i>	<i>7-Days Heat of Hydration (J/g)</i>	<i>28-Days Heat of Hydration (J/g)</i>
<i>C0</i>	78.33	206.13	248.75
<i>C15</i>	68.10	191.10	235.48
<i>C30</i>	62.80	171.20	212.42
<i>C45</i>	68.39	161.00	198.00
<i>G0</i>	36.00	129	188.10
<i>G15</i>	34.12	119.25	171.00
<i>G30</i>	25.10	104.35	150.00
<i>G45</i>	25.80	97.65	141.70

During this study, HOH of cement pastes was also measured with designed calorimeter in accordance with EN 196-8. Although it was not experimented because of technical and economic problems, the reason why EN 196-8 was chosen instead of ASTM C1702 at the beginning is that cement samples can be cured at high pressure first and then be tested if EN 196-8 is used. Thus, the effect of pressure on the HOH is not ignored.

After all HOH tests were finished, the results of two methods were compared with each other. Theoretically, as expected, the results given in Table 6-3 and 6-5 should have been the same but as shown in Table 6-6, there are some minor differences in between results of two methods. The rate of the chemical reactions is highly dependent on temperature. Any fluctuation affects the rate of chemical reaction and simultaneously the rate and the amount of evolved heat are also affected for exothermic reactions. The results given in Table 6-6 were normalized according to heat values obtained from isothermal conduction calorimetry. As shown in the table, the difference is increasing with age. This is probably because of the fact that the curing temperatures are not same for the methods (20 °C for EN 196-8 and 23 °C for ASTM C1702), the rate of hydration of same cement sample at a given age is also different for each method. As seen in Figure 6-8, 3 °C difference does not create significant effect at early ages however it creates almost 20% increase at later ages.

Table 6-6: Normalized Difference between the results of two methods

<i>Cement Type</i>	<i>1-Day</i>	<i>7-Days</i>	<i>28-Days</i>
<i>C0</i>	0.024	0.027	0.099
<i>C15</i>	-0.013	0.015	0.141
<i>C30</i>	-0.025	0.034	0.138
<i>C45</i>	0.104	0.005	0.112
<i>G0</i>	-0.306	-0.003	0.112
<i>G15</i>	-0.210	0.035	0.175
<i>G30</i>	-0.444	0.031	0.184
<i>G45</i>	-0.287	0.007	0.188

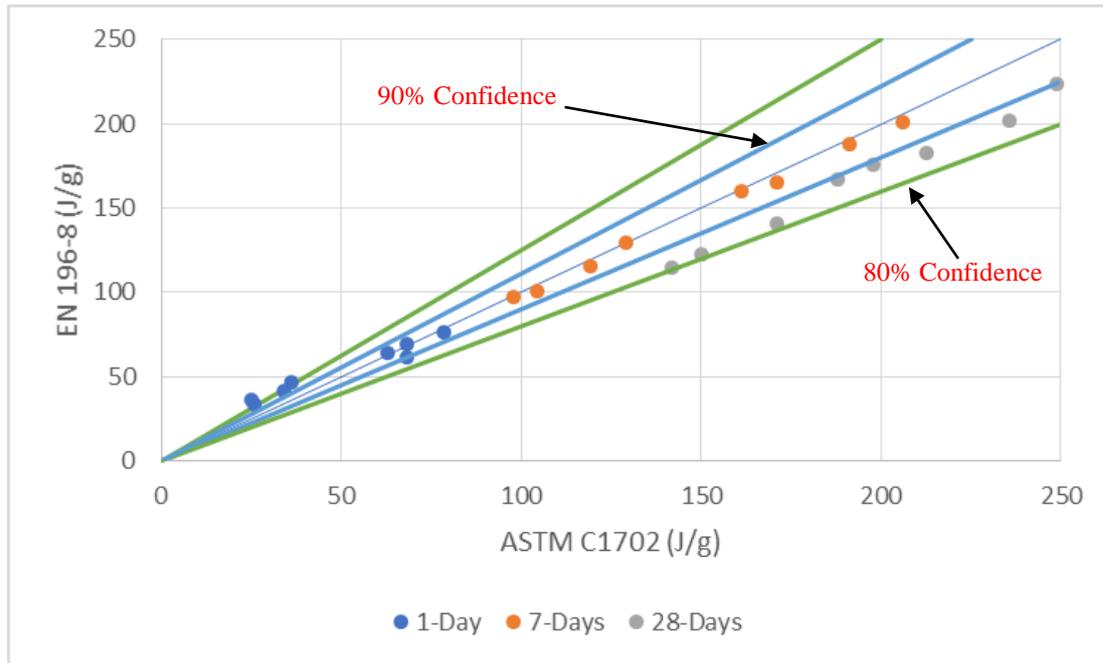


Figure 6-8: Comparison of ASTM C1702 vs EN 196-8

6.4 Porosity

Mean values of porosity of hardened cement pastes is listed in Table 6-7. For each type of cement, three different specimens were prepared and tested by using same cylindrical vials with a diameter and length of 36mm and 55mm. Details of porosity measurement data are also given in Appendix C.

Table 6-7: Porosity of hardened cement pastes

CEMENT TYPE	1-day Porosity (%)	7-days Porosity (%)	28-days Porosity (%)
C0	32.55	30.21	24.18
C15	35.27	31.22	28.50
C30	37.67	32.55	28.62
C45	39.61	34.87	30.15
G0	36.74	33.63	30.21
G15	40.37	36.41	31.22
G30	43.97	39.43	32.55
G45	46.83	42.50	34.87

According to Table 6-7, porosity decreases with age in all pastes. The porosity of C-cements always lower than G-cements at all ages, however the difference is comparable small at later ages.

Heikal et al. (2000) studied the effect of addition of limestone to the cement. They found that the addition of limestone reduces the total porosity, whereas the free lime and combined water increase with limestone content

During hydration of low W/C mixes, a portion of the cement often remains unhydrated. By replacing that cement with a relatively inert material such as limestone, the degree of hydration increase (Bonavetti, Donza, Menendez, Cabrera, Irrasar, 2003).

6.5 Permeability

Steady state gas permeameter was used to measure the permeability of hardened cement pastes. Same specimens using for porosity measurements (3 different specimen for each composition) were also used for permeability measurements and results are shown in Table 6-8. Detailed data is given in Appendix D. In order to eliminate the possibility of cracking, CT device was used for investigation of cracks for all core samples.

All samples were put into same cylindrical vials as porosity measurements during curing so that coring was not applied. To avoid thermal deformation during drying operations, temperature was increased/decreased gradually. Before permeability measurements, CT device was used for investigation of cracks and connected pores. 12 different images were taken for each core. The distance between 2 taken images is 5mm. The images of core specimens were analyzed in order to investigate fractures and inter-connected pores. The images of C0 cement at 28-days are shown in Figure 6-9 and 6-10. All images are also shown in Appendix F.

Table 6-8: Permeability of hardened cement pastes

CEMENT TYPE	1-day (mD)	7-days (mD)	28-days (mD)
C0	0.045	0.022	0.014
C15	0.094	0.067	0.072
C30	0.224	0.113	0.024
C45	0.623	0.187	0.019
G0	0.051	0.028	0.022
G15	0.101	0.069	0.081
G30	0.216	0.133	0.075
G45	0.227	0.165	0.136

According to Table 6-8, permeability of cements is low at all ages. C-cements have lower permeability than G-cements. Although increasing amount of limestone also increases the permeability of hardened cement pastes, maximum permeability value is still lower than 0.15 mD at 28-days.

CHAPTER 7

CONCLUSION & RECOMMENDATION

7.1 Conclusion

The aim of this study was to investigate the applicability of limestone blended cements in deepwater gas hydrate containing environments. Effects of limestone amount on properties of prepared cements were determined. Cylindrical vials with a length and diameter of 55mm and 36mm was used for all tests. The first type of analysis was compressive strength tests. Compressive strength tests were performed at 1st, 7th and 28th days. Curing temperature was 15°C. After compressive strength tests, heat of hydration of blended cements were determined by using both isothermal conduction calorimeter in accordance with ASTM C1702 and heat of solution calorimeter which was manufactured according to EN 196-8. All samples were tested at 1st, 7th and 28th days same as compressive strength tests. However, curing temperature was 20°C. The third type of analysis which applied to hardened cement pastes was porosity measurements. All samples were dried before tests to remove moisture and stop further hydration. Testing pressure was about 7 bar and used gas is helium. After porosity measurements, same samples were used for permeability measurements. Steady state gas permeameter was used for testing. The outcomes of the analyses are as follows:

- The increasing amount of limestone decreases compressive strength of blended cements. At lower replacement levels, limestone added blended cements show admissible strength reduction. However, the increase in limestone content dramatically decreases the strength values for later ages. Incorporation of 45% limestone causes a strength reduction of 30% for CEM-I and 70% for Class G cement at 28-days. Because of higher fineness value of CEM-I cement, compressive strength reduction is much lower than Class G cement at a given age.

- Heat of hydration analysis performed on limestone blended cements showed that the addition of limestone decreases the heat of hydration. One another outcome is that addition of limestone increases the rate of cement hydration in other words decreases the required time to reach the end of the acceleration period. Because of higher fineness value of CEM-I cement, the rate of heat of hydration is higher than Class G cements. However, the effect of fineness on the rate of heat of hydration is more significant than C_3S content for this study, although C_3S content of cement contributes heat of hydration directly. Additionally, during this study heat of hydration was measured by using both isothermal conduction calorimeter and heat of solution calorimeter in accordance with ASTM C1702 and EN 196-8, respectively. The results obtained from two different method compared with each other. Although the results of heat of hydration of same cement sample show some minor differences at 28-days, results were almost same for 1-day and 7-days.
- Limestone existence in the blends increases the porosity of hardened cement pastes especially at early ages. However, because of the fact that hydration products of cement and limestone in the cement paste fill the pores, the effect diminishes at later ages with increasing the degree of hydration. The results of permeability analysis were consistent with the results obtained from porosity analysis. Although increasing amount of limestone increases the permeability of hardened cement pastes, permeability value is still very low. In order to investigate the possibility of cracking, CT device was used. 12 different images (5mm space between two image) were taken from each hardened cement paste at 28-day and as a result of analysis of images, possibility of cracks was eliminated.

According to these results, it can be possible to use limestone as a cement replacement material for cementing wells drilled in deepwater gas hydrate containing environments. It is important to keep in mind that the most important parameter which taken into consideration in this study was heat of hydration of blended cements. The Class G cement paste with a 45% of limestone shows better results compared to neat

cement paste. Its heat of hydration, porosity and permeability are favourable. However, it showed the lowest compressive strength –almost 70% reduction. This should be taken into consideration when higher compressive strength is needed.

7.2 Recommendations

The following recommendations can be useful for future studies.

- The fineness values of CEM-I and API Class G cements did not same. The effect of limestone amount on the behavior of the cement pastes could be investigated by choosing fineness value of CEM-I and API Class G identical.
- Strength development is important factor especially for offshore operations. In order to observe compressive strength development of the cement pastes, Ultrasonic Cement Analyzer could be used.
- During measuring of heat of hydration of cement samples, room temperature could be kept as constant as possible. If it is possible, relatively small room should be used for the measurements. Molarity of HNO_3 is important parameter for EN 196-8, hence it is important to preparing the acid mixture by using digital measuring tools if possible or pre-prepared HNO_3 solutions can be purchased.
- Chemical additives are frequently used in well cementing operations in order to obtain required properties. Therefore, the effects of chemical additives on the limestone blended cements can be investigated.
- At the beginning of this study, the plan was to cure the blended cement pastes at reservoir conditions in other words low temperature and high pressure conditions. But because of technical and economic problems, curing chamber was not manufactured and all test were done at atmospheric pressure. Therefore, it may present some other meaningful results if high pressure curing chamber is used to cure the cement pastes before the tests.
- During heat of hydration tests, curing temperatures were different for the methods. This temperature difference did not create major differences at early ages but the gap between results increased at later ages. In order to compare

two method with each other more accurately, the curing temperature can be chosen as 23°C for heat of solution method.

REFERENCES

- ACI E3-01, Cementitious Materials for Concrete, USA: American Concrete Institute, 2001.
- API RP 40, “Recommended Practices for Core Analysis”, American Petroleum Institute, February, 1998.
- API Specification 10, “Specification for Materials and Testing for Well Cements”, American Petroleum Institute, January, 1995.
- ASTM C 1702, Standard Test Method for Measurement of Heat of Hydration of Hydraulic Cementitious Materials Using Isothermal Conduction Calorimetry. ASTM International, 2009.
- Benge, O. G., Jones, R. R., Drescher, T. D., & Dolan, R. T. (1982). A New Low-Cost Permafrost Cementing System. *Proceedings of SPE California Regional Meeting*. <http://doi.org/10.2523/10757-MS>
- Bonavetti, V., Donza, H., Menendez, G., Cabrera, O., and Irassar, E. F., 2003, “Limestone filler cement in low w/c concrete: a rational use of energy,” *Cement and Concrete Research*, Vol. 33, No. 6, pp. 865-871.
- Boncan, V.G., Mueller, D.T., Rogers, M.J., and Bray, W.S. (1997). U.S. Patent No. 6,145,591. Washington, D.C.: U.S. Patent and Trademark Office.
- Boswell, R. & Collett, T.S. 2006. The gas hydrates resource pyramid. *Fire in the Ice: Methane Hydrate Newsletter*, 6, (3), 5–7.
- Boswell, R., Hunter, R., Collett, T. S., Digert, S., Hancock, S., Weeks M., and M. E. S. Team, Vancouver, Canada, 2008.

- Chen SC, Wang YS. Gas hydrate mining techniques. *Sci Dev* 2007; 412:26–31.
- Chong, Z. R., Yang, S. H. B., Babu, P., Linga, P., & Li, X. Sen. (2016). Review of natural gas hydrates as an energy resource: Prospects and challenges. *Applied Energy*, 162, 1633–1652. <http://doi.org/10.1016/j.apenergy.2014.12.061>
- Collett, S.T., Dallimore, S.R. “Detailed Analysis of Gas Hydrate Induced Drilling and Production Hazard.” Proceedings of the Fourth International Conference on Gas Hydrates, Yokohoma, 10-23 May, pages 47-52, 2002.
- Domone, P, Illstone, J., *Construction Materials: Their nature and behaviour*, 4th edition, Spon Press, New York, 2010.
- EN 196-8, *Methods of testing cement – Part 8: Heat of Hydration – Solution Method*. European Committee for Standardization, 2010.
- EN 197-1, *Cement-Part 1: Compositions and conformity criteria for common cements*”, European Standards, June, 2000.
- Go Boncan, V.C. (2000).U.S. Patent No. 6,626,243. Washington, D.C.: U.S. Patent and Trademark Office.
- GRID, A. (2009). *Gas Hydrate Production Methods*. Retrieved February 15, 2017, from <http://www.grida.no/resources/6596>
- Halliburton. *Cementing: HydrateCem™ Cement System*. Retrieved from (Accessed on August 7, 2016): http://www.halliburton.com/public/cem/contents/Data_Sheets/web/H/H05892.pdf
- Harrison, S. (2010). *Natural Gas Hydrates*. Retrieved July 13, 2017, from <http://large.stanford.edu/courses/2010/ph240/harrison1/>

- Hannegan, D., Todd, R., Pritchard, D.M., Jonasson, B. “MPD-Uniquely Applicable to Methane Hydrate Drilling.” Paper SPE/IADC 91560 presented at the 2004 SPE/IADC Underbalanced Technology Conference and Exhibition held in Houston, Texas, USA 11–12 October.
- Heikal, M., El-Didamony, H., and Morsy, M. S., 2000, “Limestone-filled pozzolanic Cement,” *Cement and Concrete Research*, Vol. 30, No. 11, pp. 1827-1834.
- Klinkenberg, L. . (1941). *The Permeability of Porous Media to Liquids and Gases*.
- Kuleli, O. (2009). Çimento mühendisliği el kitabı. (1st ed.). Ankara: Türkiye Çimento Müstahsilleri Birliği.
- Kurihara, M. and Narita, H. Gas Production From Methane Hydrate Reservoirs, *Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011)*, Edinburgh, Scotland, United Kingdom, 2011.
- Kurihara, M., Ouchi, H., Narita, H., & Masuda, Y. (2011). Gas production from methane hydrate reservoirs. *Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011)*, (Icgh).
- Kvenvolden K.A. Methane hydrate — a major reservoir of carbon in the shallow geosphere? *Chem Geol* 1988; 71:41–51.
- Kvenvolden, K.A. and Lorenson, T.D. The global occurrence of natural gas hydrate, in: C.K. Paull, W.P. Dillon (Eds.), *Natural Gas Hydrates: Occurrence, Distribution, and Detection*, American Geophysical Union, Washington, DC, 2001, pp. 3–18.
- Labahn, O., *Cement Engineers’ Handbook*, Bauverlag, Berlin, 1983.
- Lea, F. M., *The Chemistry of Cement and Concrete*, 3rd edition, Chemical Publishing Co., New York, 1971.

- Lu, S. M. (2015). A global survey of gas hydrate development and reserves: Specifically in the marine field. *Renewable and Sustainable Energy Reviews*, *41*, 884–900. <http://doi.org/10.1016/j.rser.2014.08.063>
- Luke, K., Fitzgerald, R.M.), Zamora, F., and Sandy, J.M. (2004). U.S. Patent No. 7,219,733. Washington, D.C.: U.S. Patent and Trademark Office.
- Max, M. D., & Johnson, A. H. (2014). Hydrate petroleum system approach to natural gas hydrate exploration. *Petroleum Geoscience*, *20*(2), 187–199. <http://doi.org/10.1144/petgeo2012-049>
- Mazzini, A., Ivanov, M. K., Parnell, J., Stadnitskaia, A., Cronin, B. T., Poludetkina, E., Van Weering, T. C. E. (2004). Methane-related authigenic carbonates from the Black Sea: Geochemical characterisation and relation to seeping fluids. *Marine Geology*, *212*(1–4), 153–181. <http://doi.org/10.1016/j.margeo.2004.08.001>
- Menendez, G., Bonavetti, V., and Irassar, E. F., 2003, “Strength development of ternary blended cement with limestone filler and blast-furnace slag,” *Cement and Concrete Composites*, Vol. 25, No. 1, pp. 61-67.
- Merey, S., & Sinayuc, C. (2016). Analysis of the Black Sea Gas Hydrates, *10*(8), 904–912.
- Moridis, G. J., & Collett, T. S. (2003). Author : From Hydrate Accumulations Under Various Geological And Reservoir Conditions.
- Moridis, G. J. and Collett, T. S. *Adv. Study Gas Hydrates*, 2004, 83–97, DOI: 10.1007/0-306-48645-8_6.
- Moridis, G. J., Collett, T. S., Dallimore, S. R., Satoh, T., Hancock, S., and Weatherill, B., *J. Pet. Sci. Eng.*, 2004, *43*, 219–238.

- Nelson, E. B., "Portland Cements Characterized, Evaluated," Oil and Gas Journal, pp 73-77. 1983.
- Nelson, E. B., Well Cementing, Schlumberger Educational Services, Texas, 1990.
- Neville A. M., Properties of Concrete, Fourth Edition, Pearson Education Limited, England, 2003.
- Odler, I., Hydration, setting and hardening of Portland cement, in P. Hewlett (ed.), Lea's chemistry of cement and concrete, 4th edition, Arnold, London, U.K., 2004.
- Ohara, J., Dallimore and S.R., Fercho, E. "JAPEX/JNOC/GSC MALLIK 2L-38 Gas Hydrate Research Well, Mackenzie Delta, N.W.T, Overview of Field Operations." Paper SPE 59795 presented at the 2000 SPE/CERI Gas Technology Symposium held in Calgary, Alberta Canada, 3–5 April.
- Paull, C., Reeburgh, W., Dallimore, S. R., Enciso, G., Green, S., Koh, C. A., ... Riedel, M. (2010). *Realizing the Energy Potential of Methane Hydrate for the United States. Energy.*
- Popescu, I., De Batist, M., Lericolais, G., Nouzé, H., Poort, J., Panin, N., ... Gillet, H. (2006). Multiple bottom-simulating reflections in the Black Sea: Potential proxies of past climate conditions. *Marine Geology*, 227(3–4), 163–176. <http://doi.org/10.1016/j.margeo.2005.12.006>
- Ramachandran, V. S. and Beaudoin, J. J.: "Hydration of C₄AF+ Gypsum: Study of Various Factors." Proc. Seventh Intl. Cong. Chem. Cement, Paris (1980) 2,11/25-II/30.
- Ravi, K., Iverson, B., & Moore, S. (2008). Cement-Slurry Design To Prevent Destabilization of Hydrates in Deepwater Environment. Mumbai.

- Reddy, B. R. (2008). Novel Low Heat-Of-Hydration Cement Compositions for Cementing Gas Hydrate Zones, 1–8.
- Reed, G. “Shallow Geohazard Risk Mitigation; A Drilling Contractors Perspective.” Paper IADC/SPE 74481 presented at the IADC/SPE Drilling Conference held in Dallas, Texas, USA, 26–28 February.
- Romero, J., & Loizzo, M. (2000). The Importance of Hydration Heat on Cement Strength Development for Deep Water Wells. *SPE Annual Technical Conference and Exhibition*. <http://doi.org/10.2118/62894-MS>
- Schlumberger. DeepCrete Low-Temperature Cementing Solution. Retrieved from (Accessed on February 4, 2017): http://www.slb.com/~media/Files/cementing/product_sheets/deepcrete_ps.pdf
- Schofield, TR., Judgis, A., Yousif, M.” Stabilization of In-situ Hydrates Enhances Drilling Performance and Rig Stability.” Paper SPE 38568 presented at the 1997 SPE Annual Technical Conference and Exhibition held in San Antonio, Texas, USA 5-8 October.
- Shaw, D. J., *Introduction to Colloid and Surface Chemistry*, Butterworth & Co. Ltd., London (1970).
- Shryock, S.H., George, C.R., and Cunningham, W.C. (1975). U.S. Patent No. 3,937,282. Washington, D.C.: U.S. Patent and Trademark Office.
- Tokyay M., Erdogdu K., Türker P., Comparison of intergrinding and separate grinding for the production of natural pozzolan and GBFS-incorporated blended cements, *Cement and Concrete Research* Vol:29 pp.743-748, 1999
- Tsivilis S, Tsantilas J, Kakali G, Chaniotakis E, Sakellariou A. “The permeability of Portland limestone cements concrete”. *Cement Concrete Research* 2003; 33(9):1465–71.

- U.S. Energy Information Agency. (2013). International Energy Outlook 2013. *Outlook 2013*, 312. [http://doi.org/EIA-0484\(2013\)](http://doi.org/EIA-0484(2013))
- Wilson, W.N. (1979). U.S. Patent No. 4,216,022. Washington, D.C.: U.S. Patent and Trademark Office.
- Xu, C. G., & Li, X. S. (2015). *Research progress on methane production from natural gas hydrates*. *Rsc Advances* (Vol. 5). <http://doi.org/10.1039/c4ra10248g>
- Yamamoto, K., & Dallimore, S. (2008). Aurora-JOGMEC-NRCan Mallik 2006- 2008 Gas Hydrate Research Project Progress. *Fire in Ice, Methane Hydrate Newsletter*, *National Energy Technology Laboratory*, 8, 1–20.

APPENDIX A

RESULTS OF COMPRESSIVE STRENGTH TESTS

Table A-1: 1-day compressive strength

<i>Cement Type</i>	<i>CS-1 (Mpa)</i>	<i>CS-2 (Mpa)</i>	<i>CS-3 (Mpa)</i>	<i>CS-4 (Mpa)</i>	<i>Length (mm)</i>	<i>Average (Mpa)</i>
<i>C0</i>	27	28,8	19,6	27,3	53	27,7
<i>C15</i>	23,8	23,3	21,8	24	54	23,2
<i>C30</i>	20,3	20,5	21	20,9	54	20,7
<i>C45</i>	15,3	14,6	13,4	13,9	54	14,3
<i>G0</i>	11,8	10,9	11,9	10,4	53	11,3
<i>G15</i>	9,8	11,7	9,5	9,6	53	10,2
<i>G30</i>	8,9	8,3	8,8	8,5	54	8,6
<i>G45</i>	5,4	4,9	4,9	5,1	54	5,1

Table A-2: 7-day compressive strength

<i>Cement Type</i>	<i>CS-1 (Mpa)</i>	<i>CS-2 (Mpa)</i>	<i>CS-3 (Mpa)</i>	<i>CS-4 (Mpa)</i>	<i>Length (mm)</i>	<i>Average (Mpa)</i>
<i>C0</i>	47,9	40,6	41,3	42,2	54	41,4
<i>C15</i>	38	40,3	37,7	37	54	38,3
<i>C30</i>	31	30,6	30	31	55	30,7
<i>C45</i>	23	21,8	21,8	22,9	55	22,4
<i>G0</i>	28,1	23,8	21,7	24,1	53	23,2
<i>G15</i>	15,7	16,2	16,3	18,4	54	16,7
<i>G30</i>	15,4	17,2	15,9	16,8	54	16,3
<i>G45</i>	7,9	7	7,8	8,3	54	7,8

Table A-3: 28-day compressive strength

<i>Cement Type</i>	<i>CS-1 (Mpa)</i>	<i>CS-2 (Mpa)</i>	<i>CS-3 (Mpa)</i>	<i>CS-4 (Mpa)</i>	<i>Length (mm)</i>	<i>Average (Mpa)</i>
<i>C0</i>	65	61,7	62	64,3	55	63,3
<i>C15</i>	53,7	54,1	53	52,6	55	53,4
<i>C30</i>	47	48,7	47,6	48	54	47,8
<i>C45</i>	31,6	29,9	30,7	29,8	54	44,0
<i>G0</i>	38	36,8	38,6	22	54	37,8
<i>G15</i>	32,2	34,5	26,5	33,7	53	33,5
<i>G30</i>	26	25,8	26,8	31	54	26,2
<i>G45</i>	11	10,8	12	15	54	11,3

APPENDIX B

RESULTS OF HEAT OF HYDRATION TESTS

Table B-1: Heat of hydration of cement samples at 1-day

<i>Cement Type</i>	Heat of Hydration (J/g)	Heat of Hydration (J/g)	Average (J/g)	Difference (J/g)
<i>C0</i>	75.3	77.7	76.46	2.42
<i>C15</i>	66.4	71.7	69.00	5.30
<i>C30</i>	68.3	60.4	64.35	7.96
<i>C45</i>	55.7	66.2	60.95	10.50
<i>G0</i>	43.8	50.3	47.00	6.50
<i>G15</i>	43.2	39.4	41.30	3.80
<i>G30</i>	35.5	37.0	36.25	1.50
<i>G45</i>	28.4	38.0	33.20	9.60

Table B-2: Heat of hydration of cement samples at 7-days

<i>Cement Type</i>	Heat of Hydration (J/g)	Heat of Hydration (J/g)	Average (J/g)	Difference (J/g)
<i>C0</i>	203.3	198.0	200.65	5.38
<i>C15</i>	193.4	182.9	188.15	10.50
<i>C30</i>	168.1	162.5	165.30	5.64
<i>C45</i>	162.7	157.7	160.20	5.00
<i>G0</i>	132.7	126.1	129.36	6.58
<i>G15</i>	114.6	115.7	115.13	1.06
<i>G30</i>	105.3	96.9	101.10	8.40
<i>G45</i>	101.3	92.8	97.00	8.50

Table B-3: Heat of hydration of cement samples at 28-days

<i>Cement Type</i>	Heat of Hydration (J/g)	Heat of Hydration (J/g)	Average (J/g)	Difference (J/g)
<i>C0</i>	218.0	229.0	223.5	11.00
<i>C15</i>	206.7	197.8	202.2	8.90
<i>C30</i>	183.4	182.6	183.0	0.80
<i>C45</i>	171.3	180.4	175.8	9.10
<i>G0</i>	171.5	162.5	167.0	8.94
<i>G15</i>	138.4	143.7	141.0	5.30
<i>G30</i>	120.1	124.7	122.4	4.54
<i>G45</i>	116.9	113.2	115.0	3.70

APPENDIX C

RESULTS OF POROSITY MEASUREMENTS

Table C-1: Porosity of hardened cement pastes at 1-day

<i>Cement Type</i>	<i>Core#1 (%)</i>	<i>Core#2 (%)</i>	<i>Core#3 (%)</i>	<i>Average (%)</i>
<i>C0</i>	32.33	33.00	32.33	32.55
<i>C15</i>	34.80	34.80	36.23	35.27
<i>C30</i>	37.31	37.31	38.39	37.67
<i>C45</i>	39.49	39.49	39.86	39.61
<i>G0</i>	36.53	36.75	36.95	36.74
<i>G15</i>	39.66	40.67	40.77	40.37
<i>G30</i>	43.75	44.28	43.88	43.97
<i>G45</i>	46.73	46.99	46.79	46.83

Table C-2: Porosity of hardened cement pastes at 7-days

<i>Cement Type</i>	<i>Core#1 (%)</i>	<i>Core#2 (%)</i>	<i>Core#3 (%)</i>	<i>Average (%)</i>
<i>C0</i>	29.18	29.83	31.61	30.21
<i>C15</i>	31.57	29.42	32.66	31.22
<i>C30</i>	31.94	31.94	33.76	32.55
<i>C45</i>	34.87	34.87	34.87	34.87
<i>G0</i>	33.63	33.63	33.63	33.63
<i>G15</i>	36.74	36.53	35.96	36.41
<i>G30</i>	39.63	38.74	39.94	39.43
<i>G45</i>	42.62	42.72	42.16	42.50

Table C-3: Porosity of hardened cement pastes at 28-days

<i>CEMENT TYPE</i>	<i>Core#1 (%)</i>	<i>Core#2 (%)</i>	<i>Core#3 (%)</i>	<i>AVERAGE (%)</i>
<i>C0</i>	20.31	27.67	24.55	24.18
<i>C15</i>	29.79	26.62	29.09	28.50
<i>C30</i>	29.46	27.67	28.72	28.62
<i>C45</i>	29.79	30.86	29.79	30.15
<i>G0</i>	29.18	29.83	31.61	30.21
<i>G15</i>	31.57	29.42	32.66	31.22
<i>G30</i>	31.94	31.94	33.76	32.55
<i>G45</i>	34.87	34.87	34.87	34.87

APPENDIX D

RESULTS OF PERMEABILITY MEASUREMENTS

The permeability of some specimens could not be measured and labelled as NM.

Table D-1: Permeability of hardened cement pastes at 1-day

<i>CEMENT TYPE</i>	<i>Core#1 (mD)</i>	<i>Core#2 (mD)</i>	<i>Core#3 (mD)</i>	<i>AVERAGE (mD)</i>
<i>C0</i>	0.069	0.022	NM	0.045
<i>C15</i>	0.094	NM	0.094	0.094
<i>C30</i>	NM	0.133	0.315	0.224
<i>C45</i>	0.513	0.734	NM	0.623
<i>G0</i>	0.048	0.053	0.052	0.051
<i>G15</i>	0.093	0.118	0.093	0.101
<i>G30</i>	0.218	0.211	0.218	0.216
<i>G45</i>	0.211	0.243	NM	0.227

Table D-2: Permeability of hardened cement pastes at 7-days

<i>CEMENT TYPE</i>	<i>Core#1 (mD)</i>	<i>Core#2 (mD)</i>	<i>Core#3 (mD)</i>	<i>AVERAGE (mD)</i>
<i>C0</i>	0.024	0.023	0.021	0.022
<i>C15</i>	0.073	0.067	0.061	0.067
<i>C30</i>	0.134	0.074	0.132	0.113
<i>C45</i>	NM	0.188	0.187	0.187
<i>G0</i>	0.029	0.03	0.025	0.028
<i>G15</i>	0.07	0.072	0.066	0.069
<i>G30</i>	0.132	0.136	0.132	0.133
<i>G45</i>	0.166	0.163	0.165	0.165

Table D-3: Permeability of hardened cement pastes at 28-days

<i>CEMENT TYPE</i>	<i>Core#1 (mD)</i>	<i>Core#2 (mD)</i>	<i>Core#3 (mD)</i>	<i>AVERAGE (mD)</i>
<i>C0</i>	0.010	NM	0.017	0.014
<i>C15</i>	0.115	0.029	0.071	0.072
<i>C30</i>	0.034	0.024	0.015	0.024
<i>C45</i>	0.017	NM	0.022	0.019
<i>G0</i>	0.023	0.023	0.02	0.022
<i>G15</i>	0.082	0.081	0.081	0.081
<i>G30</i>	NM	0.075	0.075	0.075
<i>G45</i>	0.138	0.138	0.133	0.136

APPENDIX E

DETAILS OF THE CALORIMETER DESIGN PHASE

Heat of solution calorimeter was manufactured according to the EN 196-8 standard. Details are given as follows:

- Elimko PR-110 data logger (Figure F-1a) and Pt-100 thermometer with an accuracy of 0.001 °C (Figure F-1b) were used to collect data. Exterior surface of the thermometer was coated with acid resistant very thin material.
- KGW Isotherm type 9C Dewar flask (Figure F-2) was used as a dissolution vessel which is also acid resistant material. But waxing can be applied to interior surface of flask to extend the lifetime.
- Hinged cubic box with a side length of 424mm (Figure F-3) was used to isolate the vessel. Cubic box was filled up with polystyrene which is a foam-like plastic material to prevent heat loss.
- Isolab high speed mixer was used to stir the acid solution as described in the specification (Figure F-4).
- Propeller was purchased from Matest and it is conforming to EN 196-8 specifications (Figure F-5).
- Cylindrical plug with a diameter of 75mm was manufactured by using acid resistant material which is polytetrafluoroethylene, commonly known as Teflon (Figure F-6). 1 vertical and 2 inclined holes were drilled to insert the thermometer, funnel and propeller.



Figure F-1: a) PR-110 data logger b) Pt-100 thermometer



Figure F-2: KGW Dewar flask

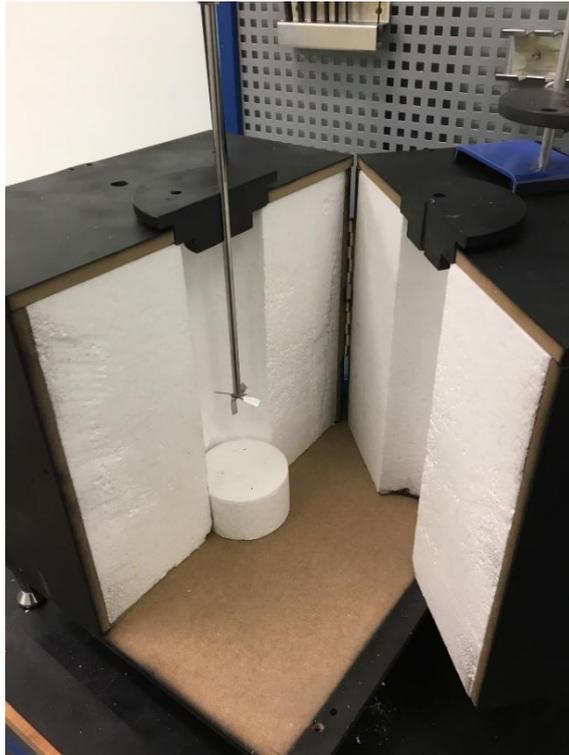


Figure F-3: Hinged cubic box



Figure F-4: Isolab high speed mixer



Figure F-5: Matest propeller

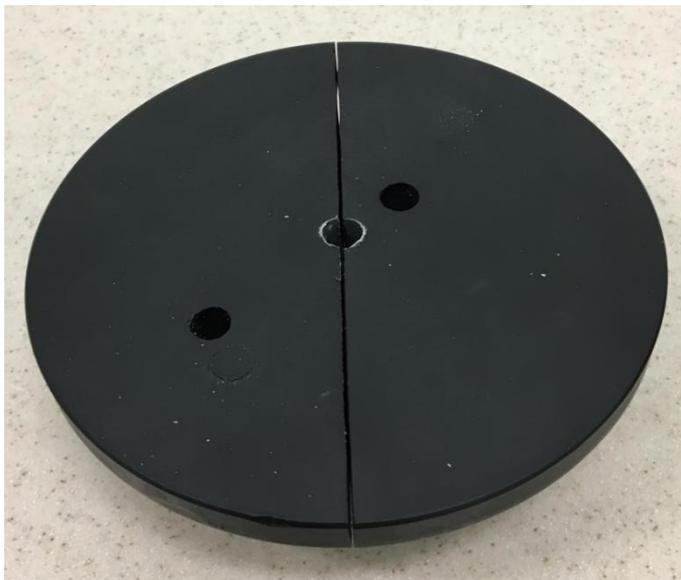


Figure F-6: Teflon plug

APPENDIX F

CT IMAGES

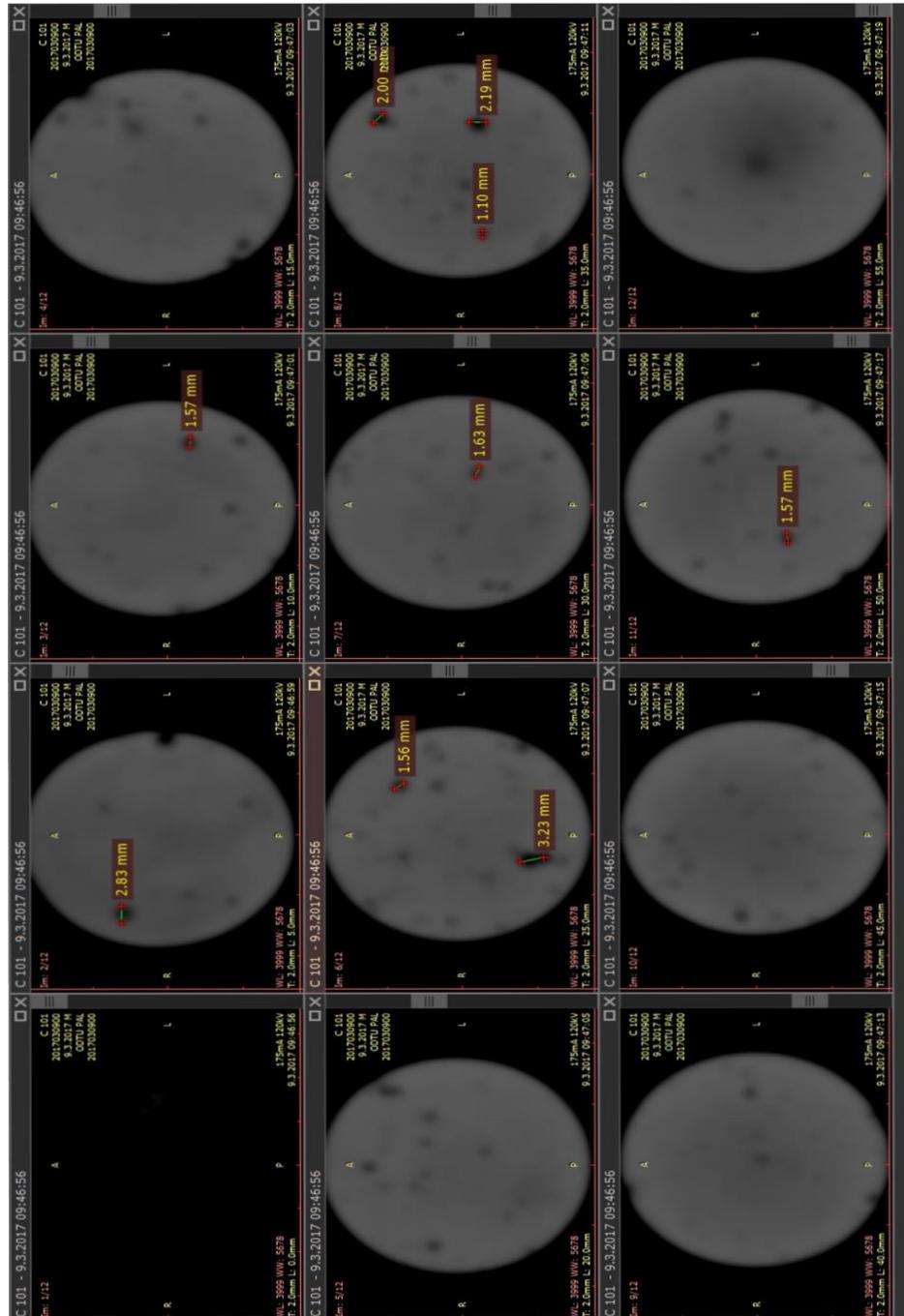


Figure F-1: CT images of C0 cement at 28 days

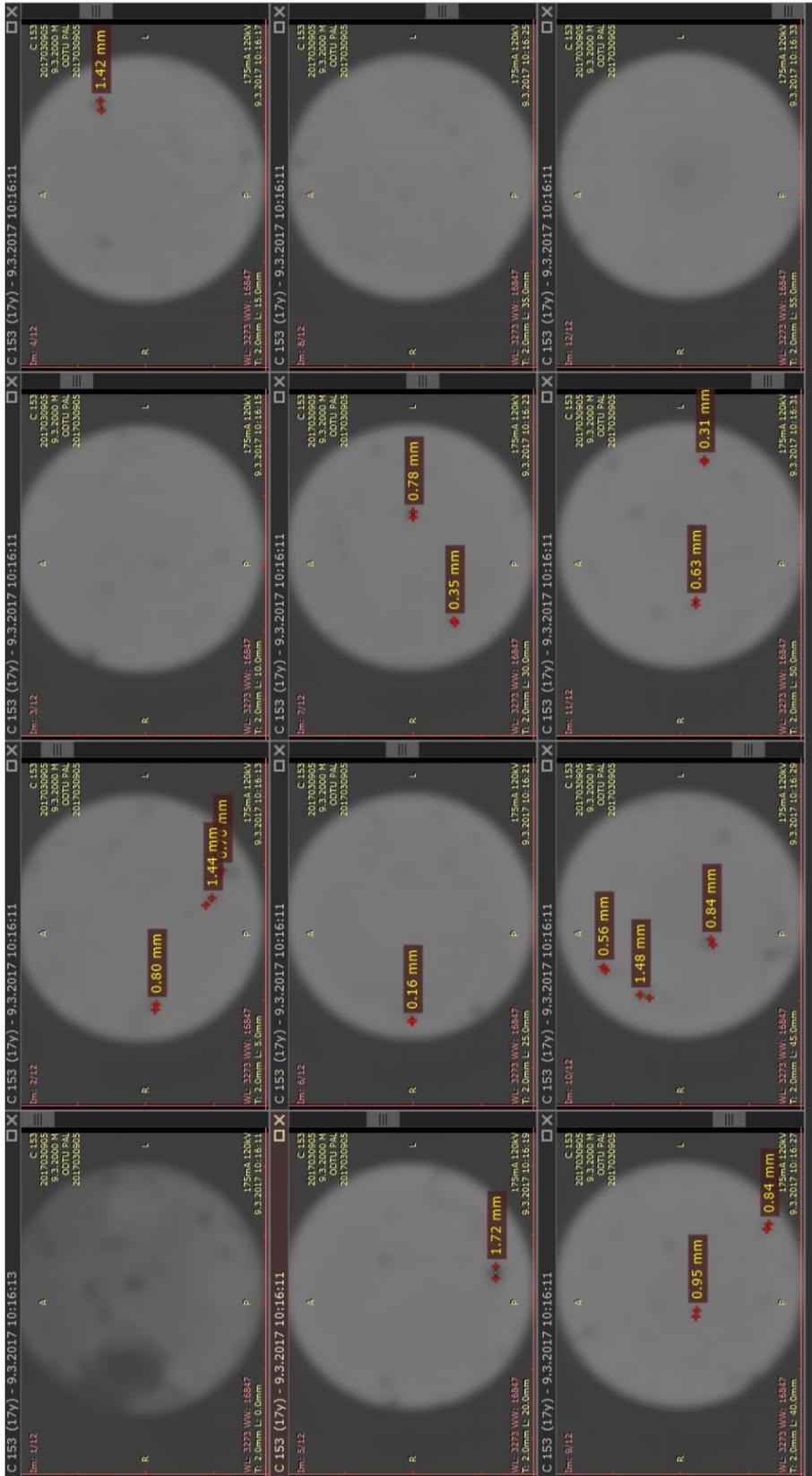


Figure F-2: CT images of C15 cement at 28 days

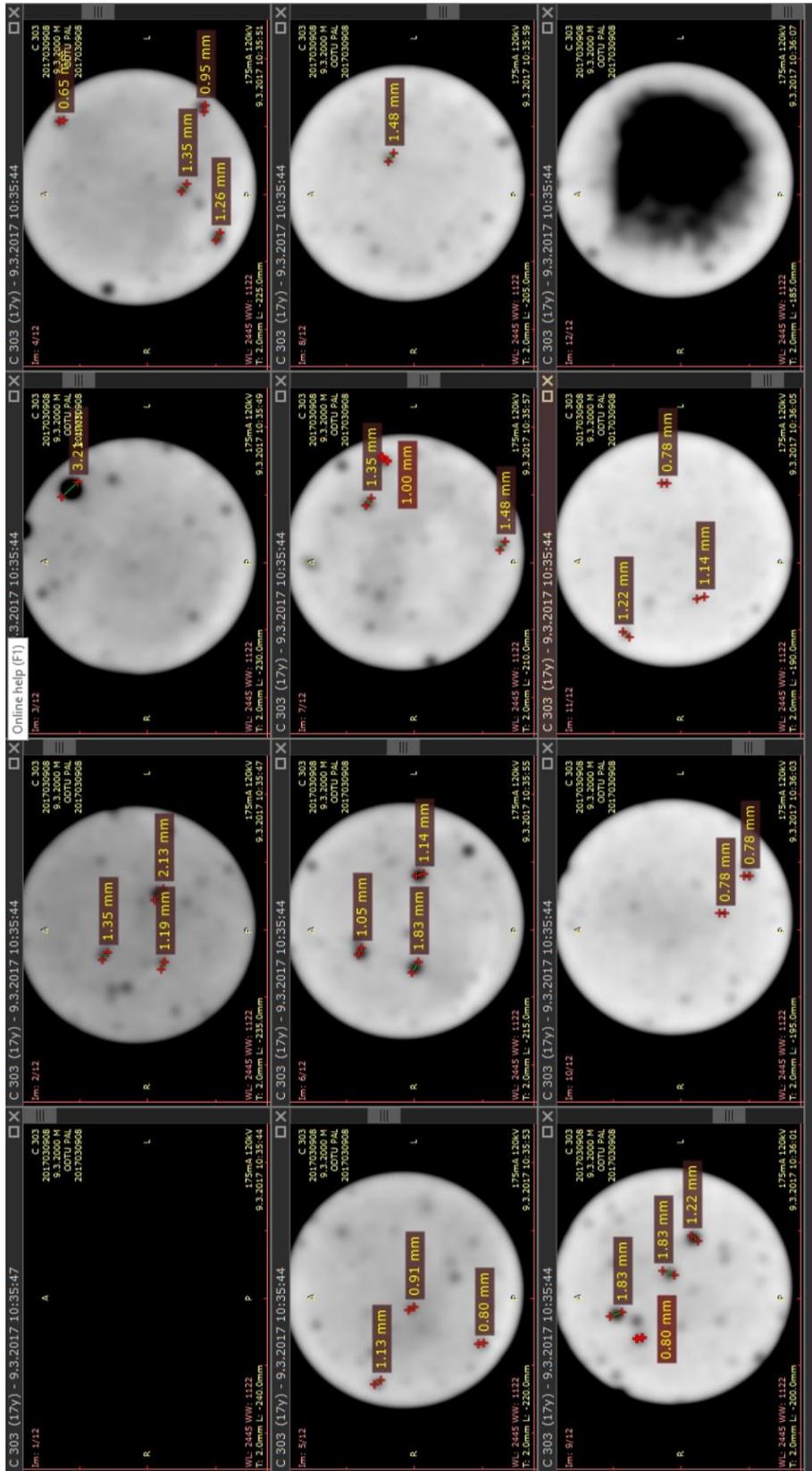


Figure F-3: CT images of C30 cement at 28 days

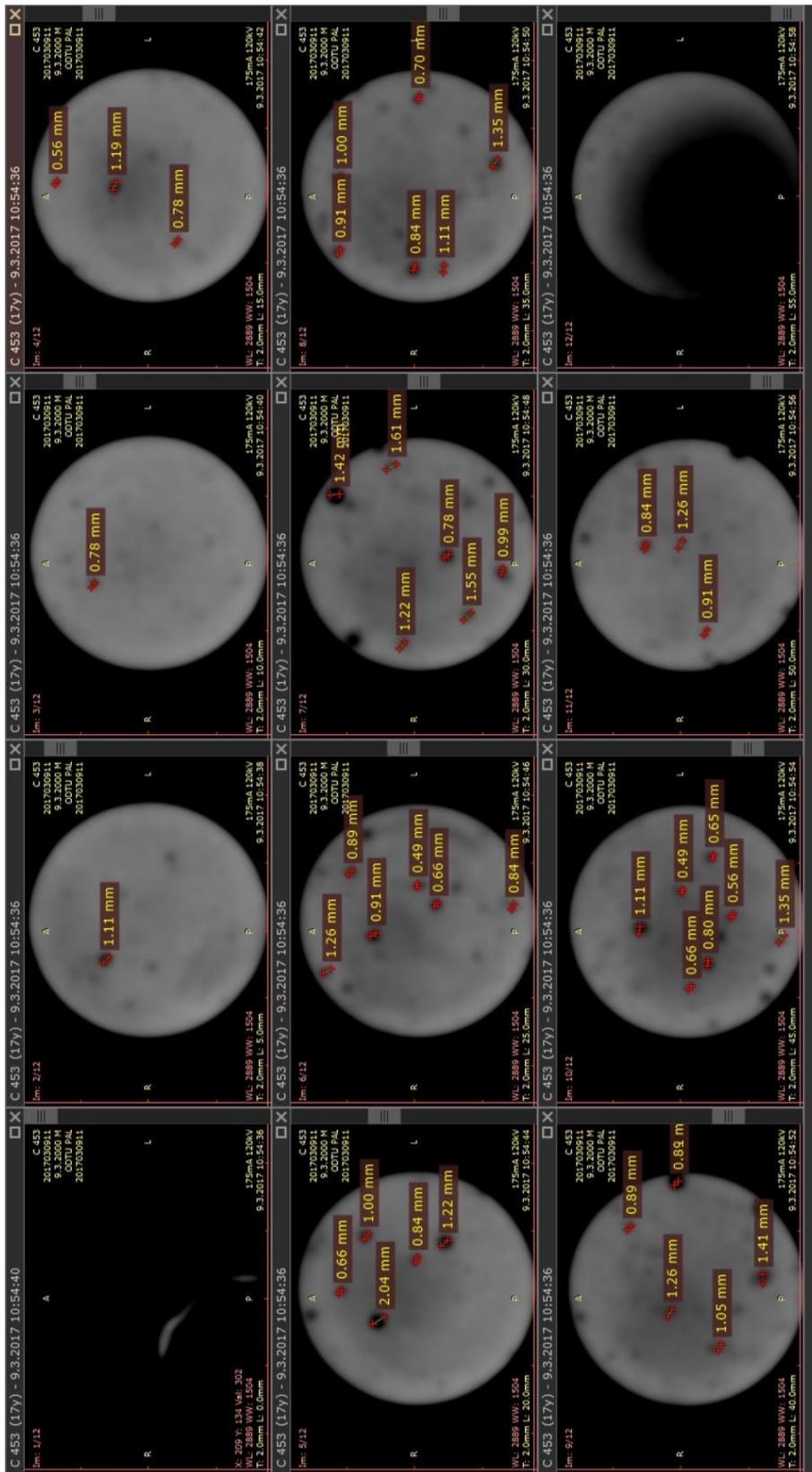


Figure F-4: CT images of C45 cement at 28 days

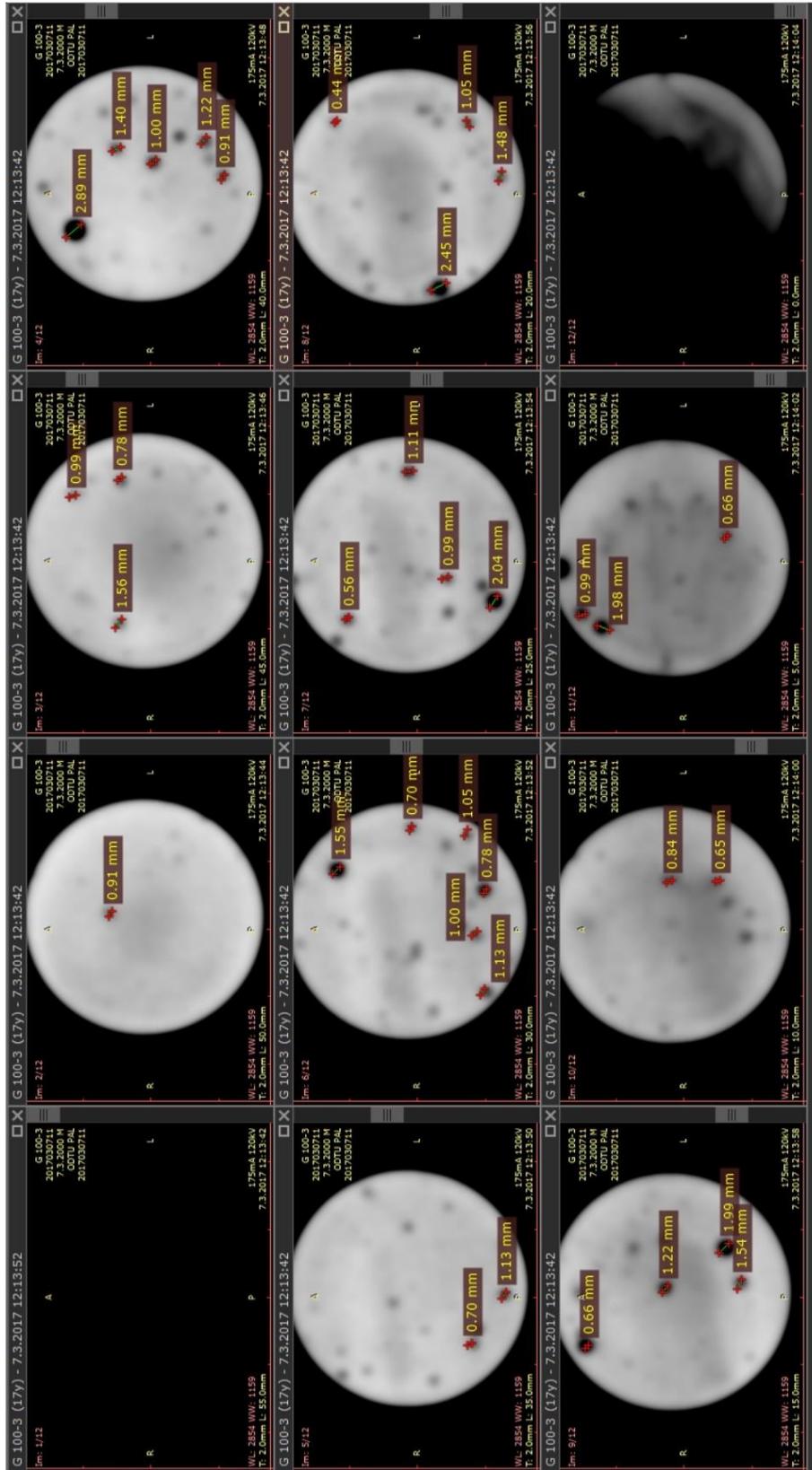


Figure F-5: CT images of G0 cement at 28 days

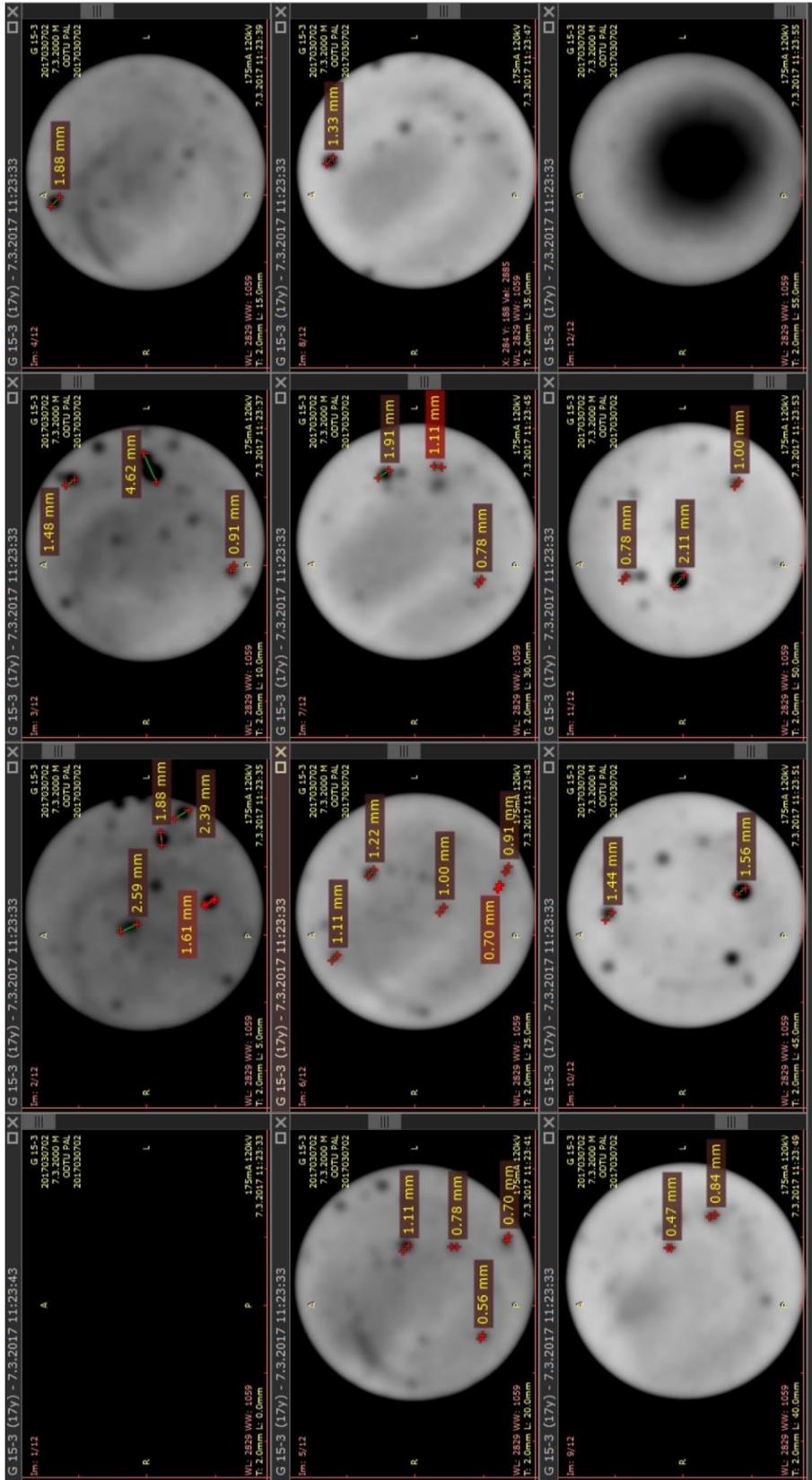


Figure F-6: CT images of G15 cement at 28 days

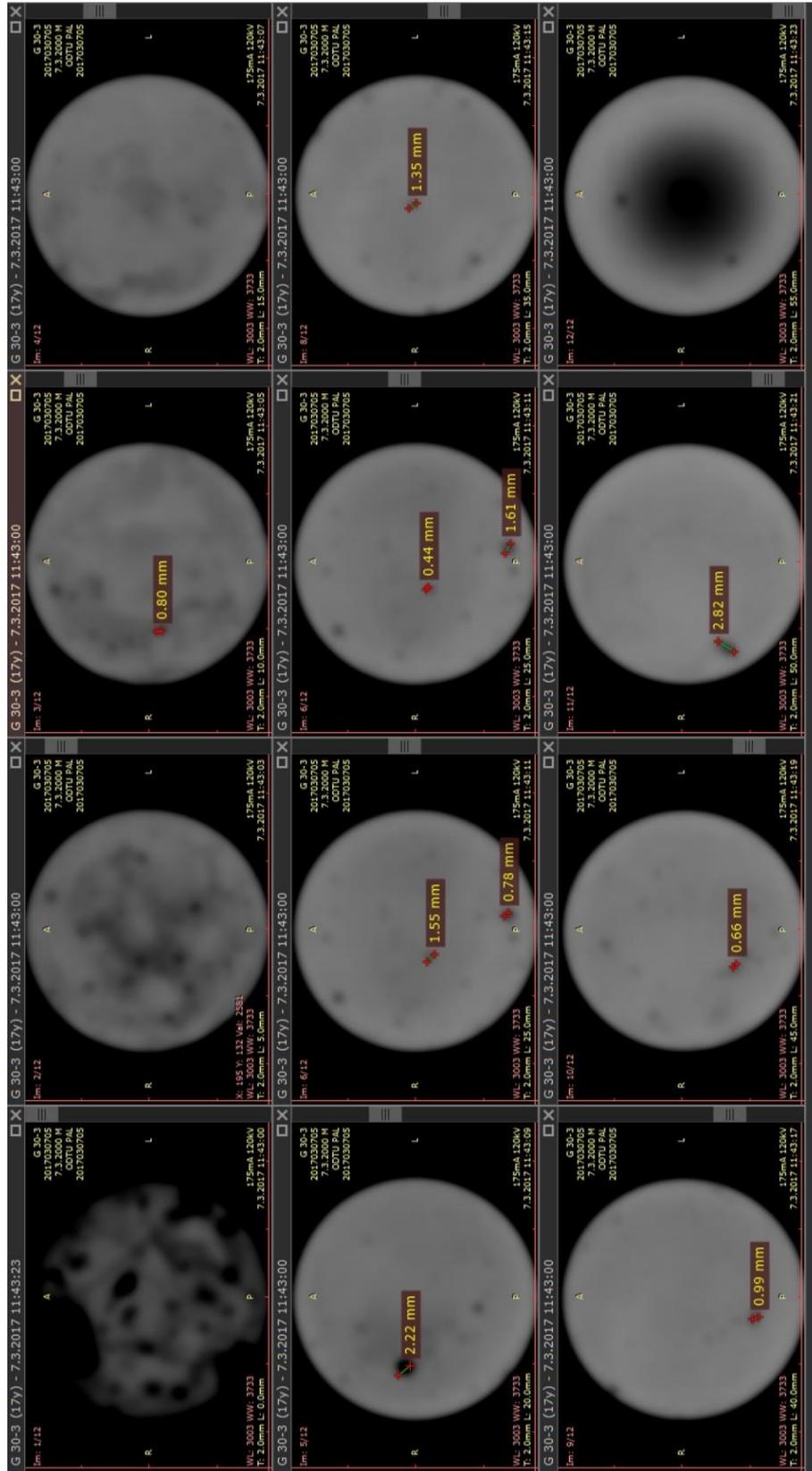


Figure F-7: CT images of G30 cement at 28 days

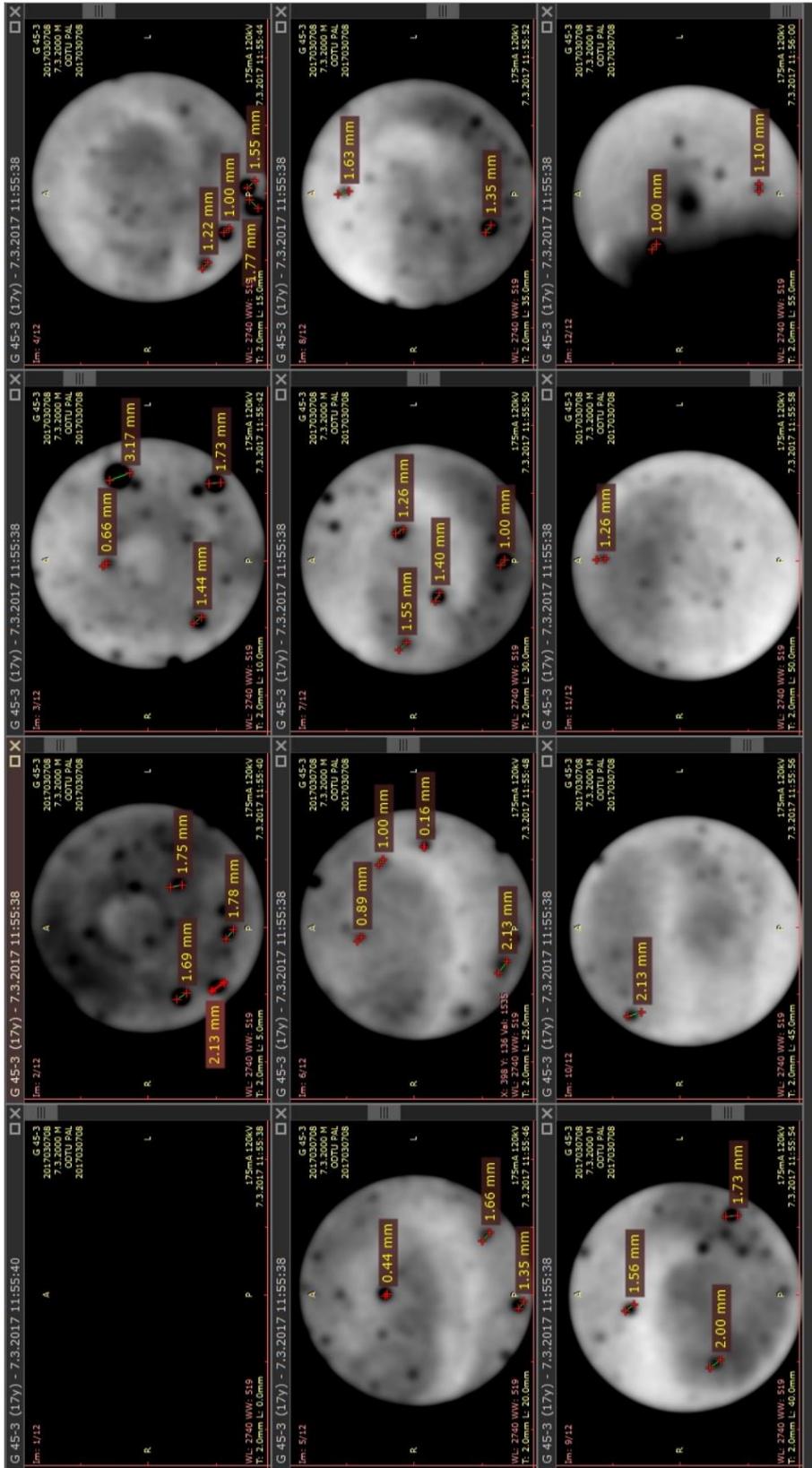


Figure F-8: CT images of G45 cement at 28 days