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NOVEL CHEMICALLY-BONDED PHOSPHATE CERAMIC BOREHOLE SEALANTS (CERAMICRETES) FOR ARCTIC ENVIRONMENTS

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**NOVEL CHEMICALLY-BONDED PHOSPHATE CERAMIC BOREHOLE
SEALANTS (CERAMICRETE) FOR ARCTIC ENVIRONMENTS**

FINAL REPORT

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ABSTRACT

Novel chemically bonded phosphate ceramic borehole sealant, i.e. Ceramicrete, has many advantages over conventionally used permafrost cement at Alaska North Slope (ANS). However, in normal field practices when Ceramicrete is mixed with water in blenders, it has a chance of being contaminated with leftover Portland cement. In order to identify the effect of Portland cement contamination, recent tests have been conducted at BJ services in Tomball, TX as well as at the University of Alaska Fairbanks with Ceramicrete formulations proposed by the Argonne National Laboratory. The tests conducted at BJ Services with proposed Ceramicrete formulations and Portland cement contamination have shown significant drawbacks which has caused these formulations to be rejected. However, the newly developed Ceramicrete formulation at the University of Alaska Fairbanks has shown positive results with Portland cement contamination as well as without Portland cement contamination for its effective use in oil well cementing operations at ANS.

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ABBREVIATIONS

ABAQUS	general-purpose nonlinear finite element analysis (FEA) program by ABAQUS Inc.
ANL	Argonne National Laboratory
ANS	Alaska North Slope
API	American Petroleum Institute
ASTM	American Society of Testing and Materials
Bc	Bearden unit of consistency
Ceramicrete	abbreviation for chemically-bonded phosphate borehole sealant
CPC	California Portland Cement
CSI	Construction Specification Institute
CTE	Compression Testing Equipment
DoE	Department of Energy
FL	Fluid Loss
GRACE	Viscometer manufacturing company
HTHP	High Temperature High Pressure
UAF	University of Alaska Fairbanks
UCA	Ultrasonic Cement Analyzer
WOC	Wait on Cement

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NOVEL CHEMICALLY-BONDED PHOSPHATE CERAMIC BOREHOLE SEALANTS (CERAMICRETES) FOR ARCTIC ENVIRONMENTS

EXECUTIVE SUMMARY

One of the basic material requirements in oil and gas exploration and completion operations in the permafrost region is suitable insulating cement that will provide good seal to gas leakage and at the same time keep the permafrost region undisturbed during the production of the oil and gas. Conventional Portland cement has difficulty in setting and performing suitably in permafrost regions due to various reasons such as freezing and expansion of water in the pores and capillaries of the cement leading to development of cracks in the structure, or freezing of the water before setting of the cement. In addition, the thermal conductivity of conventional cement is not adequately low. New cementing approaches could help reduce the safety and environmental hazards created by cementing failures. A phosphate-bonded ceramic borehole cement developed at Argon National Laboratory (ANL) may fulfill this need. A chemically-bonded phosphate ceramic, known generically as Ceramicrete and developed by ANL, appears attractive as a cement replacement in arctic well construction. This material contains no Portland cement and does not have its limitations under cold conditions.

Experimental tests were conducted on Ceramicrete according to industry specifications in order to compare its material behavior against that of Portland cement as a viable alternative under arctic oilfield conditions. These tests, including a compatibility test, a thickening time test, a compressive strength test, and a fluid loss and rheological evaluation were initially conducted at BJ Services' Tomball R&D Center in Houston using specified proposed formulations of Ceramicrete with and without contamination by Portland cement. The tests showed positive results for the use of Ceramicrete that satisfied American Petroleum Industry (API) standards for oilfield cement in regard to pumping and working time.

Simulation results obtained from the use of ABAQUS software showed that Ceramicrete with 10% contamination by dry Portland cement can cause the thawing of the permafrost zone around the wellbore after 3.5 hrs., i.e. the setting time, by as much as 9 cm. Thawing of the permafrost zone around the wellbore can cause casing collapse, which will eventually lead to a loss of well integrity. However, the proposed Ceramicrete formulation with 5% dry Portland cement showed other properties that satisfy the characteristics of ideal permafrost cement, except that it developed a crack after an

expansion test at 40 degrees F. This was thought to be as a result of higher or lower concentration of MgO in the Ceramicrete compared to the concentration of KH_2PO_4 .

Further tests were conducted at the University of Alaska Fairbanks (UAF) Laboratory to determine the optimum concentration of MgO in the Ceramicrete binder to optimize permafrost Ceramicrete formulation for the Alaska North Slope (ANS). Results from the tests of the new formulations of Ceramicrete binder showed that:

1. The newly developed formulation of Ceramicrete binder: MgO (22.9%), KH_2PO_4 (28.5%), C-class fly ash (10.6%), Wollastonite (10.6%), and Boric Acid (0.1%), showed slurry expansion without crack development.
2. In addition, the new formulation did not flash set or show reduced strength in the presence of Portland cement impurities and its compressive strength was the same with and without contamination of 5% California Portland cement (CPC) “G” grade, i.e. 2800 psi.
3. A slurry with less fluid loss without fluid loss additives does not lead to a temperature increase after setting (as in the case of the new formulation of Ceramicrete binder) and can thus prevent the thawing of the permafrost around the wellbore when used as an oil-well cement on the ANS.

In summary, laboratory test results indicate that the new formulation of Ceramicrete has the ability to provide improved well integrity and can reduce the thawing problem of the permafrost region around the wellbore, if used on the ANS. The material will significantly improve oil and gas operations in the Arctic by helping to control shallow gas migration problems. From the results of the laboratory tests, it is envisaged that the lightweight cement will be more efficient for ANS operators to use in shallow arctic completions. Additionally, this material holds tremendous potential to assist the development of shallow viscous oil and gas hydrates in the Arctic by protecting the permafrost in these shallow wells.

It is recommended in this report that a yard test of the newly-formulated Ceramicrete binder be conducted to confirm the optimal performance of the new formulation of Ceramicrete binder.

CHAPTER 1

INTRODUCTION

1.1 Purpose of Oil-Well Cementing

The oil-well cementing process is used throughout the world and has grown in complexity, with many people, organizations, and technologies contributing to the development of state-of-the-art technologies. Oil-well cementing is a process of mixing a slurry of cement and water and pumping it down through a steel casing to critical points in the annulus around the casing or into the open hole below the casing string. The primary purpose of cementing is to restrict the fluid movements between the formations and to bond and support the casing.

In addition to isolating oil, gas, and water-producing zones, cement also aids in:

- protecting the casing from corrosion.
- preventing blowouts by quickly forming a seal.
- protecting the casing from shock loads when drilling deeper.
- sealing off zones of lost circulation and thief zones (Smith, 1990).

1.2 Definition of the Problem and General Temperature Limitations

Set Portland cement is a remarkably durable and adaptable material; however, there are limits beyond which the material will become less than desirable. In regions with temperatures below the freezing point of water, temperature effects become a dominant force in the development of cement's material properties. The primary issue in these cold regions is premature freezing of the cement slurry. Rather than the slurry setting and developing strength as expected, the slurry water within the poured product freezes to form a network of interconnected ice crystals within the setting product (Morris, 1970).

The presence of these ice crystals greatly affects the properties of the set cement. Ice has significantly different loading behavior than Portland cement, leading to a frozen product that is significantly weaker than a true set product. As a result, the ultimate strength of cement in cold regions tends to be nominal and is frequently below what is demanded from an engineering and safety perspective. Freezeback is another identified

problem, and occurs when drilling or cementing operations pass through regions of thick permafrost. A conventionally cemented well is likely to thaw these permafrost regions, with the thaw zone extending as far as a meter or more beyond the boundary of the wellbore (Nelson and Drecq, 2001). Casing collapse is a serious concern in cold regions if no preventative steps are taken.

Furthermore, the existence of a connective network of ice crystals within the set product has the effect of increasing porosity. During the setting process, the formation of an ice network displaces the setting cement slurry, resulting in a mass of channels within the final product. While frozen, the ice network serves to fill and plug these channels, decreasing the effective porosity of the set cement product. However, the network is easily subjected to disruption by the heat of produced and/or drilling fluids, as well as by seasonal temperature changes. Upon sufficient heating, the ice network is disturbed and the effective permeability of the set product rapidly increases (Nelson and Drecq, 2001). Thus, a frozen cement wellbore casing is very likely to experience future problems with oil and gas migration, a costly and environmentally-damaging situation for a producing well.

Cycling temperature effects also decrease the product life of Portland cement when it is used in cold regions. Oilfield cements are not homogenous products but rather are composed of a collection of aggregates, namely a mixture of calcium, silicon and aluminum oxides (Bonen, 2004). Each aggregate has significantly varying coefficients of contraction and expansion. As the set product proceeds through several freeze-thaw cycles, the mismatch in these coefficients leads to internal stress within the product, surface and volume flaws, and the creation of microfractures within the cement. As these microfractures grow and multiply, the fatigue-resistance of the cement is greatly diminished. As a result, arctic cementing jobs frequently require repair and/or replacement (Wagh, 2004).

Finally, cement performs inadequately as an insulation between the formation and the wellbore. One primary function of a well casing in northern regions is that of an insulative barrier, protecting the surrounding formation from the heat of drilling, production, and possible fluid injection. In this regard, cement functions adequately, but improvements in these properties would be welcomed by the oil and gas industry. Should

cement become more insulative, more work could be done in northern climates without fear of environmental damage, formation subsidence, or hole collapse (Smith, 1986). Table 1 summarizes the negative effects that sub-freezing temperatures can have on Portland cement and its performance as an oilfield borehole cement.

General Temperature Limitations
<ul style="list-style-type: none"> • Premature freezing of the setting product • Weakening of the final product • Shortened product life • Increased dangers of gas and oil migration

Table 1: Negative Effects of Cold Temperatures upon Portland Cement

1.3 Problems Associated with Conventional Cements

It is a challenge to design a cement for very cold climates that is capable of setting at subzero temperatures but features a low heat of formation to avoid thawing the permafrost.

Portland cement has been used over the years for oil well cementing in cold climates and is one of the most widely used cements in today's oil and gas industry world-wide. Significant work has been done to improve the properties of Portland cement and to adapt it to cold climate regions, especially permafrost zones on the ANS. Set Portland cement is a durable and adaptable material. However, there are limits beyond which the material will become less than desirable (Morris, 1970).

Conventional Portland cement has difficulty setting and performing suitably in freezing environments for various reasons (Wagh et al., 2005).

1. The water in the cement may freeze even before the cement sets.
2. The water in the pores and capillaries of the cement may freeze and expand; this may ultimately lead to crack development and poor compressive

strength.

3. Mismatch of constituent materials' expansion coefficients may produce flaws in cement during the "freeze-thaw cycle."

Thus, using Portland cement as permafrost cement may cause casing collapse and the loss of well integrity.

Conventional cements have also been shown to develop a connective network of ice when used in permafrost well-cementing operations. During the setting process, the ice network displaces cement slurry, resulting in a mass of channels in the set cement. This process ultimately leads to a decrease in effective porosity, but the ice network can be easily disrupted by heat; therefore, a frozen cement wellbore is very likely to experience future problems with oil and gas migration and loss of well integrity (Nelson and Drecq, 2001).

The important function of cement used in permafrost cementing operations is to act as an insulative barrier between the formation and the wellbore (Smith, 1986). However, the high heat of hydration of conventional permafrost cement can cause permafrost thawing around the wellbore, which in turn can lead to formation subsidence and casing collapse.

1.4 Permafrost Cementing

Permafrost is a permanently frozen subsurface formation which exists in arctic regions such as the Canadian Northwest, the Arctic Islands, and the ANS (Maier et al., 1971); permafrost forms where annual temperatures remain at the freezing point or colder all year. Permafrost depth may vary from 500 ft. to 2000 ft. on the ANS (Morris, 1970). The typical depth of permafrost at on the NS is about 1800 ft.

Cementing of casing in the permafrost zones on the ANS presents unique operational problems. Permafrost sections can vary from unconsolidated sands and gravels with ice lenses to some areas of ice-free, consolidated rock. Drilling a well and cementing the surface casing in permafrost requires the prevention of wellbore enlargement due to thawing as well as cement that sets with low heat of hydration. Thus, in order to maintain well integrity, it is necessary to develop cement which sets with low heat of hydration and does not cause thawing of permafrost (Maier et al, 1971).

Any cement system that is used in permafrost cementing operations must be kept from freezing until after the setting reaction is complete (Morris, 1970). Different types of systems have been suggested and are used to solve this problem. However, conventional cement systems commonly used in oil-well cementing are not satisfactory for use in the permafrost regions. Conventional cement slurry freezes at the sub-freezing permafrost zone temperatures, thus, cement does not set when placed in the low temperature environment. In the permafrost regions where the operating temperatures are below the freezing point of water, conventional cement has shown undesirable properties such as shortened product life, poor compressive strength, and uncontrolled expansion (Goodman, 1977).

The arctic regions contain huge conventional and unconventional oil and gas resources. In order to tap these resources while providing safe operations, it is important to understand the unique cementing issues in cold regions and to develop materials better suited for use in these cold climates. Though various attempts have been made to improve the cement properties for cold climates, no technology currently exists that can make suitable cement for cold-climate oil well cementing.

1.5 Ideal Permafrost Cement Properties

Effective permafrost cement should exhibit the following properties:

1. It should be pore-free so that it does not trap pore fluids. Pore fluids could freeze and expand, causing a crack in the matrix.
2. It should have very low thermal conductivity so that it does not thaw the formation and destabilize the casing.
3. It should have low heat of hydration.
4. It should have inherent superior mechanical properties if used for load-bearing applications.
5. It should be fast-setting cement so that if it is used in permafrost regions, it will allow little time for water to freeze.
6. It should exhibit good bonding properties with earth materials such as downhole rocks and also with casing steel.
7. The cement slurry should allow at least 3 hrs. of pumping time before it sets.

8. It should not be deteriorated by the freeze-thaw cycle.
9. It should have a wait-on-time of less than one day, developing a minimum of 500 psi compressive strength within this time (Wagh et al., 2005).

1.6 Project Scope

One of the basic material requirements for oil and gas exploration in permafrost regions is a suitable insulating cement that will keep the permafrost undisturbed during production and transportation of oil and gas. However, conventional Portland cements do not provide adequate insulation or material strength under these conditions. New approaches to cementing could help reduce the safety and environmental hazards created by cementing failures. Using the criteria outlined for an ideal cementing system; Ceramcrete is evaluated as a borehole cement for drilling through the permafrost/gas hydrate intervals on the North Slope of Alaska.

CHAPTER 2

LITERATURE REVIEW

2.1. Limitations for Consolidated Formations

Until the discovery of large oil deposits on the ANS, very little information had been collected on well completions in cold environments. In the 40 years since that time, the burgeoning oil industry in areas such as northern Canada, Russia, the Arctic Islands, and Alaska has led to significant research into proper oilfield practices for these environments. However, the techniques appropriate for a cold formation vary widely depending on the geological and physical properties of the cold formation (Maier, 1971).

In areas such as the Arctic Islands, the cold formation is fairly well consolidated. Consolidated formations are advantageous because thawing during drilling and cementing do little to disrupt the area surrounding the wellbore. As a result, there are few concerns about well practices that may lead to thaw subsidence, casing stress, hole collapse, or environmental damage. Freezing of a cement slurry can be prevented through external heating, e.g. by using a warm displacement fluid. There is no particular need for specialty material use as the primary problem of freezing can be controlled through numerous measures, limited only by the environmental laws of the area. Table 2 summarizes various methods of slurry protection that are appropriate for a consolidated cold formation (Maier, 1971).

Instead of modifying cement properties to meet the needs of the environment, one can temporarily change the environment to allow for proper setting of the cement. Heating the slurry water, adding a warm displacing fluid, or even localized heating of the air in areas of slurry placement can all raise the formation temperature above freezing, protecting the cement slurry from any adverse effects. A frozen consolidated formation that is unharmed by thawing can likely be cemented with any slurry that will adequately set at the existing curing temperature. However, in areas where the frozen formation contains ice lenses and is incompetent in the material sense, where the formation must not be allowed to thaw, specialized slurries must be called upon to do the job (Maier, 1971).

Methods of Slurry Protection in Consolidated Formations
<ul style="list-style-type: none"> • Pre-heated slurry water • Warm displacement fluid • Localized heating of the air

Table 2: Methods to Avoid Premature Freezing in a Consolidated Frozen Formation

2.2. Limitations for Unconsolidated Formations

A more difficult problem arises during cementing operations in the unconsolidated permafrost/gas hydrate regions of the world, namely the Canadian Northwest Territories and the ANS. In regions with unconsolidated formations, the use of an external heat source to prevent slurry freezing is not an effective or safe option (Maier, 1971). In these areas, drilling and cementing need to be accomplished with a minimum amount of thawing around the wellbore. Melting can cause the thawed formation to subside, particularly in the upper 200 ft of the well. If the permafrost melts, drag forces can be transferred from the soil to the casing. Furthermore, hole sloughing and possible collapse become realistic possibilities (Smith, 1986). For these reasons, no external heat source should be used to prevent freezing and the cement must itself exhibit a low heat of hydration.

Permafrost behavior varies greatly depending on region. The Mackenzie Delta and other continental regions of Canada, for example, exhibit shallow formations frequently consisting of ice lenses and frozen muskegs. By contrast, Alaska's permafrost has no real consistency, but rather varies greatly depending on the area of the state in which drilling is occurring. Permafrost thins out in the ocean and lake areas, and disappears completely offshore in water depths of 10 ft or more. The permafrost also varies in ice content, with some sections showing as little as 20% ice and others as much as 90%. Permafrost in the arctic region of Alaska at times resembles snow, while elsewhere ice lenses can vary in thickness from a fraction of an inch to several feet. The permafrost in these arctic regions is reported to vary from unconsolidated sands and

gravels with ice lenses to some areas of ice-free, consolidated rock. For this reason, permafrost is defined only in the broadest of possible terms; it is generally described as a formation that remains frozen for two consecutive years. The depth of this permafrost soil may vary from 500 feet to 2000 ft, depending on location, with the permafrost temperature varying from 15 °F to 32 °F (-9.4° to 0 °C).

State of Alaska environmental conservation laws and regulations dictate that drilling and cementing operations in Alaska must have minimal environmental impact on regions of permafrost (a rule of thumb describes permafrost as the upper 300 ft. of a formation). Thus, formation thaw protection becomes not only sensible industry practice but a legal requirement. More information on these laws can be found in Alaska statute 20 AAC 25.030, presented in Appendix A.

2.3. Current Industry Practices

Currently, there is no standard casing program for well completions in permafrost regions. Each area has a different casing design based on the drilling objectives of that particular well and upon the economics of the field. One standard practice is to set all surface pipe several hundred feet below any permafrost and cement it back up to the surface. Surface casings of 3,000 to 4,000 ft are not uncommon (Smith, 1990). Numerous additional precautions must be taken in a permafrost area, including the use of high-strength ductile casing designed for sub-freezing conditions, casing designs that protect the formation from injection fluids and warm oil produced over the life of the well, and the need to leave no fluid in the annulus that might freeze and damage the casing.

Field experience has shown that the cement casing needs to show only a minimal amount of early strength for drilling operations to continue. Acceptable Wait-On-Cement (WOC) times are less than one day, but after this time the set product need only provide approximately 500 psi of compressive strength. An experienced field engineer may be capable of working with as little as 250 psi of strength in 24 hours time, though 500 psi is a more appropriate measure for safety reasons (Benge, 1982). Most slurries in the permafrost region, regardless of composition, must have a working time of 2 to 4 hours because the larger pipes used require more cement than normal, thus requiring more

placement time. A safety margin for unexpected problems is also included in this working time (API Spec. 10, 2004).

2.4. Background Information on Portland Cement

Portland cement is the most common type of cement in general usage, as it is a basic ingredient of both concrete and mortar. As stated earlier, it is composed of a mixture of various oxides, most commonly calcium, silicon, and aluminum. Portland cement, and similar materials, is made by heating limestone with clay or sand and then grinding the product. The resulting powder, when mixed with water, will become a hydrated solid over time (Banfill, 2003).

Production of Portland cement is broken into three fundamental stages:

1. Preparation of the raw material
2. Production of the clinker
3. Final preparation of the cement

The raw materials for Portland cement production are calcium oxide, silicon oxide, aluminum oxide, ferric oxide, and magnesium oxide, in the proportions illustrated in Figure 1.

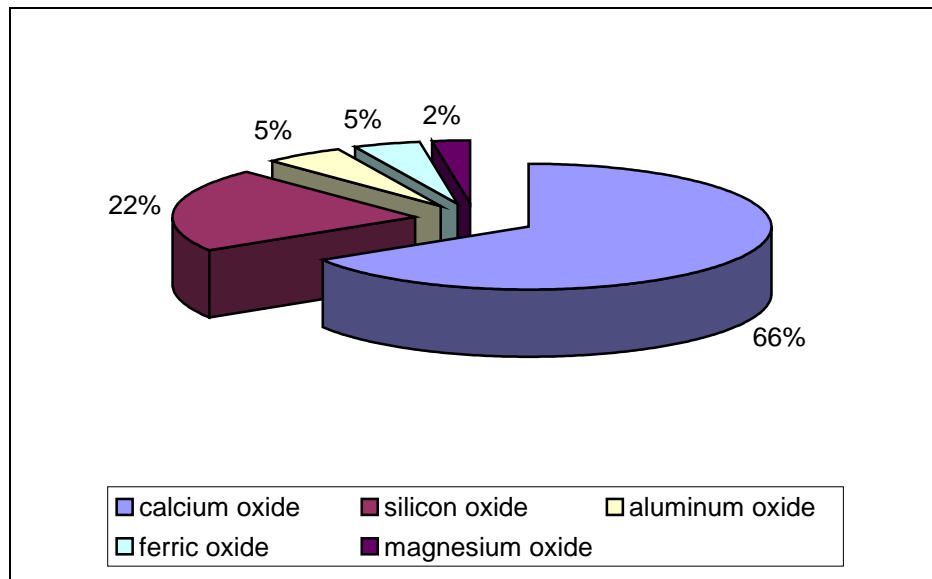


Figure 1: Raw materials required for Portland cement clinker

The production of clinker can be described as follows:

“The raw mixture is heated in a kiln, a gigantic slowly rotating and sloping cylinder, with temperatures increasing over the length of the cylinder to roughly 1480° C. Temperature regulation is especially important during this sintering process, as too low a temperature causes insufficient sintering but too high a temperature results in a molten mass or glass-like product. In the lower temperature part of the kiln, calcium carbonate turns into calcium oxide and carbon dioxide. In the high temperature part, calcium oxides and silicates react to form dicalcium and tricalcium silicates. Small amounts of tricalcium aluminate and tetracalcium aluminoferrite are also formed.”

The resulting material is clinker, which is pulverized into a powder with roughly 2% gypsum by weight. The finished cement has approximately the following composition: calcium oxide (64%), aluminum oxide (5.5%), silicon oxide (21%), ferric oxide (4.5%), magnesium oxide (2.4%), and sulfate (1.6%). This make-up is graphically illustrated in Figure 2.

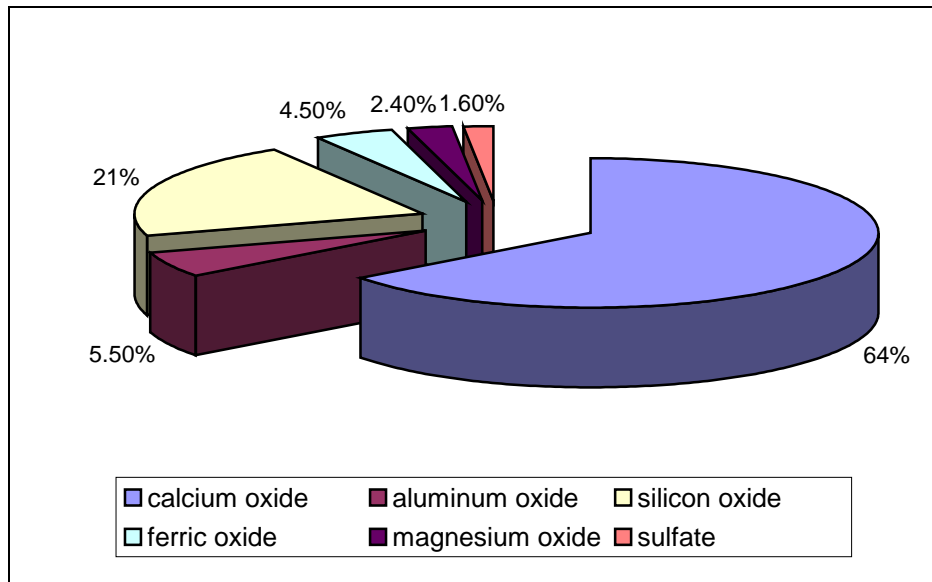


Figure 2: Composition of Portland cement

2.5. The Use of Freeze-Depressing Additives

Early work in freeze-protected cementing systems made extensive use of freezing point depressants for the slurry water. Many different materials were used, including salts, alcohols, and specialty polymers, with varying success. However, one trend remained consistent across all the additives that were used: in quantities necessary to prevent the freezing of the slurry water, additives had a side-effect of making the set cement product weak to the point of uselessness. Thus, the use of additives has been abandoned as a primary solution to the freezing problem, and additives are used only in conjunction with other freeze-prevention methods, such as specialty extended permafrost systems (Nelson and Drecq, 2001).

2.6. Existing Extended Permafrost Systems

2.6.1. High-Aluminate Cements

Calcium aluminate cements are special-use cements of limited production and premium price. Their general use is for preparing fire-brick mortar; however, they are gaining wider acceptance for industrial use and for cold-weather construction. The high-aluminate cements contain no free lime and none is produced upon hydration, as is the case with the American Petroleum Institute (API) classes of cement; therefore, adding fly ash or pozzolans creates only diluents and no cementitious reaction occurs (Smith, 1986).

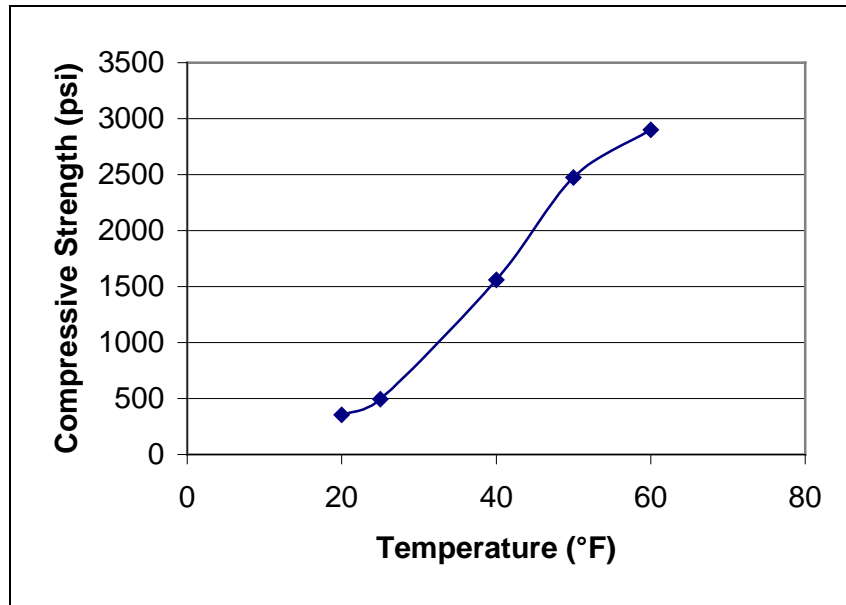


Figure 3: Strength Development of Calcium Aluminate Cements at Different Temperatures (Nelson and Drecq, 2001)

As shown in Figure 3, high-aluminate cements will set and gain strength rapidly at low temperatures, reaching about 95 percent of the ultimate strength in 24 hours. These cements exhibit a high heat of hydration, and since the hydration reaction occurs rapidly, high cement-column temperatures may occur. Performance characteristics of these cements change drastically with the addition of small quantities of other materials. Sodium chloride will severely retard the setting time; lime, calcium chloride, and the API classes of cements may cause an instantaneous (flash) set. Extreme care must be taken to avoid contamination (Smith, 1986). Besides contamination, another concern with calcium aluminate cements is degradation. Degradation occurs if the cement becomes warm and moist. Degradation is caused by a change from a metastable crystalline structure to a cubic form, and is accompanied by a color change from near black to a reddish brown (Smith, 1990).

Through the use of chemical extenders and freeze depressants, a high-alumina cement can be used to make a highly-extended permafrost cement system. The system exhibits a heat of hydration great enough to enhance the setting process, but uses large

quantities of water to moderate the heat generated during hydration, eliminating the need for fly ash (Benge, 1982).

Unlike Portland cement, whose principal constituent is tricalcium silicate, the principal constituent in high-alumina cements is mono-calcium aluminate. During hydration of Portland cement, mono-calcium silicate is formed and lime is liberated. For high-alumina cements, hydration forms dicalcium aluminate, with alumina liberated in place of lime. The chemical reaction in high-alumina cement generates heat much more rapidly than the reaction in Portland cement (Nelson and Drecq, 2001).

A high-alumina cement cannot be blended with Portland cement, since blending of the two will cause extreme acceleration of the high-alumina cement, resulting in severe gelation or “flash” setting. Operators must use extreme caution to prevent contamination of a high-alumina cement system with Portland cement. The chance of contamination can be minimized with astringent cleaning of field bins, bulk trucks, and storage facilities before and after each job that uses a high-alumina cement system. However, under normal operations it becomes almost impossible to eliminate the chance of cross-contamination.

High-alumina cements have been used to cement through the permafrost both in Canada and on the ANS. Two high-alumina cements have been marketed under the tradenames of Luminite and Ciment Fondu (Nelson and Drecq, 2001).

2.6.2. Gypsum-Cement Blends

Gypsum-cement blends, with a mixing-water freezing temperature depressant, have unique properties that make them attractive for low and freezing subsurface temperature environments. The gypsum phase sets and gains strength rapidly at these temperatures, providing adequate strength for continuing well operations. Protected from freezing, the more slowly-setting Portland cement phase then hydrates, providing the cement with high ultimate strength and durability (Maier, 1971).

Figure 4 illustrates how gypsum-cement slurries were designed for use at temperatures between 80° F and 15° F (26.7° to -9.4°C), with salt added to help prevent freezing at temperatures less than 32° F (0° C). Like conventional cements, gypsum-

cement slurries also become exceptionally permeable if allowed to freeze before setting. A very low heat of hydration is realized, less than 20 BTU per lb of slurry (Maier, 1971).

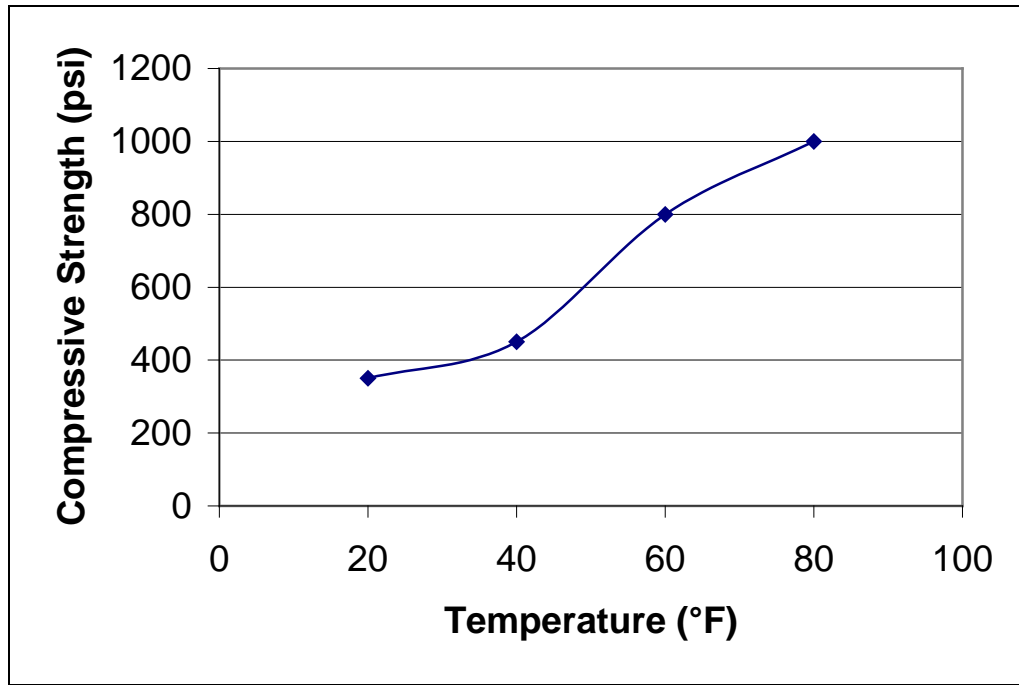


Figure 4: Strength Development of Gypsum Cements at Varying Temperatures (Nelson and Drecq, 2001)

Though these gypsum-cement blends have become the primary method of cementing in permafrost areas, they have significant drawbacks. Additional freezing point depressants need to be added to the slurry water, and strength development is poor when compared to conventional Portland cement or even calcium aluminate cements. Furthermore, high cost makes gypsum-cement blends less than ideal for widespread use.

CHAPTER 3

DEVELOPMENT OF CHEMICALLY-BONDED PHOSPHATE CERAMICS (CERAMICRETE)

Chemically-bonded phosphate ceramics are formed by an acid-base reaction between an acid phosphate (e.g., potassium, ammonium, or aluminum) and a metal oxide (e.g., magnesium, calcium, or zinc) (Wagh, 2005). A powder blend of the two is mixed with water to make a slurry. The slurry sets at room temperature within minutes or hours, depending on the additives. It forms a dense ceramic that can be tailored to develop desirable properties. Though this material maintains a number of desirable ceramic properties, such as high strength and thermal resistivity, it sheds the energy-intensive process of sintering that most non-silicon-based ceramics require to obtain their final shape and material properties (Wagh, 2004).

Ceramicrete is a trade name given to the process of generating magnesium potassium phosphate ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$) by reacting magnesium oxide (MgO) with a solution of potassium phosphate (KH_2PO_4). Developed at Argonne National Laboratory (ANL), this novel form of ceramic production was originally intended for the stabilization and transport of radioactive and hazardous waste (Wagh, 2003). Since its development, the material has undergone some adaptation for niche applications where the properties of a ceramic may be desirable but the workability of cement is needed. In the case of oilfield operations, research has been performed by ANL to increase the strength and insulative properties of Ceramicrete while also reducing the cost of the material to allow it to compete with the price-point of existing oilfield solutions. The permafrost-formulation of Ceramicrete has seen the addition of c-class fly ash and wollastonite to improve material properties. Fly ash is a common industrial byproduct, both cheap and easily acquired in bulk quantities. In addition to increasing the strength of the final set product, fly ash adds to the insulative properties of Ceramicrete and will reduce the cost of the blended powder. Additionally, by adding fly ash one mitigates the exothermic reaction of Ceramicrete, reducing its thawing effect upon the surrounding

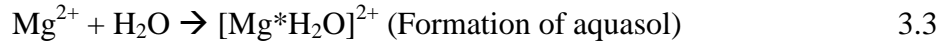
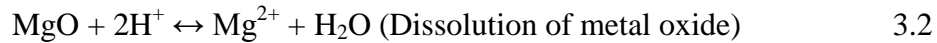
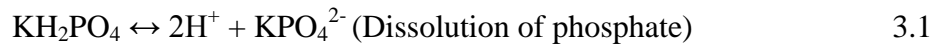
formation. Wollastonite, like fly ash, adds to the strength and thermal resistivity of Ceramicrete, but also adds a thickening effect to the Ceramicrete slurry (Wagh, 2004).

A major advantage that Ceramicrete possesses over other possible cement alternatives is that, despite a novel chemistry, handling techniques for Ceramicrete are no different than those for conventional cement. No new equipment or training is required for the use of Ceramicrete, and the hardened product can be assumed to behave in an equivalent manner to cement. A Ceramicrete slurry, in the field, would be prepared by bulk mixing a dry mix powder with water in a batch mixer, just as with Portland cement. The set product has an appearance and texture similar to that of cement, and like cement exhibits the ability to bond to itself, to formation materials, and to steel (Wagh, 2005).

3.1. Dissolution Model for Ceramicrete Production

3.1.1. Dissolution of Oxides and Formation of Sols by Hydrolysis

Generation of a Ceramicrete product begins with the dissolution of potassium phosphate (KH_2PO_4). As dissolution of this chemical occurs, two key effects are obtained: first, the addition of free phosphate serves as a freezing point depressant for the water in solution, while a secondary effect is the evolution of a high-acidity environment. When metal oxides are stirred into an acid solution, the oxide generally separates into two component parts, a metal cation and an oxygen-containing anion. The metal cation reacts with free water molecules and forms positively charged ‘aquasols’ by hydrolysis. In the case of MgO , the generation of these aquasols is dependent on a solution pH lower than 12. Any mildly acidic solution is more than suitable for the creation of chemically-bonded phosphate ceramics (Wagh, 2003). The key reaction formulas are present below.



The dissolution and hydrolysis of these metal cations are the controlling step in the formation of chemically-bonded phosphate ceramics. To drive this reaction forward, Le Chatalier’s principle is judiciously used in the creation of the Ceramicrete blend. An excess of KH_2PO_4 drives the reaction forward towards the creation of a ceramic product, and pushes the hydrolysis of Mg^{2+} cations to restore equilibrium. The dissolution rate of

KH₂PO₄ is far less of a concern, chemically, as this chemical has a remarkably high rate of dissolution (Wagh, 2003).

3.1.2. An Acid-Base Reaction and Formation of a Gel by Condensation

The aquasols generated by the hydrolysis of Mg²⁺ react with the aqueous phosphate anions to form hydrophosphate salts. Reacting in parallel, free protons and oxygen react to form water. The newly-formed hydrophosphate salts react together to form a network in the aqueous solution that leads to the formation of a gel composed of magnesium potassium phosphate, as shown below (Wagh, 2003).



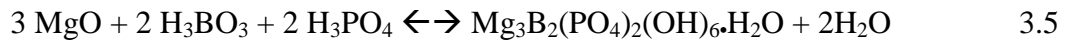
3.1.3. Saturation and Crystallization of the Gel into a Ceramic

As the reaction proceeds, more and more hydrophosphate salts are “added” to the gel and the Ceramicrete slurry thickens. This creation of a gel structure is identical to the sol-gel process of non-silicate ceramics. As increasing numbers of cations are released into the colloidal gel solution, previously isolated sols experience a condensation reaction and become connected to other sols. Chains of connected sols begin to form and percolate throughout the solution to form a gel (Wagh, 2003).

When sufficiently thickened, the gel is essentially a saturated phosphate solution in which a significant amount of undissolved metal oxide particles remain and are uniformly distributed. As precipitation of the phosphates occurs, these metal oxides provide nucleation points for crystallization into a well-connected crystal lattice. Thus it is important that some unreacted particles are available to provide a good stable ceramic. Formation of a well-crystallized ceramic or a poorly crystallized precipitate will depend on how rapidly the dissolution of the oxides occurs in the acid solution. The overall acid-base reaction is exothermic and heats the reaction slurry; if the reaction temperature is higher than the boiling point of the slurry, the slurry will boil over and disrupt the formation of the ceramic. Thus, upper and lower boundaries of ceramic production are adopted according to the dissolution of the metal oxide: high oxide solubility results in a precipitate, while low oxide solubility will result in a non-reaction (Wagh, 2003).

3.2. Effects of Boric Acid on Solubility of MgO

In large batches, Ceramicrete has a mixing time of only a few minutes before the exothermic acid-base reaction between MgO and KH_2PO_4 begins. Therefore, chemical retardants are necessary for any sort of large-scale mixing operation. Boric acid is useful for this purpose. When a very small quantity of boric acid is mixed into a Ceramicrete powder blend, a coating develops on the MgO particles and retards early dissolution, thus delaying the acid-base reaction (Wagh, 2003). The reaction leading to the coating of MgO is shown in the formula below:



The addition of boric acid to the powder blend leads to the creation of a polymeric coating upon MgO, identified by X-ray diffraction in the literature as lunebergite. When boric acid containing MgO is mixed into the phosphate solution, lunebergite is formed on the grains of MgO and coats them. This prevents the grains from dissolving into the acid solution. Subsequently, as the pH of the solution rises, the coating slowly dissolves and re-exposes the grains to the acid solution. Thus, because the dissolution of MgO is delayed, the rate of dissolution is reduced and the acid-base reaction is retarded (Wagh, 2003).

CHAPTER 4

DETERMINATION OF THAWED PERMAFROST ZONE AROUND THE WELLBORE

4.1 Introduction

One of the problems associated with oilfield operations on the ANS is permafrost thawing around the wellbore due to heat produced during setting of the cement slurry in the annular volume between the casing and the wellbore. The thawing may destroy the bond between the cement and the permafrost, cause instability and subsidence of the soil around the wellbore, and place high mechanical stresses on the casing. To prevent damage to the well, permafrost thawing is controlled by insulation, refrigeration, or insulation of the top several hundred feet of the well, while the rest of the permafrost is allowed to thaw uncontrolled.

In order to design a well completion that is economic, thermal behavior of permafrost and cement slurry to be used should be examined (Sengul and Brigham, 1983). The Stefan problem is used to forecast the rate of advancement of thawing front and temperature distribution in a thawed permafrost region. A common feature of the Stefan problem is the existence of a moving interface separating liquid and solid phases. The thermal properties of the two phases differ on either side of the moving interface, where the heat is absorbed or released. The interface moves either into the solid region (melting) or into the liquid region (solidification), depending on the relative temperature gradients of the two phases; the position of the moving interface is determined as a function of time, along with the temperature distributions in the liquid and solid regions.

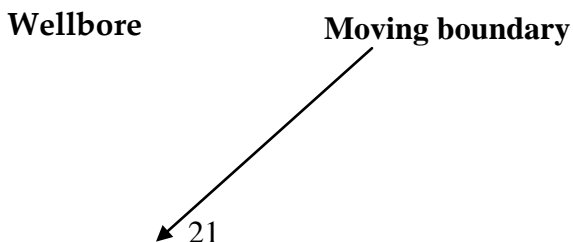
Recent tests at BJ Services have shown that a mixture of 95% Ceramicrete and 5% set CPC “G” grade has undergone “flash setting”, with the final temperature of the slurry being in the range of 55 degree F to 120 degree F. Thus, in this chapter the numerical solution is used to get a preliminary indication of a thawed zone distance around the wellbore, if the Ceramicrete and set Portland cement mixture slurry undergoes a flash setting. Simulations were carried out to determine the thawed zone radius around a wellbore in a permafrost zone using ABAQUS software, assuming a mixture of 90% Ceramicrete and 10% dry Portland cement and a slurry setting time of 3.5 hrs.

4.2 Numerical Method of Determining the Thawed Permafrost Zone Around the Wellbore

A practical way of determining the radius of the thawed permafrost region around a wellbore is presented in this chapter. A new numerical method was used to generate the solutions for a radial thawing of the permafrost with axial symmetry; the solution was shown to be a function of three dimensional parameters plus dimensionless time and radius. The model generated solutions for the range of values of the three parameters for conditions on the ANS. The dimensionless radius of the thawed permafrost region was related to the dimensionless time through simple power law equations containing two constants. The developed correlations were used in a computer model to find the thawed permafrost radius (Sengul and Brigham, 1983). The numerical solution is used to make a tentative estimate of the thawed zone near a wellbore during the flash setting of a slurry mixture of 95% of Ceramicrete and 5% set Portland cement.

4.2.1 Physical System Representing Permafrost Thawing Around the Wellbore

Figure 3 shows the schematic around the well in the permafrost region after flash setting of a slurry mixture of 95 % of Ceramicrete and 5 % set Portland cement in annular volume between the casing and the wellbore. Around the wellbore, two regions (thawed permafrost and permafrost) are separated by a moving boundary. As heat is supplied to a moving boundary, due to the exothermic reaction occurring during the setting of cement slurry, permafrost undergoes thawing and the thaw front moves away from the wellbore.



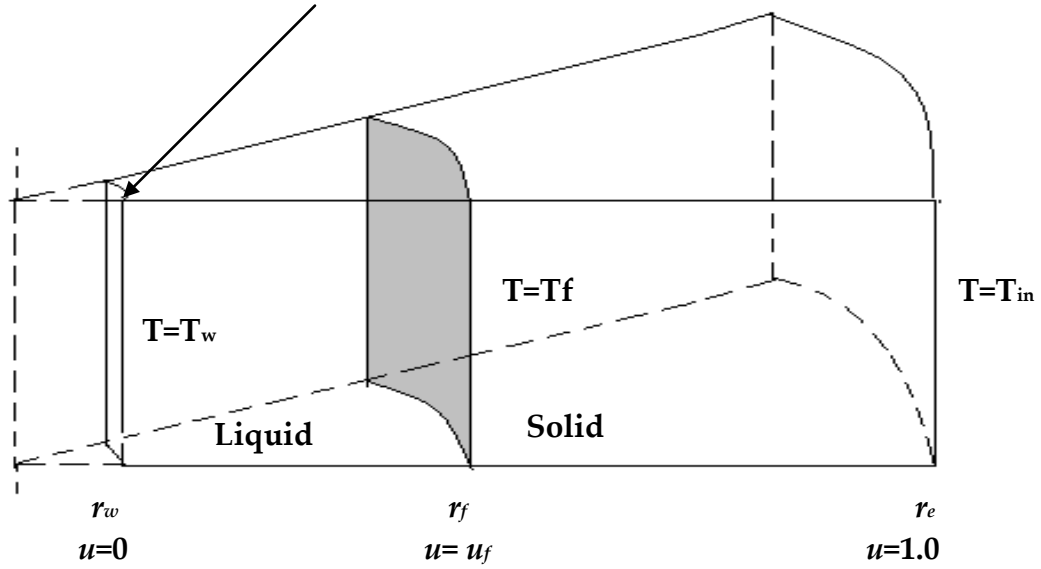


Figure 5: A Schematic Representing Permafrost Thawing Around the Wellbore (Sengul and Brigham, 1983).

4.2.2 Assumptions

To simplify the mathematical formulation of the physical system in Figure 5 several assumptions were made (Sengul and Brigham, 1983)

1. Permafrost and thawed permafrost are isotropic, homogeneous, and incompressible.
2. Thermal conductivity, specific heat, and density are constant within the two regions.
Thermal conductivity and specific heat differ on either side of the thaw front, but densities are the same on either side of the thaw front.
3. There is no free convection in the thawed permafrost region. Heat transfer in the thawed permafrost and permafrost is by conduction only.
4. There are no heat sources or sinks in the system

4.2.3 Mathematical Formulation of Physical System

Assuming axial symmetry and constant thermal properties, the differential equation describing unsteady-state heat conduction in an isotropic solid in cylindrical co-ordinates can be expressed as (Sengul and Brigham, 1983):

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} (r, t) \right) = \frac{1}{D} \frac{\partial T}{\partial t} (r, t) \quad (4.1)$$

$$D = \frac{k}{\rho \cdot Cp} \quad (4.2)$$

Where D is the diffusivity of the solid.

It is useful to describe the mathematical model for the problem described in Figure 5 in dimensionless form. For this purpose, a logarithmic transformation is used to transform the radial co-ordinates ($r_w \leq r \leq r_e$) into normalized co-ordinates ($0 \leq u \leq 1$).

$$u = \ln (r/r_w) / \ln (r_e/r_w) \quad (4.3)$$

Similarly, dimensionless time for the thawed permafrost (t_D) and the permafrost region (t_{DS}) can be given as:

$$t_D = K_L \cdot t / \rho_L \cdot C_{PL} \cdot r_w^2 \quad (4.4)$$

$$t_{DS} = t_D / \gamma \quad (4.5)$$

Where γ is the ratio between thawed permafrost and permafrost diffusivities (D_L/D_S).

Dimensionless temperature in the thawed permafrost region and the permafrost region can be given as

$$\theta_L (u, t_D) = (T (r, t) - T_f) / (T_w - T_f) \quad (4.6)$$

$$\theta_s (u, t_{DS}) = (T_f - T (r, t)) / (T_{in} - T_f) \quad (4.7)$$

Assuming that heat transfer occurs only by conduction in both the thawed permafrost and the permafrost regions, and that thawing occurs at a specific temperature, there are two equations corresponding to the equation describing the unsteady state heat conduction in the thawed permafrost and the permafrost regions.

Thawed permafrost region:

$$\frac{(r_e/r_w)^{-2u}}{[\ln(r_e/r_w)]^2} \frac{\delta^2 \theta_L(u, t_D)}{\delta u^2} = \frac{\delta \theta_L(u, t_D)}{\delta t_D} \quad (4.8)$$

Where $0 < u < u_f(t_D)$

Permafrost region:

$$\frac{(r_e/r_w)^{-2u}}{[\ln(r_e/r_w)]^2} \frac{\delta^2 \theta_s(u, t_D)}{\delta u^2} = \gamma \frac{\delta \theta_s(u, t_D)}{\delta t_D} \quad (4.9)$$

Where $u_f(t_D) < u < 1$.

4.2.4 Initial and Boundary Conditions

Initial condition

Initially, permafrost is at a temperature (T_{in}) lower than permafrost thawing temperature.

$$\theta_s(u, 0) = (T_f - T_{in}) / (T_{in} - T_f) = -1 \quad (4.10)$$

Boundary conditions

Temperature of the inner boundary is constant (T_w) and greater than the permafrost thawing temperature.

$$\theta_L(0, t_D) = (T_w - T_f) / (T_w - T_f) = 1 \quad (4.11)$$

The outer boundary, assumed to be at infinite distance from the well, stays at the same temperature as T_{in} throughout the thawing process.

$$\theta_s(1, t_D) = (T_f - T_{in}) / (T_{in} - T_f) = -1 \quad (4.12)$$

Moving boundary conditions

From the continuity of the temperature at the thaw front

$$\theta_L(u_f, t_D) = \theta_s(u_f, t_D) = 0 \quad (4.13)$$

Stefan Condition – from the heat conservation consideration at the moving boundary

$$\frac{(r_e/r_w)^{-2u}}{\ln(r_e/r_w)^2} \left[\phi \frac{\partial \theta_s(u, t_D)}{\partial u} - \frac{\partial \theta_L(u, t_D)}{\partial t_D} \right] u - u_f = \sigma \frac{du_f(t_D)}{dt_D} \quad (4.14)$$

$$\phi = K_s(T_{in} - T_f) / (K_L(T_w - T_f)) \quad (4.15)$$

$$\sigma = L_f / C_{pL}(T_w - T_f) \quad (4.16)$$

A solution for this model is taken as the temperature distribution in the thawed permafrost and the permafrost separately and to determines the position of the thaw front.

4.2.5 Results and Discussion

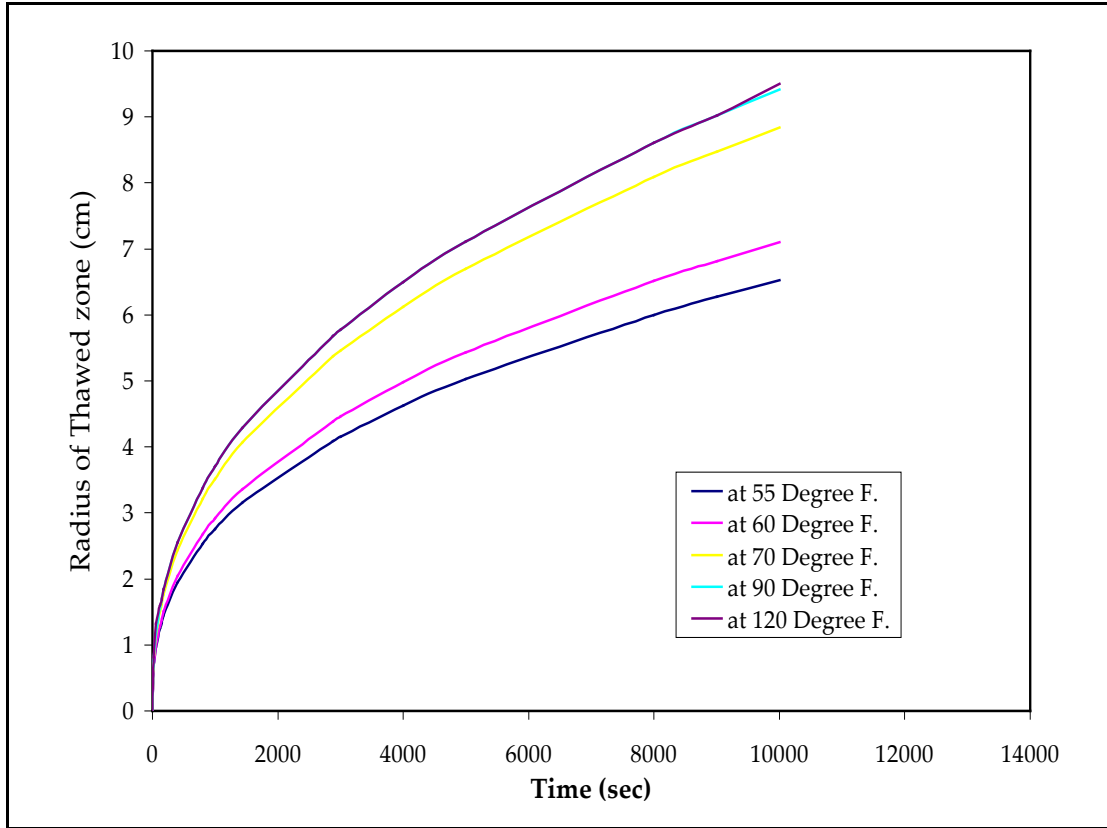


Figure 6: Radius of Thawed Permafrost Zone Around the Wellbore, r_f (cm) vs. time (min.) for Thawing.

The plot of radius of thawed zone, r_f (cm) is plotted against the time (min) for thawing at different temperatures, ranging from 55 degree F to 120 degree F as shown in Figure 6. It can be seen that as the slurry mixture of Ceramicrete (95%) and set Portland cement (5%) undergoes setting in the annular volume between the casing and the wellbore the permafrost zone around the wellbore starts thawing; as the permafrost thaws, there is a chance of soil subsidence around the wellbore, which can lead to casing collapse. However, as the slurry in the annular volume is “flash setting”, there are chances of rapid freeze-back of the thawed zone, which might prevent casing collapse and, thus, loss of well integrity. Figure 6 does not give the exact solution; however, it can be used to make a preliminary estimate of permafrost thawing during flash setting of mixed Ceramicrete (95%) and Set Portland cement (5%) around the wellbore on the ANS before conducting simulations using ABAQUS software.

4.3 Determining the Thawed Permafrost Zone Around the Wellbore Using ABAQUS Software

ABAQUS software is used to determine the thawed permafrost zone around a wellbore and it has many advantages over numerical solutions for determining these zones. This useful software can generate a physical view of thawing phenomena under particular slurry temperature conditions. The main advantage of ABAQUS software is that each and every material property of both the slurry mixture of Ceramicrete and dry Portland cement powder and the thawed permafrost zone can be incorporated into it, which improves the accuracy of the results. In order to generate results using ABAQUS software, four different cases have been considered. In case 1 (section 4.3.3), it was assumed that the final temperature of Ceramicrete slurry after setting for 3.5 hrs is 50 degrees C. However, in case 2 (section 4.3.4), it was assumed that instead of 50 degrees C, the Ceramicrete slurry reaches 32 degrees C after setting for 3.5 hrs. In the next two cases, it was assumed that after the Ceramicrete slurry set for 3.5 hrs with a final temperature of 50 degrees C, the temperature reached either -1 degree C or 10 degrees C; the effect on the permafrost zone around the wellbore was examined.

4.3.1 Material Properties Used in ABAQUS Software

Properties of the slurry of 90% Ceramicrete and 10% dry CPC “G” grade and of permafrost that were used in ABAQUS software to generate the results are as given in Table 3. Phase change temperature and water content of slurry and permafrost are listed in Table 4.

MATERIAL	Dry density (Kg/m ³)	Thermal conductivity (J/(day-m- degree C))		Specific heat capacity (J/(kg- degree C))		Latent Heat (J/m ³)
		Thawed	Frozen	Thawed	Frozen	
Slurry	1900	44928		879		-
Permafrost	1521	97198	179442	2436	1848	93,436

Table 3: Material Properties of a Ceramicrete and Dry Portland Cement Powder Slurry and Permafrost

MATERIAL	Phase change temperature (degree C)		Water content (%)	
	Solidus	Liquidus	Normal	Unfrozen
Slurry	-		-	
Permafrost	-0.3	0	40	12

Table 4: Phase Change Temperature and Water Content of a Ceramicrete and Dry Portland Cement Slurry and Permafrost

Note: Slurry consists of 90% Ceramicrete and 10% dry Portland cement and setting time for the slurry of this mixture is assumed to be 3.5 hrs in all simulation runs.

4.3.2 Dimensions of a Typical Well on the ANS

For determination of thawed permafrost zone around the wellbore, a typical well on the ANS is selected as shown in Table 5.

Open hole diameter	26"
Surface casing diameter	20"
Depth of the permafrost zone	1800'

Table 5: Dimensions of Typical Well on the ANS

The above material properties and well dimensions are used in the “ABAQUS” software to generate the results shown below:

4.3.3 Thawing of the Permafrost Zone Around the Wellbore After 3.5 hrs at 50 Degrees C.

The physical view (top view) of thawing of the permafrost zone around the wellbore after 3.5 hrs at 50 degrees C is shown in Figure 7. The slurry takes approximately 3.5 hrs. to set in an annular space between the wellbore and the casing

with the temperature assumed to be 50 degrees C (based on the test conducted at BJ Services). The thawed-zone radius after the slurry has set is indicated by the blue color band (partially thawed zone) in Figure 7. However, the temperature (degrees C) vs. thawed-zone radius (m) (Figure 8) indicates a thawed-zone radius of 9 cm (shown as dotted lines in Figure 8).

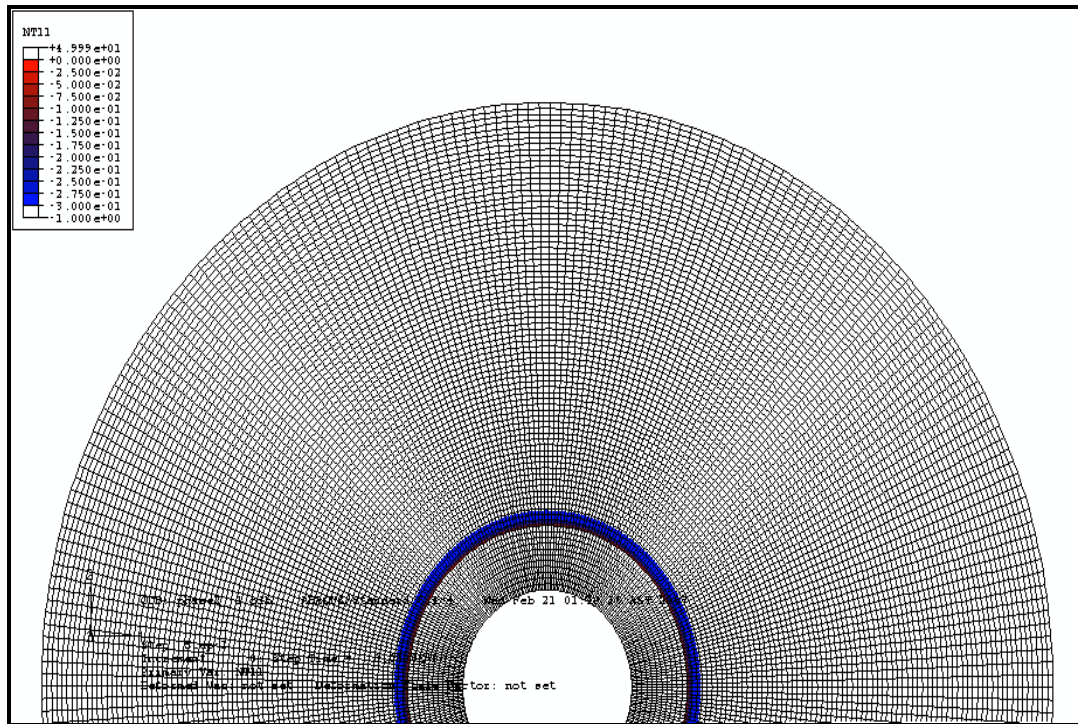


Figure 7: Contour Diagram Showing Thawed Zone Around the Wellbore at 50 Degrees C.

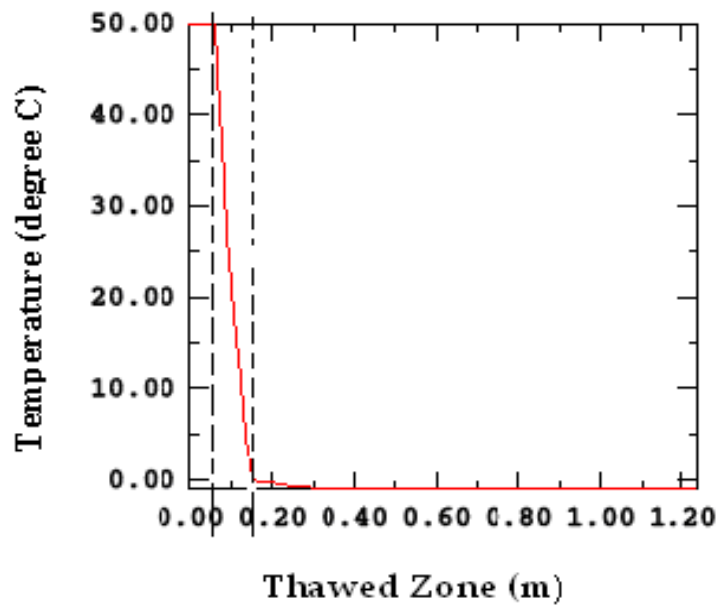


Figure 8: Temperature Profile of Thawed Zone at 50 Degrees C.

4.3.4 Comparison Between Thawed Zones Around the Wellbore After 3.5 hrs. at 50 Degrees C and at 32 Degrees C.

In this case, it was assumed that instead of 50 degrees C, a slurry of the Ceramicrete (90%) and Portland cement (10%) will reach 32 degrees C after setting for 3.5 hrs and a comparison of the thawed zone around the wellbore after 3.5 hrs at 50 degrees C and at 32 degrees C was carried out.

The thawed zone around the wellbore at 32 degrees C (3.5 hrs) is approximately 8.5 cm (shown as dotted lines in Figure 10), while it is 9 cm at 50 degrees C (3.5 hrs).

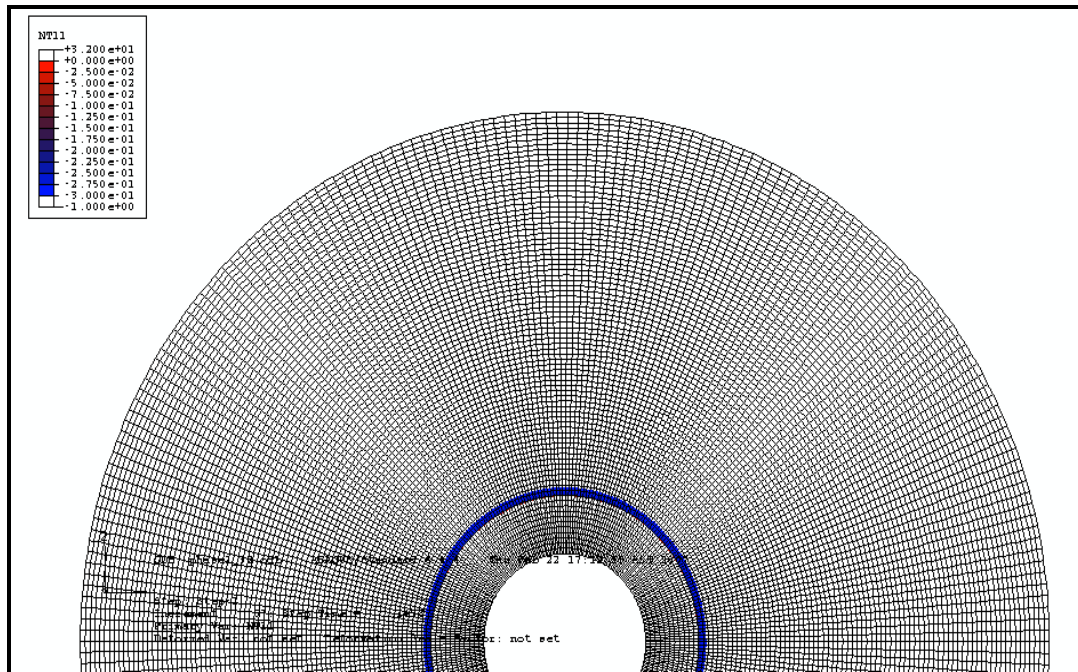


Figure 9: Contour Diagram Showing Thawed Zone Around the Wellbore at 32 Degrees C.

A comparison between thawed zones around the wellbore after 3.5 hrs. at 50 degrees C and at 32 degrees C is shown in Figure 10.

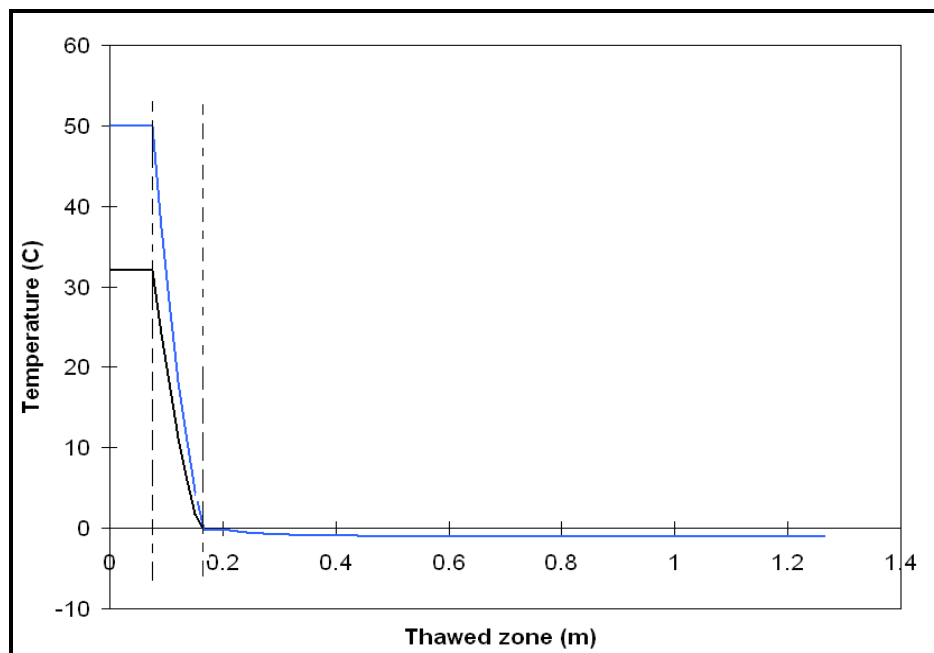


Figure 10: Comparison of Thawed Zone Around the Wellbore at 32 Degrees C and 50 Degrees C.

4.3.5 Freeze-Back of Thawed Zone at -1 Degree C.

In this case, it was assumed that after a slurry mixture of Ceramicrete and dry Portland cement has set for 3.5 hrs and reached a final temperature of 50 degrees C, it will reach an ambient temperature of -1 degree C; the effect on the thawed zone was examined.

At -1 degree C (ambient temperature), the thawed zone freezes back in about 5 hrs; different color bands in Figure 11 indicate the partially-frozen zone of permafrost.

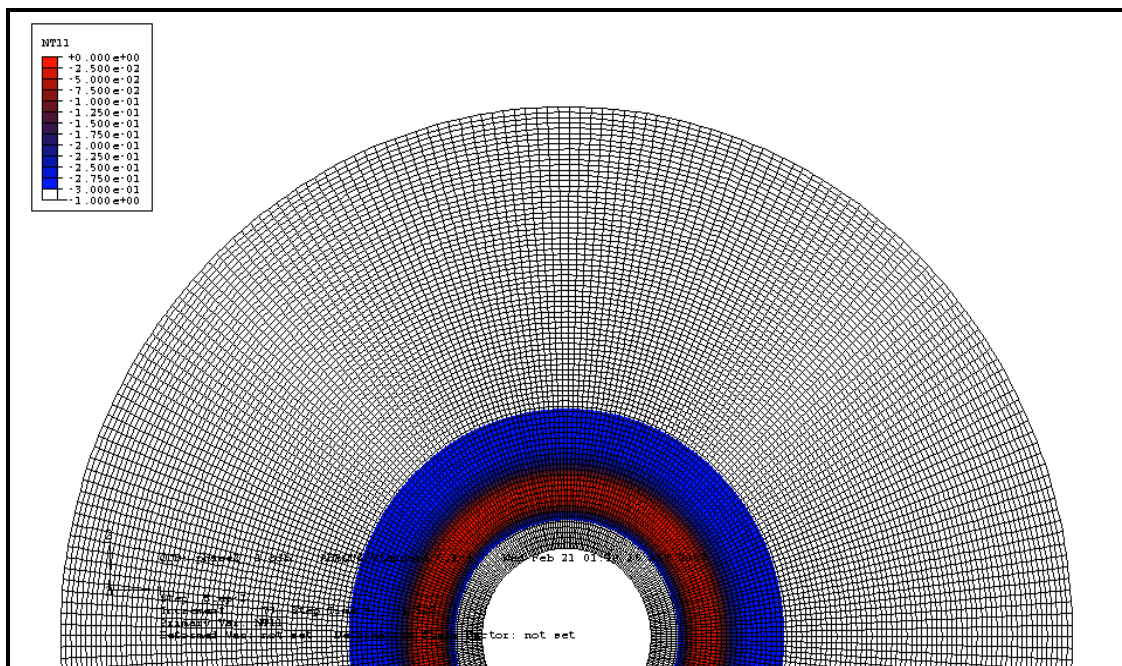


Figure 11: Contour Diagram for Freeze-Back of Thawed Zone at Ambient Temperature (-1 Degree C).

The plot of temperature (degrees C) vs. thawed-zone radius (m) (Figure 12) shows the freeze-back phenomena.

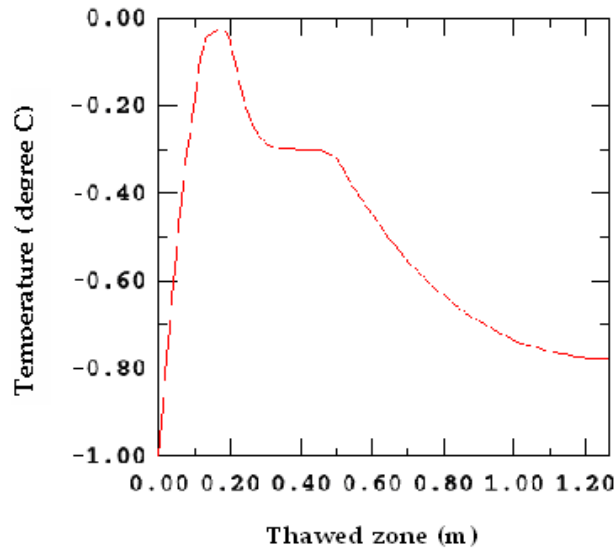


Figure 12: Temperature Profile for Freeze-Back of Thawed Zone.

4.3.6 Continuous Thawing of Permafrost at 10 Degrees C for 1 Year.

In this case, it was assumed that after a slurry mixture of Ceramicrete and dry Portland cement has set for 3.5 hrs and reached a final temperature of 120 degrees C, it will reach 10 degrees C, instead of ambient temperature, i.e. -1 degree C. The thawed zone around the wellbore at 10 degrees C is shown in Figure 13.

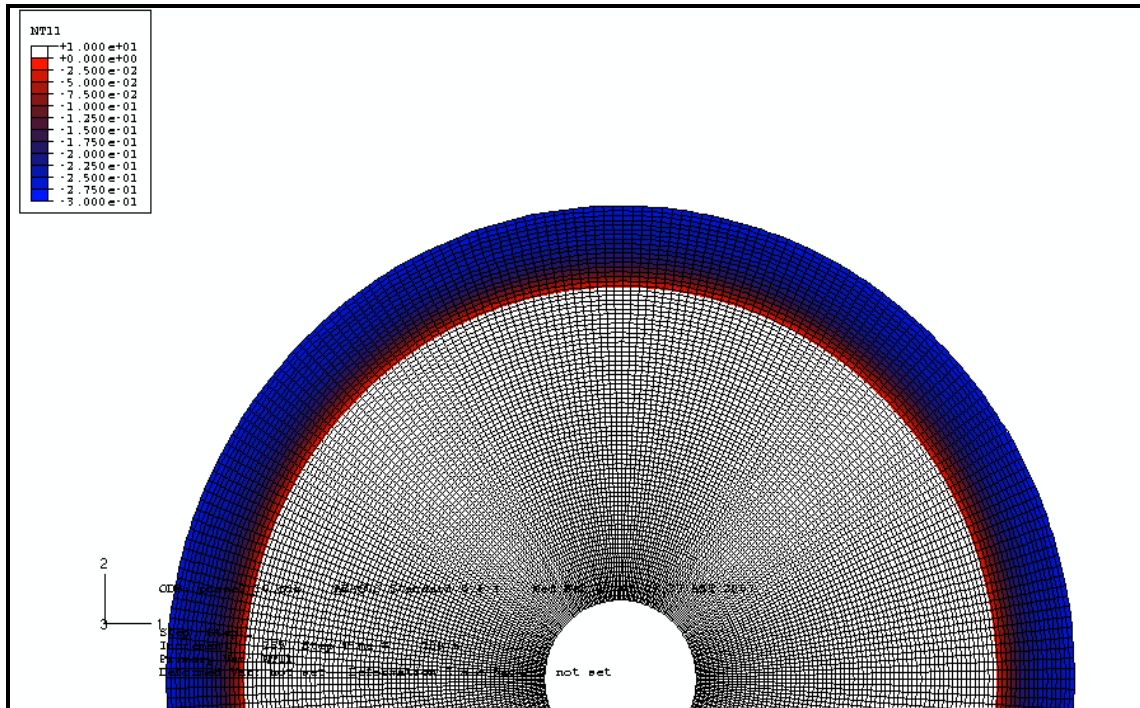


Figure 13: Contour Diagram for Continuous Thawing of the Permafrost at 10 Degrees C for 1 Year.

If it is assumed that the final temperature (50 degrees C after 3.5 hrs.) of the slurry declines only to 10 degrees C, then a continuous increase in the thawed zone temperature is observed for 1 year which would be expected behavior in any permafrost well cement. Thus, the thawed zone (indicated by different color bands in Figure 13) will never freeze back in this case. The temperature profile in Figure 14 shows continuous thawing of the permafrost around the wellbore.

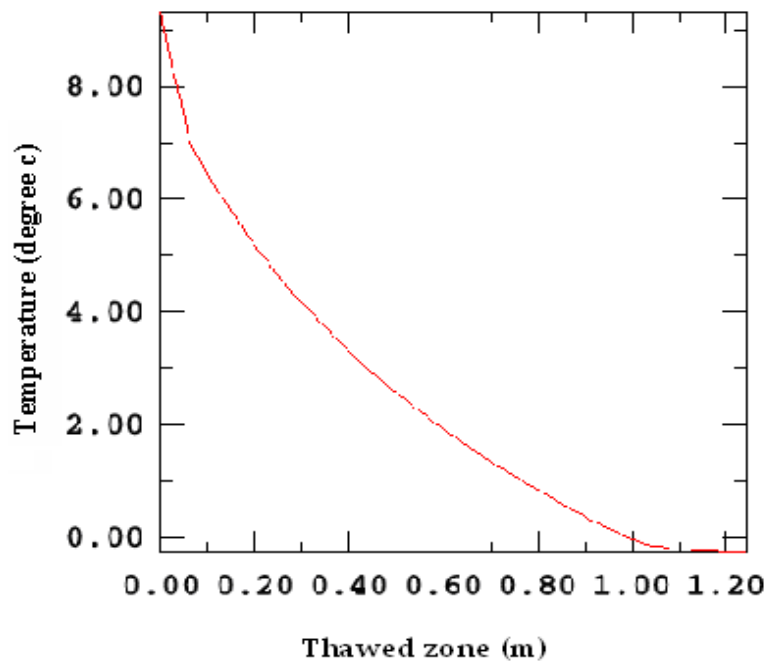


Figure 14: Temperature Profile During Continuous Thawing at 10 Degrees C for 1 Year.

4.3.7 Results and Discussion

An analysis of results was conducted to understand the effect of heat evolved during the setting of the 90% Ceramicrete and 10% dry Portland cement slurry on the permafrost region near the wellbore. Results generated by “ABAQUS” show that the thawed zone radius is 9 cm. at 52 degrees C, while it is 8.5 cm for 32 degrees C after 3.5 hrs. If the temperature drops down to -1 degree C, i.e. ambient temperature, the thawed zone will freeze back. However, if the temperature drops only to 10 degrees C, the thawed zone will never freeze back. Thus, for well integrity, it is necessary to reduce the

setting time of slurry in the annular volume between the wellbore and the casing. In order to avoid further thawing of the permafrost, the slurry should reach ambient temperature as quickly as possible. Thus, it can be seen from results generated using the Stefan method and by ABAQUS software that the permafrost zone around the wellbore undergoes thawing to a certain extent. However, if there is rapid freeze-back of the thawed permafrost zone around the wellbore, casing collapse will not occur and the well will remain intact for a longer period of time. The disadvantages of the proposed Ceramicrete formulation with contamination by either 5% or 10% dry CPC are listed in Table 6. However, considering other advantages of Ceramicrete over Portland cement, remedial measures can be taken to minimize the heat evolved during the setting of cement slurry, and thus to avoid the thawing of the permafrost zone around the wellbore.

Methodology	Ceramicrete formulations	Disadvantages
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Experimental results and numerical solution by the Stefan method	Slurry of proposed Ceramicrete formulation with 5% set Portland cement	1. Flash setting of slurry with final temperature in the range of 55 degrees F to 120 degrees F.
		2. Less compressive strength with crack development.
		3. Thawing of the permafrost zone around the wellbore to the extent of 9.5 cm in 4 hrs.
Experimental results and ABAQUS software simulations.	Slurry of proposed Ceramicrete formulation with 10% dry Portland cement.	1. Setting of the slurry after 3.5 hrs with final temperature in the range of 55 degrees F to 120 degrees F.
		2. Time required to reach -1 degree C from 50 degrees C is not considered.
		3. Final temperature of set slurry is not known.
		4. At 10 degrees C or above continuous thawing of the permafrost zone around the wellbore might lead to casing collapse, and thus loss of well integrity.

Table 6: Disadvantages of Proposed Ceramicrete Formulation

Note: As the formulation of Ceramicrete was not disclosed during testing at BJ Services, Tomball, TX, it is named “proposed Ceramicrete formulation”.

CHAPTER 5

EXPERIMENTAL PROCEDURE AND TESTING METHODOLOGY

5.1 Introduction

Various laboratory tests were carried at the R & D facility of BJ Services in Tomball, TX with BJ Services staff to predict and evaluate the performance of the Ceramicrete slurry for its effective use in permafrost cementing operations. Although other standards such as those of the American Standard for Testing Materials (ASTM) and Construction Specification Institute (CSI) exist, all these tests were standardized by the API.

A summary of the tests traditionally used in the cement slurry design as well as the API tests reference document are provided in Table 7. All of these tests were performed within the scope of this research to evaluate properties of the Ceramicrete.

Slurry Property	Laboratory Test	Test Reference
Slurry preparation for laboratory mixing and testing	Balances and high-shear mixers	API Document 10, Sec. 5
Slurry viscosity	Atmospheric thickening-time tester	API Document 10, Sec. 9
Pumping time	Consistometer testing	API Document 10, Sec. 8
Free water	Settling of slurry in 250-ml graduated cylinder after setting	API Document 10, sec. 5
Fluid loss of cement slurry	High-pressure fluid-loss cell at 1,000 psi on 325 mesh screen for 30 minutes	API Document 10, Appendix F
Slurry density	Standard Mud Balance	API Document 10, Appendix C
Rheological properties	Rotational viscometer at various shear rates	API Document 10, Appendix H
Permeability testing	Special water permeability apparatus for set cement	API Document 10, Appendix G

Table 7: API Specifications of Tests Carried out at BJ Services, Tomball, TX.

5.2 Formulation of Ceramicrete

The formulation used to carry out the tests at the R & D facility of BJ Services, Tomball, TX is given in Table 8 below:

Contents	Amount
Ceramicrete	400 grams.
Fly ash	400 grams.
Boric Acid	15 grams.
Tap Water (33.12%)	265 grams.

Table 8: Formulation of Ceramicrete Used to Carry Out Tests at BJ Services, Tomball, TX

Tests carried out at BJ Services, Tomball, TX:

The following tests were carried out according to the API standards.

1. Compatibility test
2. Thickening time
3. Density measurement
4. Compressive strength
5. Fluid loss
6. Rheology
7. Expansion test

5.3 Compatibility test

5.3.1 Introduction

In field operations, during Ceramicrete slurry preparation contamination with leftover Portland cement might occur in a mixer. If the mixture of Ceramicrete and Portland cement is not compatible, then there are possibilities that the set product may develop cracks after some time, which will eventually lead to casing collapse and loss of well integrity. Thus, it is important to establish the compatibility of Ceramicrete with Portland cement after mixing.

5.3.2 Experimental procedure:

Ceramicrete formulation shown in Table 8 (95%), with 40 grams of dry CPC "G" grade (5%) is mixed with water at a speed of 4000 RPM in a blender (Figure 15). The

blender speed is increased to 12,000 RPM for 35 seconds (according to API standards) to check the compatibility of the Ceramicrete with CPC “G” grade.



Figure 15: Blender Used to Mix 95% Ceramicrete and 5% Dry California Portland Cement "G" Grade.

5.3.3 Results and Discussion:

The mixture is found to be compatible; i.e. no separate layers of Ceramicrete (95%) and dry CPC "G" grade (5%) were observed after mixing. Hence, Ceramicrete contaminated by Portland cement "G" grade can be effectively used in oilfield cementing operations.

5.4 Thickening Time Testing

5.4.1 Introduction

Thickening time testing, also referred to as “consistometer testing”, measures the length of time the slurry will remain in a fluid state under simulated downhole conditions without any shutdown periods.

The consistometer consists of a rotating cylinder slurry container that envelops a stationary paddle. This slurry container is in turn encased within a pressure vessel and is surrounded in a “chilled” fluid that can manipulate the operating temperature. In the experimental work at BJ Services, a Chandler consistometer (Figure 16) was used and it was connected to a chiller to maintain its temperature. A downhole pressure of 1500 psi was simulated in all cases with different operating temperatures, such as 40 degree F, 55 degree F and 70 degree F.

As the consistometer maintains the slurry at a desired pressure and temperature, the torque on the stationary paddle is measured and converted into a slurry consistency, in Bc (Bearden units). According to API standard 10, the thickening time is the time at which viscosity becomes 70 Bc. Upon completion of consistometer testing, the Ceramicrete slurry is sufficiently mixed and thickened to prepare a set product.

The thickening time test is carried out for slurries of both Ceramicrete without CPC “G” grade contamination and Ceramicrete with (5%) CPC “G” grade contamination.

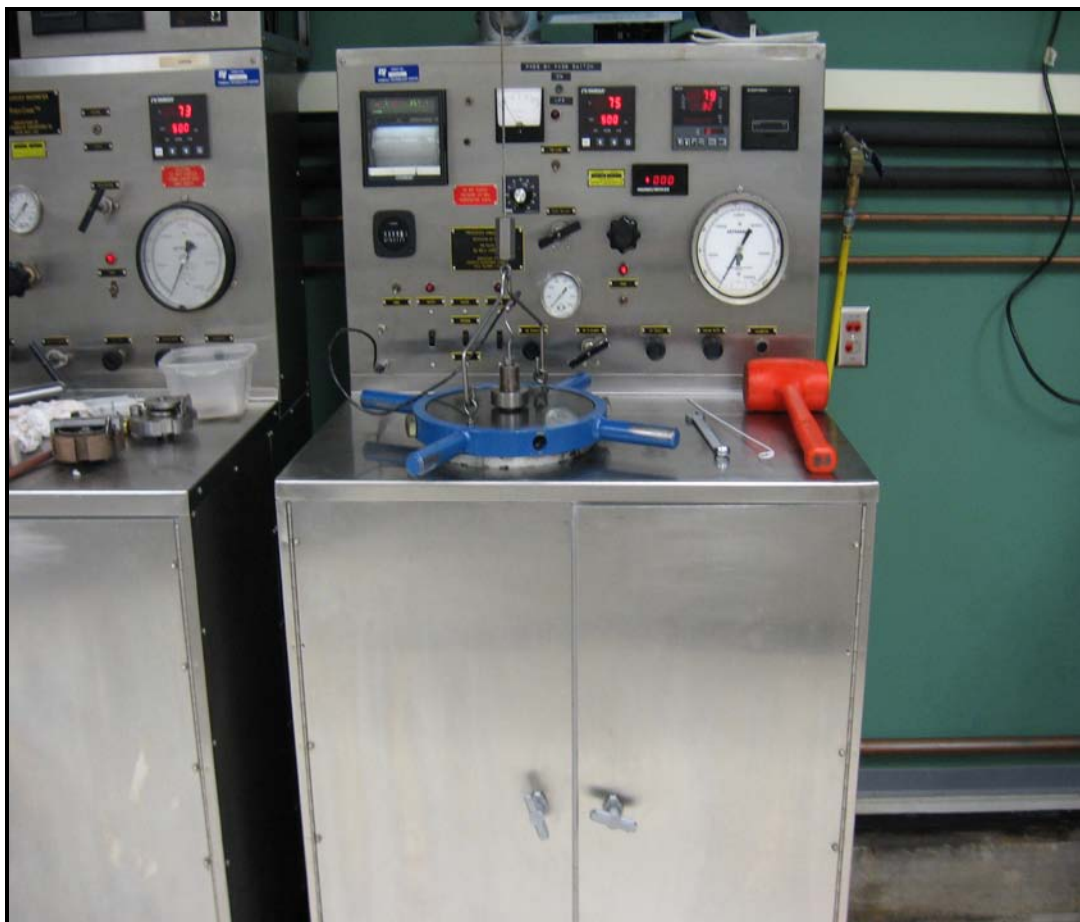


Figure 16: Chandler Consistometer for Measuring Thickening Time of Cement Slurry.

5.4.2 Results and Discussion

The API standard specifies that an oilfield cement should exhibit a pumping time ranging from 3 to 5 hrs. At BJ Services, Tomball, TX, consistometer tests were performed using the defined Ceramicrete blend, with each test occurring at 1500 psi and at different temperatures such as 40 degrees F, 55 degrees F, and 70 degrees F.

In the first case, i.e. at 1500 psi and 40 degrees F (Figure 17 and Figure 18), the thickening time (or time at which viscosity of slurry becomes 70 Bc) for both Ceramicrete with 5% CPC “G” contamination and Ceramicrete without CPC “G” contamination, is approximately 5 hrs, which meets the API standards. In the second case, i.e. at 1500 psi and 55 degrees F, the thickening time for Ceramicrete without CPC “G” contamination is approximately 2.30 hrs. In the third case, i.e. at 1500 psi and 70

degrees F, the thickening time for Ceramicrete without CPC “G” contamination is approximately 1.00 hr, which is significantly less than what is required by API standards.

It can be seen from the first case that the thickening time for Ceramicrete with or without contamination of CPC “G” is 5 hrs; because there is no change in the thickening time of Ceramicrete slurry contaminated with Portland cement “G” grade, Ceramicrete slurry can be assumed to behave ideally at 1500 psi and 40 degrees F (according to API standards) in oil-well cementing operations on the ANS. The thickening time for Ceramicrete slurry without contamination of Portland cement “G” grade at conditions mentioned in case 2 and case 3 is less than what is required by API standards. Thus, Ceramicrete slurry cannot be effectively used under the conditions of the second and third cases, i.e. for higher-temperature oil field operations.

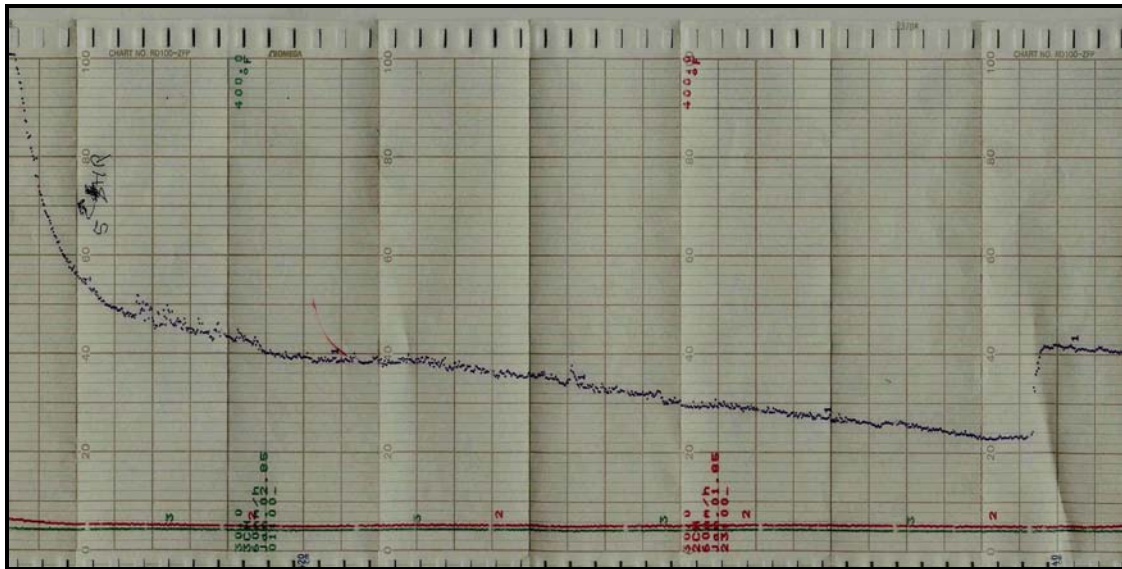


Figure 17: Thickening Time Measurement for Ceramicrete (95%) Contaminated by Dry California Portland Cement "G" Grade (5%).

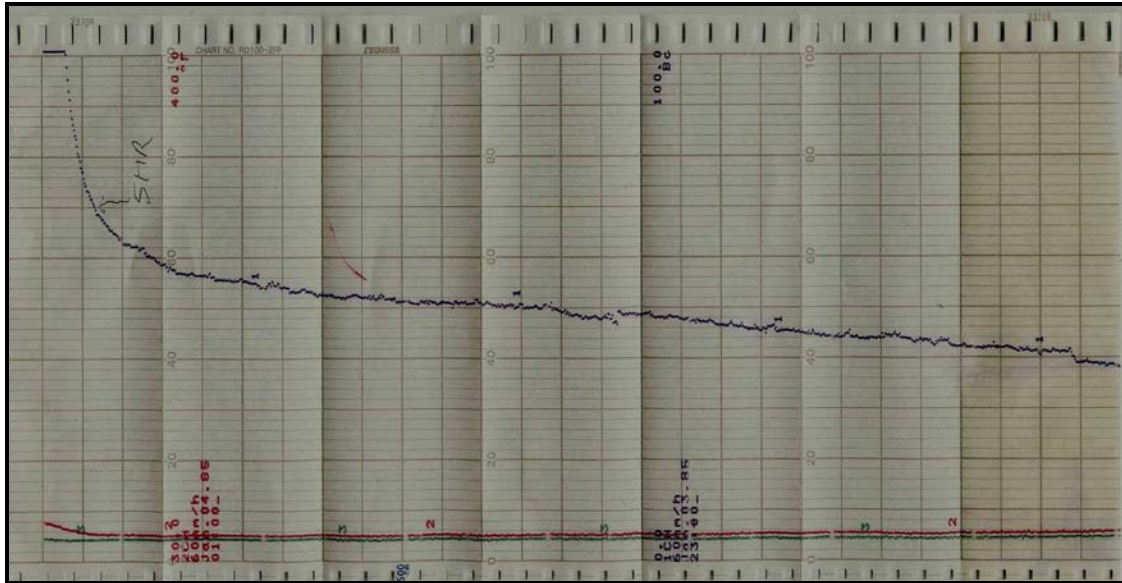


Figure 18: Thickening Time Measurement for Ceramicrete (95%) Without Contamination by California Portland Cement "G" Grade (5%).

5.5 Density measurement

5.5.1 Introduction

To achieve a satisfactory job in oil well cementing, it is extremely important to closely regulate the density of the cement slurry during the injection operation. The success of many industrial operations and processes depends on reliable measurement of the density of a liquid. In oil-well cementing operations, cement slurry is injected into an annulus formed between the pipe casing and the wall of the borehole. When the slurry reaches the desired location in the borehole it is allowed to harden. The density of cement slurry is a measure of the amount of water used with a sack of dry cement material. The amount of water in the slurry controls many physical properties of the cement. A large amount of water can increase the thickening and setting time of the cement beyond a desirable period. An excess of water in the slurry can also cause shrinkage, which will weaken the set cement. In contrast, if the slurry contains a lesser amount of water it will increase the initial viscosity and thixotropy of the cement and cause plug flow or a preliminary flash setting.

Drilling fluids and cements often have a considerable amount of air entrained or trapped within the fluid; this air may give erroneous results when determining fluid

density using conventional equipment. The air volume may be decreased to a negligible quantity by pressurizing the sample cup, yielding more accurate density readings of the fluid. Thus, the absolute density of Ceramicrete with and without contamination by CPC “G” grade can be determined accurately using Halliburton Tru-Wate™ pressurized fluid density scale (Figure 19).

The operation is similar to the conventional mud balance, with the additional capability of pressurizing the sample in the cup.



Figure 19: Halliburton Tru-Wate™ Pressurized Fluid Density Scale

5.5.2 Results and Discussion

The densities of Ceramicrete slurries without and with 5% dry Portland cement contamination were measured using a Tru-Wate™ pressurized fluid density scale.

1. The density of Ceramicrete without contamination by CPC “G” Grade: 15.6 ppg (1.88 grams/cc).

2. The density of Ceramicrete contaminated by Portland cement, i.e a mixture of 95% Ceramicrete and 5% dry CPC “G” grade): 15.7 ppg (1.88 grams/cc).

As specified by API standards, the slurry density is the same for Ceramicrete without and with contamination by 5% Portland cement “G” grade. Although the density of pure Ceramicrete and Ceramicrete contaminated by Portland cement is less than that of conventional Portland cement, there is a decrease in interstitial spacing in Ceramicrete with and without contamination by CPC “G” grade. The presence of porous spaces is one of the primary problems in arctic cementing operations. Water and other fluids fill these spaces and freezing temperatures can lead to expansion of the fluids and cracking of the set product. Ceramicrete with less density offers less pore space for potential invasion of fluids, and thus cracking of the set product at freezing temperatures is avoided. Thus, either contaminated or uncontaminated Ceramicrete can be used effectively for permafrost oil field operations because contamination with CPC “G” does not alter the density of Ceramicrete.

5.6 Compressive Strength Testing

5.6.1 Compressive Strength Measurement Using Ultrasonic Cement Analyzer

A Model 2000 UCA (Ultrasonic Cement Analyzer, Figure 20) is used to provide an indication of the relative strength development of a slurry sample while it is being cured under downhole temperature and pressure conditions. Relative strength is determined by measuring the change in velocity of an ultrasonic signal transmitted through the cement slurry specimen as it cures. As the strength of the cement specimen increases, the transit time of the ultrasonic signal through the specimen decreases, allowing the relative strength to be calculated.

The slurry sample to be tested is prepared in accordance with API-recommended practices, and then is placed in a temperature- and pressure-controlled cell to simulate the curing conditions that are expected downhole. Each cell of the Model 2000 is a stand-alone instrument designed to supply a complete data set. The data are downloaded to a computer for data archiving. An embedded controller replaces the central processor unit. This instrument is capable of running the custom software that measures the transit time of the ultrasonic signal through the slurry specimens and computes the relative

compressive strength values. Data points are measured and recorded continuously on-board in flash memory. A numeric display of the current strength measurement, temperature, and transit time, or a graphical plot of these test parameters versus time is available continuously on the 10.4 inch touch screen provided with each cell. Current temperature and pressure are always displayed numerically. A plot of pressure can be substituted for transit time if desired. The touch screen monitor also allows the user to access the control, diagnostic, and calibration functions of the embedded controller.

Temperature control is provided through a fuzzy logic control algorithm by the same embedded controller used on CTE's pressurized curing chambers and Consistometers. The desired temperature profile is easily programmed using the touch screen features of the monitor. Step by step instructions are displayed on the monitor, making the device easy to use. After the desired temperature profile is entered, a preview of the ramp is displayed graphically for pre-test inspections to prevent programming errors. The pressure is controlled manually, using an air-operated high-pressure pump and a pressure-relief valve.



Figure 20: Ultrasonic Cement Analyzer for Compressive Strength Testing

5.6.2 Results and Discussion

The compressive strength of Ceramicrete slurry with and without contamination by CPC “G” grade was determined using the UCA at 40 degrees F.

1. Compressive strength of Ceramicrete contaminated by 5% CPC “G” at 24 hrs = 42 psi.
2. Compressive strength of Ceramicrete contaminated by 5% CPC “G” at 48 hrs = 972 psi (Figure 21).
3. Compressive strength of Ceramicrete without contamination by CPC “G” at 24 hrs = 332 psi (Figure 22).
4. Compressive strength of Ceramicrete without contamination by CPC “G” at 48 hrs = 135 psi.

Thus, it can be seen that the compressive strength of Ceramicrete contaminated by CPC “G” grade at 48 hrs. (972 psi) is greater than that of pure Ceramicrete. However, in

all cases there were no signs of freezing, flash setting, or increased porosity. It can be concluded that contamination of Portland cement in Ceramicrete improves the compressive strength of the Ceramicrete. Thus, contaminated Ceramicrete is more effective to use than are other permafrost cementing formulations.

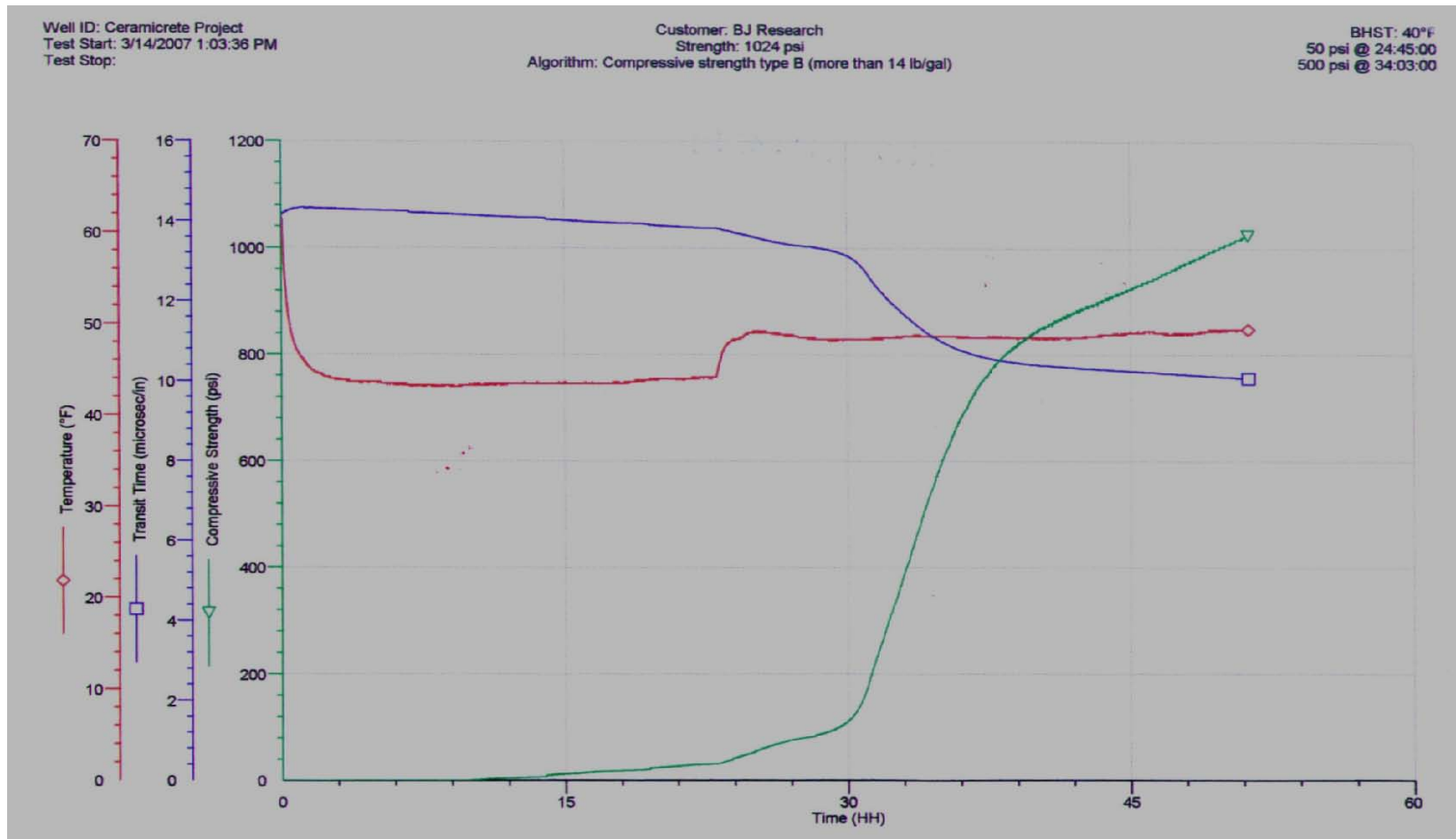


Figure 21: Compressive Strength of Ceramicrete (95%) Contaminated by Dry California Portland Cement "G" Grade.

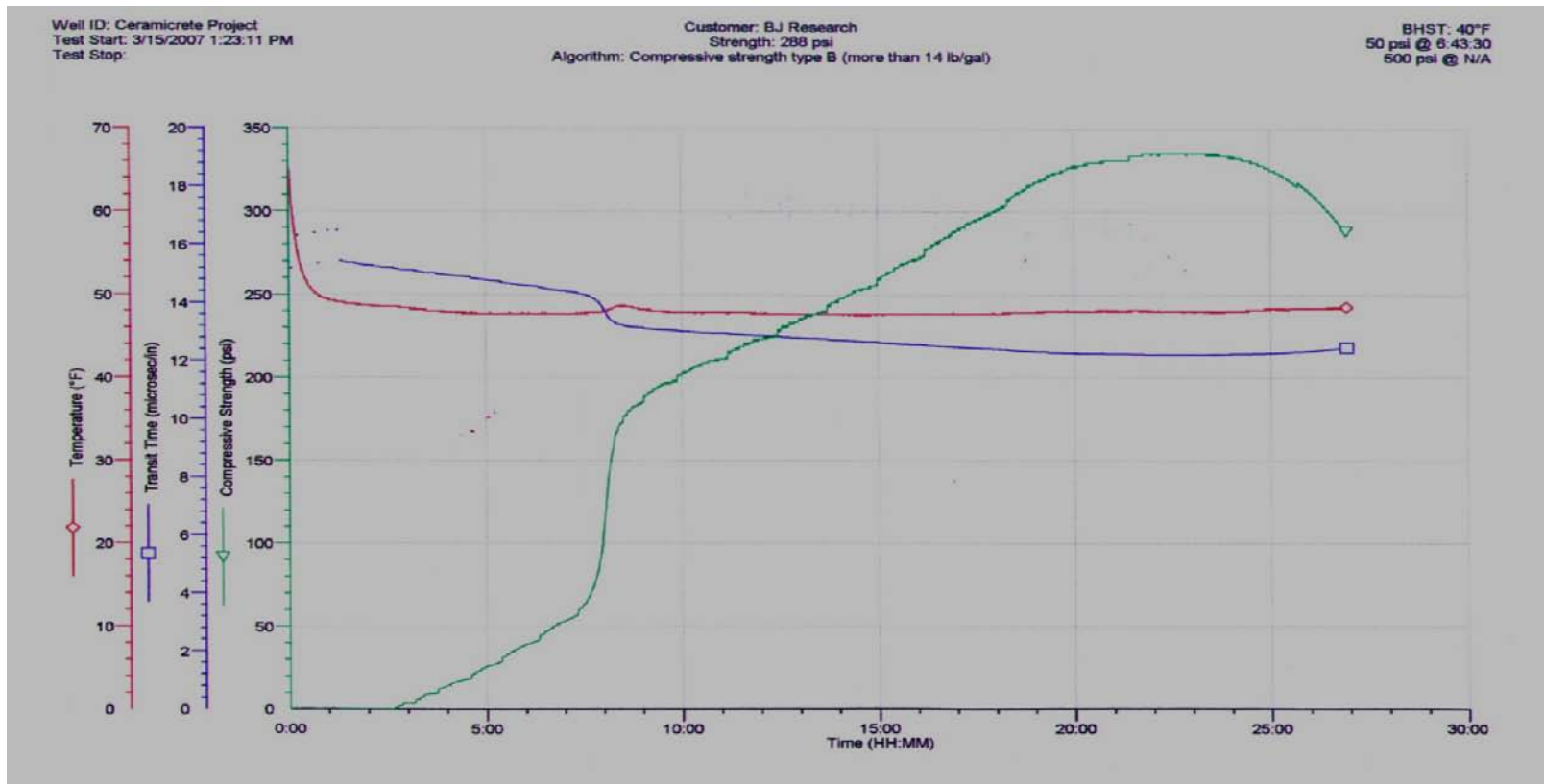


Figure 22: Compressive Strength of Ceramicrete (95%) Without Contamination by Dry California Portland Cement “G” Grade

5.6.3 Compressive Strength Measurement by Curing Method

The Model 200 High Temperature High Pressure (HTHP) curing chamber is utilized to prepare cement specimens for compressive strength tests. It is necessary to determine the amount of time required for a cement to develop compressive strength so that drilling/production operations can be resumed as quickly as possible after pouring. The HTHP curing chambers provide a means of curing cement specimens under typical downhole temperatures and pressures.

In this method, cement is first poured into a special mold (Figure 23) that produces specimens measuring 2" x 2" x 2". These molds are then kept in a water bath in the Model 200 HTHP curing chamber (Figure 24) at 40 degrees F for a time period specified by API standards, so that the specimen will develop sufficient compressive strength. The compressive strength is measured by compressing the cubes using the compressive-strength-measuring equipment shown in Figure 25. The results are recorded via a computer connected to the equipment. The compressive strength of Ceramicrete without contamination by dry Portland cement was measured after 24 hrs, while the compressive strength of a mixture of Ceramicrete (95%) and dry Portland cement (5%) was measured after 48 hrs.



Figure 23: 2" x 2" x 2" Molds with Mixture of Ceramicrete Slurry and 5% California Portland Cement "G" Grade for Compressive Strength Testing.



Figure 24: Model 200 HTHP Curing Chamber to Prepare Cement Specimens for Compressive Strength Testing



Figure 25: Instrument to Measure Compressive Strength of 2" x 2" x 2" Cubes at the R & D Center, BJ Services, Tomball, TX

5.6.4 Results and Discussion

According to API standards, the compressive strength of permafrost cement should be 500 psi after 24 hrs. The compressive strengths measured using the curing methods described are given below:

1. Compressive strength of Ceramicrete without contamination by dry California

Portland cement “G” grade after 24 hrs = 292 psi.

2. Compressive strength of Ceramicrete without contamination by dry California

Portland cement “G” grade after 48 hrs = 50 psi.

3. Compressive strength of Ceramicrete contaminated by Portland cement,

i.e a mixture of 95% Ceramicrete with 5% Portland cement, after 48 hrs =

698 psi.

The compressive strength of Ceramicrete without Portland cement contamination after 48 hrs is 292 psi, which is less than what is required by API standards. The reduction in compressive strength after 48 hrs may be due to the development of a crack in the set Ceramicrete binder after 24 hrs. In the case of Ceramicrete contaminated by 5% Portland cement, the compressive strength was not measured at 24 hrs, as it was negligible. However, there was a sudden increase in the compressive strength after 24 hrs. Hence, it can be concluded that compressive strength of the proposed Ceramicrete binder can be increased with Portland cement contamination.

5.7 Fluid Loss Testing

5.7.1 Introduction

Successfully cementing the casing string of an oil or gas well is highly dependent upon the characteristics of the cement slurry. Well cements that have poor filtration control can lead to a complete failure of the cementing operation. In addition, the invasion of filtrates into producing zones causes formation damage, which can greatly reduce the production potential of the reservoir. Developing cement slurries that have minimal filtration loss prevents expensive remedial cementing operations and reduces formation damage. The stirred fluid loss tester (Figure 26) at BJ Services, Tomball, TX was used for determining the fluid loss characteristics of the cement.

5.7.2 Experimental Procedure

Cement slurry is first prepared according to specifications with fluid loss control additives such as Fluid Loss (FL)-63 and FL-25 and then poured into the consistometer cup. The gear drive system is connected to an agitation paddle, which is dimensionally equivalent to an atmospheric consistometer paddle. The desired test temperature is maintained by a digital temperature controller, while the pressure necessary to prevent evaporation of the liquid phase is applied to the cell. When conditioning the cement in accordance with API Specification 10 guidelines, the paddle is rotated at 150 rpm for 20 minutes. Once the cement is conditioned, the test cell is rotated 180 degrees and the desired differential pressure is applied to the cell. The filtrate is collected in a back pressure receiver for 30 minutes. The API standards define fluid loss as the volume (cc) of filtrate that is collected during this 30-minute interval.



Figure 26: Stirred Fluid Loss Tester at BJ Services, Tomball, TX

5.7.3 Results and Discussion

Fluid loss measurements were carried out under following conditions:

Data:

Temperature: 77 degrees F.

Pressure: 1000 psi.

Time for filtrate collection: 30 min.

Calculations:

Filtrate is collected after 30 mins. If the test “spurts” in less than 30 minutes, fluid loss can be calculated by:

$$Q_{30} = Q_t \times 5.477 / \sqrt{t} \quad (5.1)$$

Q_{30} = Quantity of filtrate collected in 30 mins, cc

Q_t = Quantity of filtrate collected at time t, cc

t = time in minutes

1. Fluid loss for Ceramicrete without dry Portland cement or fluid loss control additives can be calculated using equation 5.1.

$$\begin{aligned} Q_{30} &= Q_t \times 5.477 / \sqrt{t} \\ &= 33 \times 5.477 / \sqrt{1.43} \\ &= 150.96 \text{ cc} \end{aligned} \tag{5.1}$$

Fluid loss = 2 * 150.96 = 301.92 cc/30 min.

2. Fluid loss for Ceramicrete without dry Portland cement but with 8% w/w FL-25 fluid loss additive can be calculated using equation 5.1.

$$\begin{aligned} Q_{30} &= Q_t \times 5.477 / \sqrt{t} \\ &= 34 \times 5.477 / \sqrt{1.76} \\ &= 213.6 \text{ cc} \end{aligned}$$

Fluid loss = 2 * 213.61 = 427.2 cc/30 min.

3. Fluid loss for Ceramicrete without dry Portland cement but with 8% w/w of FL-63 fluid loss additive can be calculated using equation 5.1.

$$\begin{aligned} Q_{30} &= Q_t \times 5.477 / \sqrt{t} \\ &= 34 \times 5.477 / 3.909 \\ &= 51.84 \text{ cc.} \end{aligned}$$

Fluid loss = 2 * 51.84 = 103.68 cc/30 min

TYPE	Q _t (CC)	Time (min)	Q ₃₀ (CC)
Ceramicrete without CPC"G" or fluid loss control additives	33	1.43	301.92
Ceramicrete without (5%) CPC"G" and 8% w/w FL-25	34	0.76	427.2
Ceramicrete without (5%) CPC"G" and 8% w/w FL-63	34	16	103.78

Table 9: Fluid Loss Measurements.

From the results in Table 9, it can be seen that the fluid loss from uncontaminated Ceramicrete with no fluid loss control additive or with 8% w/w of FL-25 fluid loss control additive is much more than from that with FL-63. Thus, FL-63 can be effectively used with Ceramicrete slurry as a fluid loss control additive in oilfield operations.

5.8 Rheology Measurements

5.8.1 Introduction

Rheology is the science and study of the flow and deformation of fluids. It describes the relationship between the flow rate (shear rate) and the pressure (shear stress) that causes movement. It enables one to determine the flow regime needed for optimum cement slurry placement, and to calculate values for friction pressure within the pipes and annulus (Schulumberger, 1984).

Rheology is an extremely important property of drilling, completion, and cement hydraulics in well operations. The flow properties of wellbore fluids (water, mud, cement slurries, mud spacers, and displacement fluids) are conventionally classified as “Newtonian” or “Non-Newtonian.”

Newtonian fluids exhibit a direct and constant proportionality between shear rate (which is related to flow velocity or rate) and shear stress (which is related to flowing pressure drop) as long as the flow regime is laminar. In this type of fluid, viscosity is independent of shear rate at a constant temperature and pressure. The behavior of non-Newtonian fluids such as cement slurries is different from that of Newtonian fluids. Frequently non-Newtonian fluids are rheologically complex particle-bearing fluids that

are usually described as “Bingham Plastics “or “power-law fluids.” In this study, the power law model is used exclusively (Banerjee, 2005); this law describes the relationship between the shear stress and shear rate of cement as an exponential relationship.

$$\zeta = k \cdot (\gamma)^n \quad (5.2)$$

Where, ζ = Shear stress (lbs/100ft²).

γ = shear rate (rpm).

n = Flow behavior index.

k = Consistency index (lbf. sec ^{n} /100ft²).

Stress (lbs/100ft²) vs. strain (RPM) plots are used to characterize the fluid based on “ n ” values, i.e.

$n = 1$ (Newtonian fluid)

$n < 1$ (Pseudo-plastic fluid)

$n > 1$ (Dilatant fluid).

However, k (lbf. sec ^{n} /100ft²) values are used to describe the fluid’s properties such as viscosity, pumping time of cement slurry, and thickening effect. In this work, Ceramicrete binder slurries either contaminated by Portland cement or uncontaminated by Portland cement are of special interest. Ceramicrete slurries with $k > 1$ exhibit high viscosity values which will eventually lead to an increase in pumping time of Ceramicrete slurry.

5.8.2 Experimental Procedure

There are two different data sets (at different rpms) of viscosities that are generated using the GRACE viscometer.

1. Viscosity measurements before conditioning: The first viscosity data set was obtained without conditioning the cement slurry. In this method, the Ceramicrete with or

without contamination by CPC “G” grade is mixed with fluid loss control additives, and then the viscosity is measured using the GRACE viscometer (Figure 27).

2. Using the atmospheric consistometer (Figure 28): The cement slurry is first poured into a consistometer cup, and then the cup is rotated at atmospheric pressure and with temperature control. In this method, temperature is measured accurately using a microprocessor-based temperature controller. Rotational speed of the slurry container is held constant by the drive motor assembly, which is factory-set at 150 rpm. Internal cooling coils provide quick cooling of the slurry. The strip chart recorder option on the Model 1250 provides a permanent record of the temperature and viscosity.

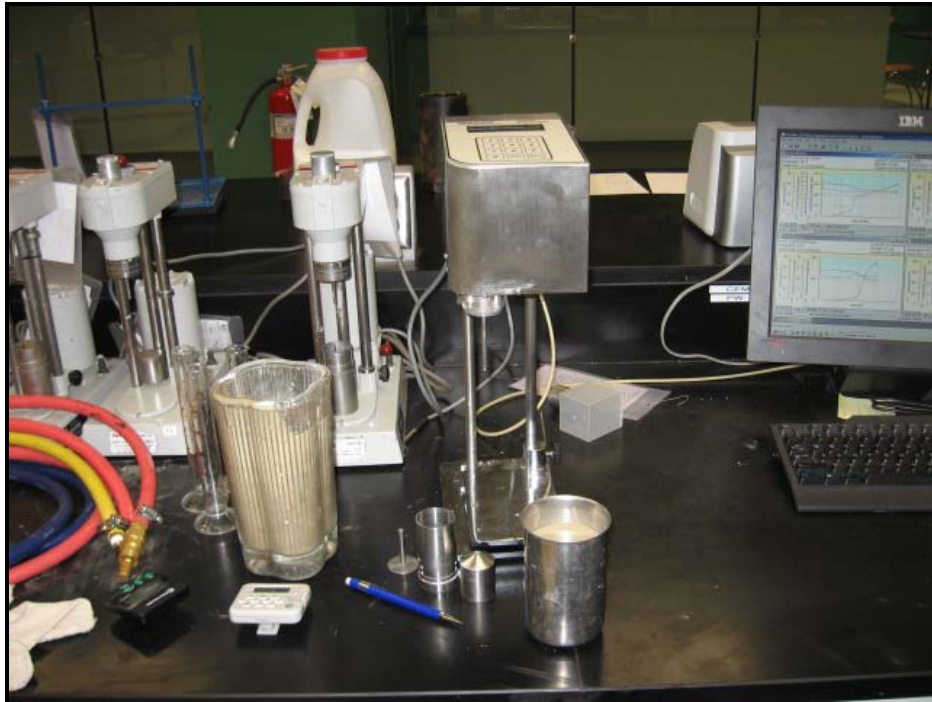


Figure 27: GRACE Viscometer for Rheology Measurements.



Figure 28: Atmospheric Consistometer for Conditioning Cement Slurry.

5.8.3 Results and Discussion

From tables 10-13 below, it can be concluded that the viscosity of the cement slurry increases after conditioning

	600 RPM	300 RPM	200 RPM	100 RPM	6 RPM	3 RPM
Without Contamination:						
Before conditioning:	155	85	63	38	12	10
After conditioning:	180	107	83	53	12	10

Table 10: Rheological Properties of Ceramicrete Without Contamination by CPC “G”
at Room Temperature

	600 RPM	300 RPM	200 RPM	100 RPM	6 RPM	3 RPM
With contamination						
Before conditioning:	106	62	43	26	9	8
After conditioning:	138	87	58	35	9	8

Table 11: Rheological Properties of Ceramicrete With Contamination by CPC “G”
at Room Temperature

Regular w/8% FL-63	600 RPM	300 RPM	200 RPM	100 RPM	6 RPM	3 RPM
Before conditioning	264	137	99	60	13	12
After conditioning	328	179	129	74	14	11

Table 12: Rheological Properties of Ceramicrete Slurry With 8% w/w of FL-63
Additive at Room Temperature

Regular w/8%FL-25:	600 RPM	300 RPM	200 RPM	100 RPM	6 RPM	3 RPM
Before conditioning:	445	254	198	114	21	14
After conditioning:	735	436	313	181	26	18

Table 13: Rheological Properties of Ceramicrete Slurry With 8% w/w of FL-25 Additive
at Room Temperature

With fluid loss control additives like FL-25, the viscosity is high. This may cause some problems while pumping the cement downhole.

Fluid characterization:

Plots (Figures 29-32) of shear stress (lbs/100ft²) vs. shear rate (RPM) were used to characterize the fluid.

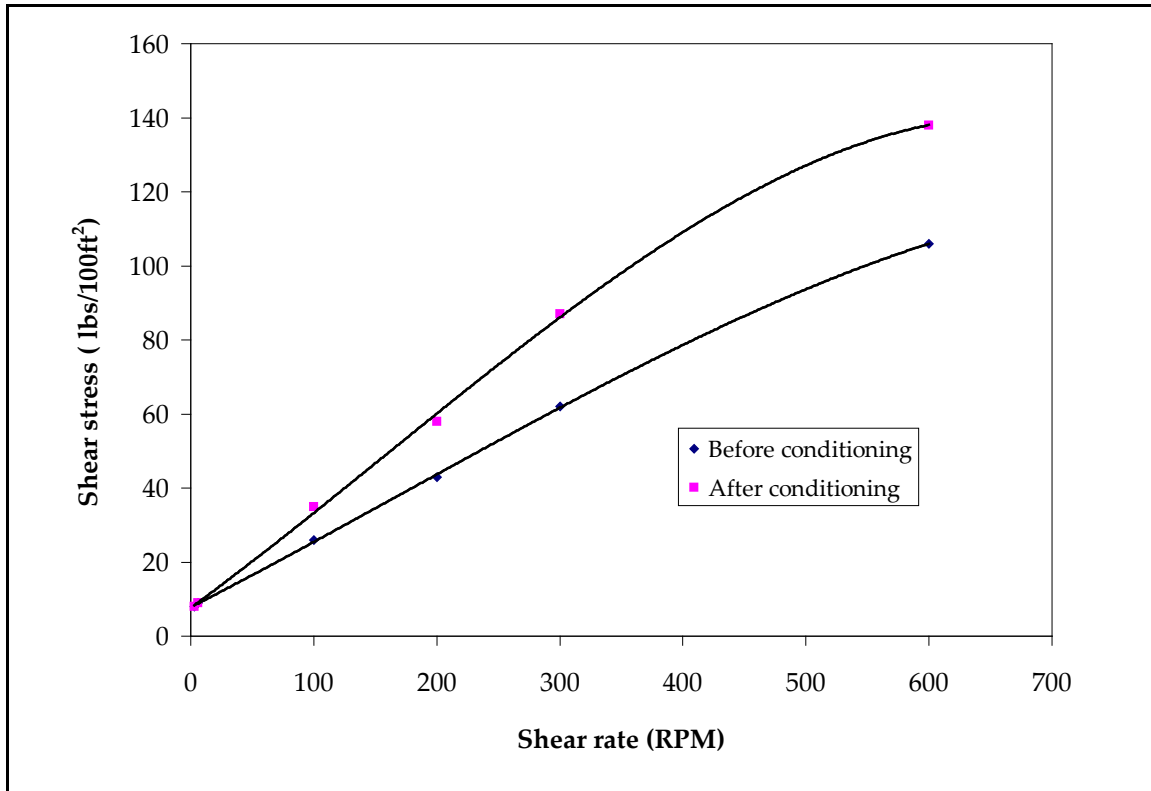


Figure 29: Rheogram for Ceramicrete Slurry at Room Temperature With Contamination by California Portland Cement "G" Grade at Room Temperature

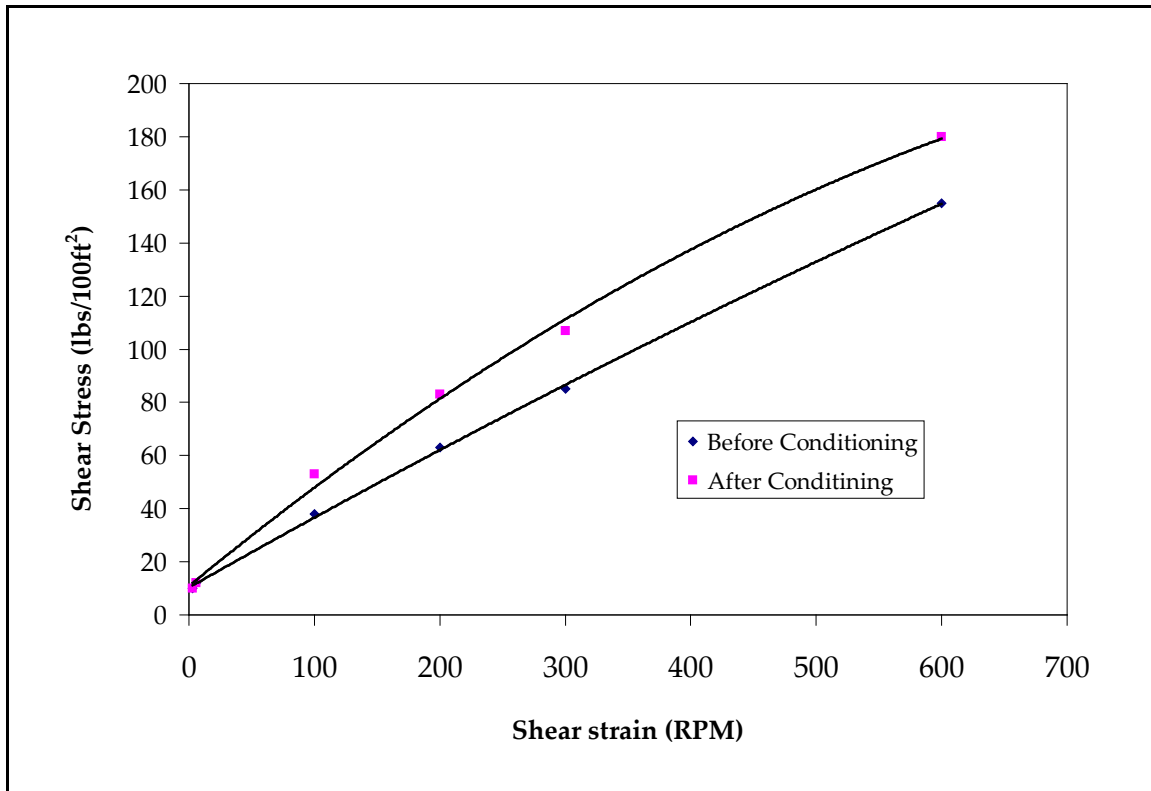


Figure 30: Rheogram for Ceramicrete Slurry at Room Temperature Without Contamination by California Portland Cement "G" Grade at Room Temperature

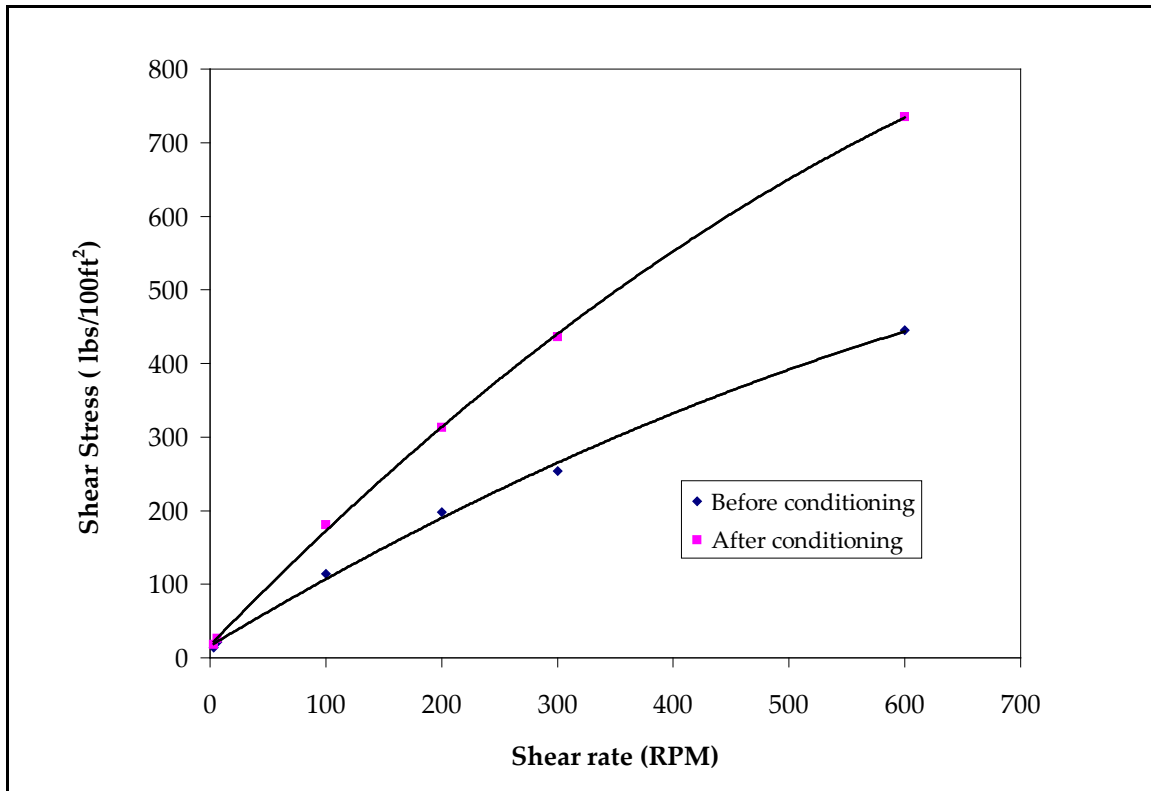


Figure 31: Rheogram for Ceramicrete Slurry at Room Temperature With 8% w/w FL-25
at Room Temperature

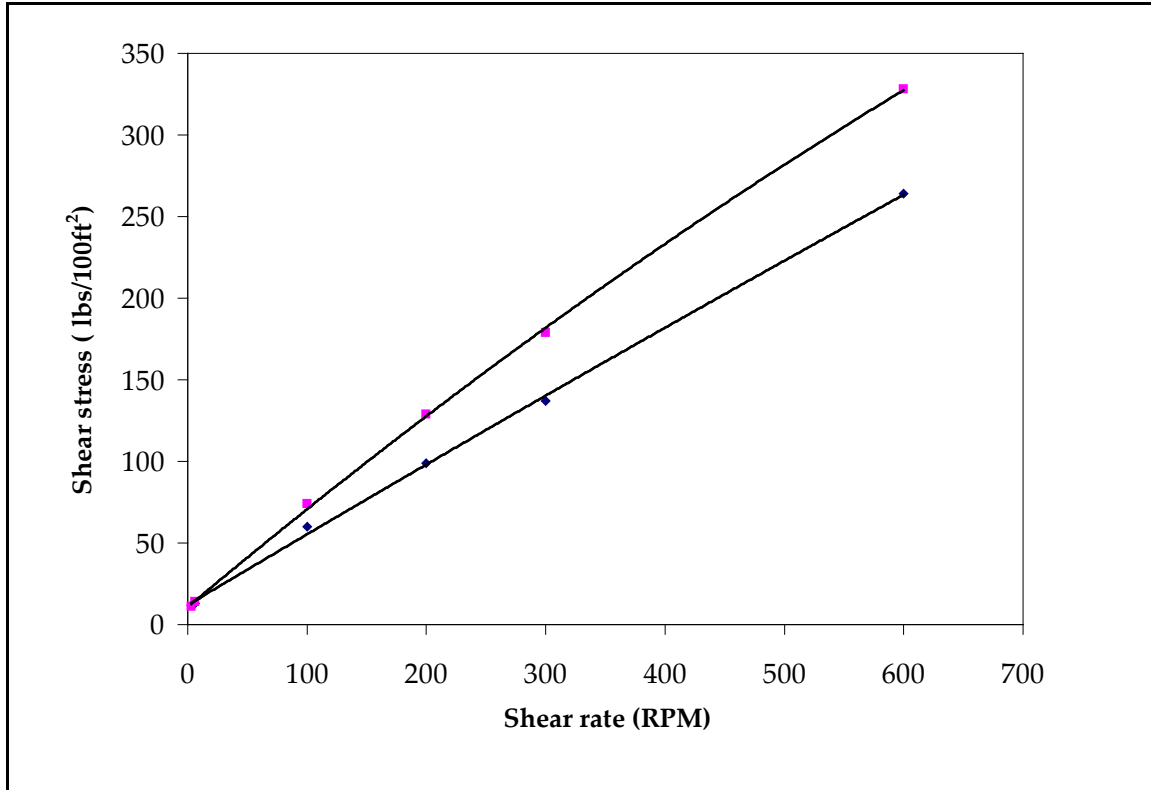


Figure 32: Rheogram for Ceramicrete Slurry at Room Temperature With 8% w/w FL-63
at Room Temperature

When shear stress (lbs/100ft²) is plotted against shear rate (RPM), it can be seen from Figures 29-32 that the various Ceramicrete slurries listed in Tables 10-13 exhibit the properties of the pseudo-plastic power-law fluid model. An exponential relationship between shear rate and shear stress in the Pseudo-Plastic Power-Law Fluid Model for the slurries listed in Tables 10-13 can be described as

$$\zeta = k \cdot (\gamma)^n \quad (5.2)$$

Where, ζ = Shear stress (lbs /100ft²)

γ = shear rate (RPM).

Since the Ceramicrete slurry properties listed in Tables 10-13 exhibit power law fluid properties, equations 5.3 and 5.4 are used to calculate the n and k (consistency index) values, respectively.

$$n = 3.32 \log (\phi_{600}/\phi_{300}) \quad (5.3)$$

$$k = \phi 600 / (1022)^n \quad (5.4)$$

where $\phi 600$ and $\phi 300$ are dial readings for GRACE viscometers at 600 rpm and 300 rpm respectively.

It can be concluded from Tables 14-17 below that all Ceramicrete slurries exhibit $n < 1$, which shows that Ceramicrete slurries listed in Table 10-13 exhibit Pseudo-Plastic Power-Law Fluid Model.

	Ceramicrete slurry without contamination	
RPM	Before Conditioning	After conditioning
3	8	8
6	9	9
100	26	35
200	43	58
300	62	87
600	106	138
N	0.773275064	0.665194648
k(lbf.secⁿ/100ft²)	0.498927389	1.373700843

Table 14: “n” and “k” Values of Ceramicrete Slurry With Contamination at Room Temperature

	Ceramicrete Slurry without contamination by CPC "G"	
RPM	Before conditioning	After conditioning
3	10	10
6	12	12
100	38	53
200	63	83
300	85	107
600	155	180
N	0.866230405	0.749950575
k(lbf.secⁿ/100ft²)	0.383091392	0.995868433

Table 15: “n” and “k” Values of Ceramicrete Slurry Without Contamination at Room Temperature

	Ceramicrete slurry with 8% w/w of FL- 25	
RPM	Before conditioning	After conditioning
3	14	18
6	21	26
100	114	181
200	198	313
300	254	436
600	445	735
N	0.808507297	0.752978821
k (lbf.secⁿ/100ft²)	1.640800028	3.982015187

Table 16 : “n” and “k” Values of Ceramicrete Slurry With 8 % w/w FL-25 at Room Temperature

	Ceramicrete slurry with 8% w/w of FL-63	
RPM	Before conditioning	After conditioning
3	12	11
6	13	14
100	60	74
200	99	129
300	137	179
600	264	328
N	0.945812754	0.873229098
k (lbf.secⁿ/100ft²)	0.375890661	0.772291208

Table 17: “n” and “k” Values of Ceramicrete Slurry With 8 % w/w FL-63 at Room Temperature

The "n" (power-law index) values for Ceramicrete slurries are similar to those of conventional cements used in oilfield operations. However, in some cases "k" (consistency index) values are more than 1, e.g. for Ceramicrete slurry with 8 % of FL-25 flow loss control additive (oth before and after conditioning) and Ceramicrete with contamination by Portland cement (after conditioning).

Thus, it can be seen that those Ceramicrete slurries which have "k" (consistency index) values more than 1 undergo a rapid thickening. With such Ceramicrete slurries ($k > 1$), high viscosity values may be found and may cause a problem during pumping the slurry downhole. In this case, FL-25 fluid loss additive leads to an increase in the “k” value of the slurry, and hence it is not suitable for the proposed Ceramicrete formulation. Thus, Ceramicrete slurry along with 8% w/w of FL-63 fluid loss control additive can be used as permafrost oil well cement formulation.

Hence, by characterizing the cement behavior, as shown in the above tables, one can quantify the pressure drop of the system, which can help in pump sizing, casing, and drill pipe design.

5.9 Expansion Test of Ceramicrete Slurry at 40 Degrees F

5.9.1 Introduction

A well-known practice in oil and gas wells is to cement a steel casing in place within the bore by placing cement slurry between the steel casing and the formation walls. Conventional permafrost cements exhibit the problem of shrinkage upon setting in annular volume between casing and wellbore at lower temperatures which leads to a poor mechanical bond between the casing and the bore wall. Such a situation may allow undesirable fluid (liquids and gases) to communicate between different formation zones penetrated by the bore, or even allow fluids produced in certain zones to undesirably leak to the surface (Cheung, 1999).

Expansive agents, when used along with cement formulation, will overcompensate for the cement shrinkage which ultimately leads to expansion of the cement slurry. Net expansion, or simply expansion of a cement means that the volume of unrestrained set cement will be greater than that of its liquid (i.e. slurry) phase. Such a net expansion helps ensure a good cement bond to both the casing and the bore wall.

The expansive agent must be designed such that, at the temperature to which the liquid cement will be exposed, it does not attempt to produce most of its expansive effect while the cement is still liquid as there will be no net expansion of the set cement (Cheung, 1999). Furthermore, for practical reasons, it will often be desirable that the expansion in the set cement must occur at a practical rate under the temperature and other conditions to which it is to be exposed.

Some wells may experience thermal shock, i.e. sudden change in temperature, which may lead to the loss of compressive strength of a set cement. Certain cement expansive additives perform well at lower temperatures and pressures; these cement additives may not perform well at higher temperatures and pressures. Thus, it is necessary to achieve an optimum concentration of the proper “expansive additive”, in order to suffer the smallest thermal shock effect.

In order to drill the well in a permafrost zone on the ANS, it is necessary to take into consideration the effect of lower temperature on the expansive additive and the proposed oil well cement expansion. However, in the case of Ceramicrete Binder, MgO (Magnesium Oxide) is used as an “expansive additive,” which also initiates the reaction required for the development of Ceramicrete binder. In order to analyze the behavior of MgO in Ceramicrete as an “expansive additive” and eventually in a proposed Ceramicrete formulation, the expansion tests have been carried out at BJ Services, Tomball, TX at lower temperatures.

5.9.2 Experimental Procedure

In order to analyze the effect of a lower temperature on Ceramicrete slurry, the slurry was poured into specialized molds and allowed to set at 40 degrees F. The specialized molds (Figure 33) at BJ Services, Tomball, TX consist of a first section that is adjacent to the base and functionally associated with a first anchor block, and a second section that is functionally associated with the first section and with a second anchor block and is adjacent to the base. Thus, a mold is comprised of the first section, the second section, and the base into which a measured amount of Ceramicrete slurry can be poured. A sensor is used to measure the movement of the first and second sections relative to each other in response to volumetric changes in the cement when the cement is exposed to lower temperatures, and the data are recorded over a period of time.

The main goal in carrying out the Ceramicrete slurry expansion test was to see whether Ceramicrete slurry had undergone expansion with or without crack development at a lower temperature; in other words, to discover whether it can be used effectively on the ANS in oil-well cementing operations.

5.9.3. Results and Discussion

It can be seen from Figure 33 that the Ceramicrete slurry has undergone expansion after setting at the temperature of 40 degrees F and that cracks have developed.

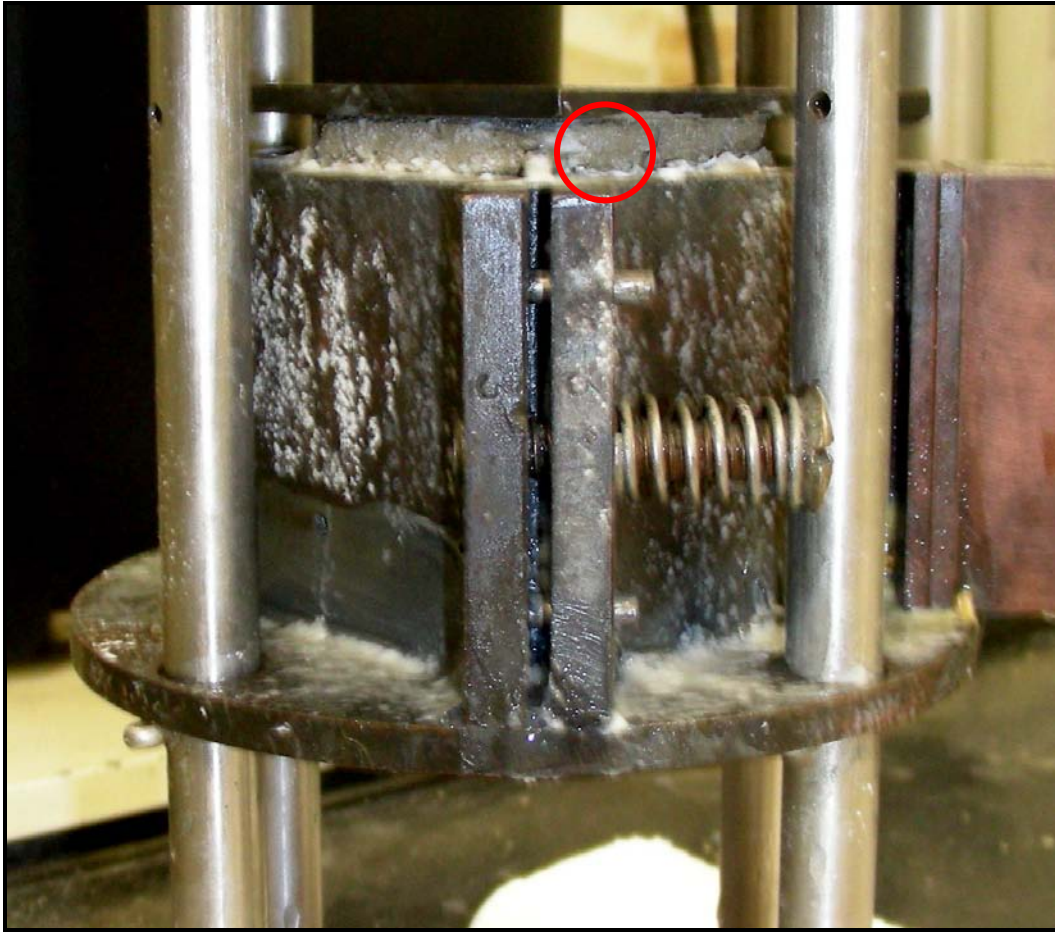


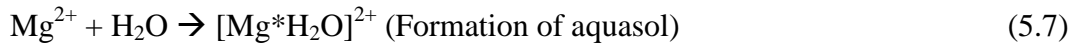
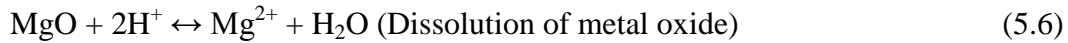
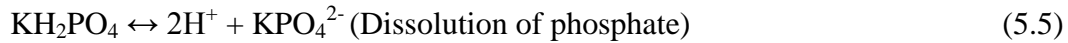
Figure 33: Crack Development in Proposed Ceramicrete Binder After Setting and Expansion at 40 Degrees F

Note: The picture was taken after the expansion test. The amount of Ceramicrete above the mold rim is due to expansion of Ceramicrete slurry at 40 degree F; the crack that developed after Ceramicrete slurry expansion at 40 degrees F is indicated by a red circle.

The possible reasons for crack development after Ceramicrete slurry setting and expansion at 40 degrees F could be “flash setting”; i.e. when the proposed Ceramicrete binder formulation is mixed with the required water quantity in a mixer, the slurry undergoes instantaneous setting in the mixer. This leads to the formation of a highly viscous Ceramicrete slurry, and further mixing of the Ceramicrete binder is not possible. The flash setting of a Ceramicrete binder slurry is also accompanied by a high amount of

heat evolution. In order to get a stable Ceramicrete after setting, it is important that some unreacted MgO particles are available in phosphate solution, as these metal oxides provide nucleation points for crystallization into a well-connected crystal lattice (Wagh, 2003; Banerjee, 2005). In the case of flash setting, there are insufficient MgO particles in acidic phosphate solution to provide nucleation points and thus, the crystallization process may remain incomplete with the possible formation of an unstable crystal lattice. The flash setting is usually observed with low MgO content in the Ceramicrete binder formulation.

Crack development can also be observed with a high MgO content for a given amount of potassium phosphate in the Ceramicrete binder formulation. Generating the Ceramicrete binder begins with the dissolution of potassium phosphate (KH_2PO_4). When metal oxides are stirred into an acid solution, the oxide generally separates into two component parts, a metal cation and an oxygen-containing anion. The metal cations react with free water molecules and form positively-charged ‘aquasols’ by hydrolysis (Wagh, 2003; Banerjee, 2005) according to the following reactions:



Eventually, the formation of a stable Ceramicrete binder depends on equation 5.7, and to drive this reaction forward an excess amount of KH_2PO_4 should be used, leading to the generation of cations required for dissolution and hydrolysis of Mg^{2+} in step 5.7 (Le Chatelier’s principal). Hence, if MgO is used in excess instead of KH_2PO_4 in a particular Ceramicrete formulation, the probable result is formation of an unstable Ceramicrete binder. Thus, it is necessary to determine the optimum percentage of MgO (expansive additive) for a given amount of KH_2PO_4 to be used in the Ceramicrete binder if crack development after setting at a lower temperature is to be prevented.

CHAPTER 6
DETERMINATION OF OPTIMUM AMOUNT OF MgO IN CERAMICRETE
BINDER

6.1 Introduction

It has been observed that a proposed Ceramicrete binder developed a crack after setting and expanded at lower temperature, i.e. at 40 degrees F. As discussed when presenting the results of the Ceramicrete expansion test at 40 degrees F, crack development could be due to a percentage of MgO in the proposed Ceramicrete binder that is either higher or lower than the percentage of KH_2PO_4 . Thus, it is very important to determine the optimum percentage of “expansive additive”, i.e. MgO, to be used in the Ceramicrete binder for a given percentage of KH_2PO_4 to avoid crack development, which can lead to the loosening of set Ceramicrete after some time. In order to avoid casing collapse and to establish well integrity, it is important to come up with a formulation of Ceramicrete binder with proper percentages of MgO (Magnesium Oxide), KH_2PO_4 (potassium phosphate), C-class fly ash, Boric acid, and Wollastonite, which are the main constituents of Ceramicrete binder.

6.2 Ceramicrete Formulation Preparation

In these experiments, MgO (25% by weight), KH_2PO_4 (27.2% by weight), C-class fly ash (10.2% by weight), Wollastonite (10.2% by weight), Boric acid (0.09% by weight), and water (27.2% by weight) (Banerjee, 2005) were used as a base formulation. The MgO concentration was decreased to values which were less than the percentage of MgO in the base Ceramicrete binder formulation (Tables 18-21). In order to take into consideration the effect of Portland cement contamination on Ceramicrete binder during its mixing in normal field practices, the selected permafrost Ceramicrete binder formulations were mixed with 5% of dry CPC “G” grade. Thus, to find out the optimum percentage of “expansive additive” (MgO) to use and eventually to come up with the optimum permafrost Ceramicrete formulation for the ANS, the following permafrost formulations were used.

Base Ceramicrete Formulation	
Contents	%
MgO	25
KH ₂ PO ₄	27.2
C-class fly ash	10.21
Wollastonite	10.2
Boric acid	0.09
Water	27.3
Total	100

Table 18: Base Formulation of Ceramicrete Binder

Sample Ceramicrete Formulation # 1	
Contents	%
MgO	22.9
KH ₂ PO ₄	28.5
C-class fly ash	10.6
Wollastonite	10.6
Boric acid	0.1
Water	27.3
Total	100

Table 19: Sample Ceramicrete Formulation #1

Ceramicrete formulation # 2	
Contents	%

MgO	21.5
KH ₂ PO ₄	29.1
C-class fly ash	11
Wollastonite	11
Boric acid	0.1
Water	27.3
Total	100

Table 20: Sample Ceramicrete Formulation #2

Ceramicrete Formulation # 3	
Contents	%
MgO	19.9
KH ₂ PO ₄	30.1
C-class fly ash	11.3
Wollastonite	11.3
Boric acid	0.1
Water	27.3
Total	100

Table 21: Sample Ceramicrete Formulation #3

All of the Ceramicrete binder formulations mentioned in the above Tables were contaminated with 5% dry CPC “G” grade for further tests. Hence, the following tests were carried out with a total of eight samples to determine the optimum permafrost cement formulation as well as the effect of CPC “G” grade on Ceramicrete binder formulations:

1. Expansion test at 32 degrees C.
2. Fluid loss testing at 1000 psi differential pressure and room temperature.
3. Uniaxial compressive strength testing.

6.3 Expansion Test at 32 Degrees F.

6.3.1 Introduction

It was demonstrated that cracks developed in Ceramicrete after setting and expanding at the lower temperature of 40 degrees F. Thus, in order to know the effect of

lower temperature on a sample Ceramicrete formulation setting and expansion, a temperature value less than 40 degree F was selected. The setting of sample Ceramicrete formulations was measured at UAF at 32 degrees F in plastic cylindrical molds measuring 4 inches high and 2 inches in diameter (Figure 34). At the same time, the effect of temperature was observed on the expansion of sample Ceramicrete formulations to discern whether cracks developed after expansion.

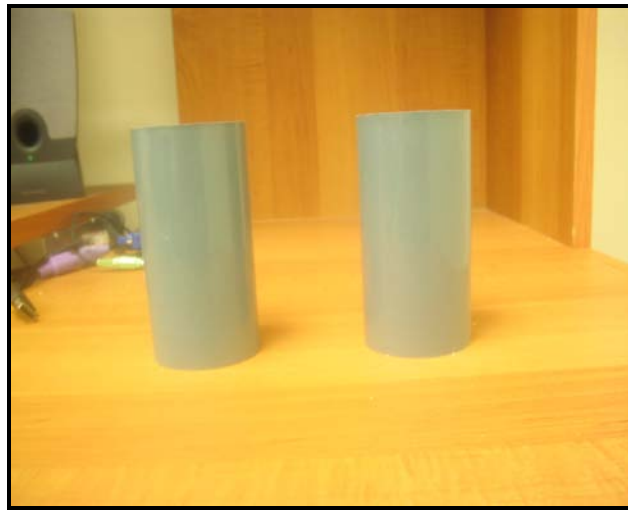


Figure 34: Plastic Molds of 4” Height and 2” Diameter Used for Setting of Sample Ceramicrete Formulations

6.3.2 Results and Discussion

It was observed that sample Ceramicrete formulation # 3 with or without 5% dry CPC “G” grade underwent “flash setting” with a high amount of heat evolution. The slurries of other sample Ceramicrete formulations, i.e. the base Ceramicrete formulation, sample Ceramicrete formulation #1, and sample Ceramicrete formulation #2 with or without 5% CPC “G” grade set successfully without any crack development when refrigerated at 32 degrees F for 24 hrs. (according to ASTM standards). Expansion of the base Ceramicrete sample contaminated by 5% dry CPC "G" grade at 32 degrees F after 24 hrs and expansion of sample Ceramicrete formulation #1 at 32 degrees F after 24 hrs are shown in Figures 35 and 36, respectively.



Figure 35: Expansion of Base Ceramicrete Sample with Contamination by 5% Dry California Portland Cement "G" Grade at 32 Degrees F After 24 hrs



Figure 36: Expansion of Sample Ceramicrete Formulation #1 at 32 Degrees F After 24 hrs

Note: The picture was taken after the expansion test. The amount of Ceramicrete above the mold rim is due to expansion of Ceramicrete slurry at 32 degrees F. In Figures 35 and 36 expansion of the base Ceramicrete sample contaminated by CPC "G" grade and Sample Ceramicrete formulation #1 are shown.

The extent of expansion observed for all Ceramicrete formulations with or without contamination was the same. The results of the expansion test at 32 degrees F are shown in Table 22.

Case 1	Base Ceramicrete formulation with and without CPC "G"	Slurry sets successfully at 32 degrees F after 24 hrs with little expansion and no crack development.
Case 2	Sample Ceramicrete formulation #1 with and without CPC "G"	Slurry sets successfully at 32 degrees F after 24 hrs with expansion higher than in case 1 and no crack development.
Case 3	Sample Ceramicrete formulation #2 with and without CPC "G"	Slurry sets successfully at 32 degrees F after 24 hrs with little expansion and no crack development
Case 4	Sample Ceramicrete formulation #3 with and without CPC "G"	Slurry underwent "flash setting" at room temperature with high expansion and crack development at 32 degrees F after 24 hrs.

Table 22: Results of Expansion Test at 32 Degrees F

6.4 Fluid Loss Testing of Ceramicrete Formulations at Room Temperature and 1000 psi Differential Pressure

6.4.1 Introduction

In cementing operations, the cement slurry may exhibit “flash setting” when it is subjected to pressure. This is due to a loss of water by filtration to the point where only interstitial water is left, resulting in a slurry that becomes unpumpable. In some cases, the slurry becomes so viscous that placement pressures exceed the fracturing pressure of a weak formation, resulting in lost circulation. By reducing the quantity of filtrate, it is possible to reduce the degree and the depth of formation damage, because when water is lost to permeable zones, it not only reduces the water/cement ratio of slurry, but the water also carries a certain amount of cementitious materials and fines with it that may damage productive formations. The final strength of a cement depends on the water/cement ratio of the slurry. Fluid-loss-control additives are used to maintain a constant water-to-solids ratio in the cement slurries. The API standards for fluid-loss laboratory tests are detailed in API spec. 10 (2004). The level of fluid-loss control is usually adjusted to the type of cementing operation (Schlumberger, 1984).

Fluid loss was determined for 8 sample Ceramicrete binder formulations using a fluid-loss measurement apparatus (shown in Figure 37) at room temperature and at 1000 psi differential pressure.



Figure 37: Fluid-Loss Measuring Apparatus at the University of Alaska Fairbanks

6.4.2 Results and Discussion

Conditions:

Temperature: 55 degrees F.

Pressure: 1000 psi.

Time for volume collection: 30 min.

Weight of Ceramicrete formulation: 290.8 grams.

Weight of water: 109.2 grams.

Calculations:

Filtrate is collected after 30 mins. If test “spurts” in less than 30 mins, fluid loss can be calculated by:

$$Q_{30} = Q_t \times 5.477 / \sqrt{t} \quad (6.1)$$

Q_{30} = Quantity of filtrate collected in 30 mins, cc.

Q_t = Quantity of filtrate collected at time t , cc.

t = time in minutes.

Case 1: Base Ceramicrete Formulation

Fluid loss for uncontaminated (without Portland cement) Ceramicrete can be calculated using equation 6.1.

$$\begin{aligned} Q_{30} &= Q_t \times 5.477 / \sqrt{t} \\ &= 10 \times 5.477 / \sqrt{16}. \\ &= 13.69 \text{ cc.} \end{aligned}$$

$$\text{Fluid loss} = 2 * 13.69 = 27.38 \text{ cc/30 min.}$$

Fluid loss was observed to be the same in the case of the base Ceramicrete formulation with contamination by dry CPC “G” grade.

Case 2: Sample Ceramicrete formulation #1

The fluid loss for sample Ceramicrete formulation #1 without contamination by dry CPC “G” grade can be calculated using equation 6.1

$$\begin{aligned} Q_{30} &= Q_t \times 5.477 / \sqrt{t} \\ &= 5 \times 5.477 / \sqrt{10} \\ &= 8.65 \text{ cc.} \end{aligned}$$

$$\text{Fluid loss} = 2 * 8.65 = 17.31 \text{ cc/30 min.}$$

The fluid loss for sample Ceramicrete formulation #1 with 5% contamination by dry CPC “G” grade can be calculated using equation 6.1.

$$\begin{aligned} Q_{30} &= Q_t \times 5.477 / \sqrt{t} \\ &= 6 \times 5.477 / \sqrt{12} \\ &= 9.48 \text{ cc.} \end{aligned}$$

$$\text{Fluid loss} = 2 * 9.48 = 18.97 \text{ cc/30 min}$$

Case 3: Sample Ceramicrete formulation #2

The fluid loss for sample Ceramicrete formulation # 2 without contamination by dry CPC “G” grade can be calculated using equation 6.1.

$$\begin{aligned} Q_{30} &= Q_t \times 5.477 / \sqrt{t} \\ &= 4 \times 5.477 / \sqrt{13}. \end{aligned}$$

= 6 cc.

Fluid loss = $2 * 6.92 = 12$ cc/30 min.

The fluid loss for sample Ceramicrete formulation #2 with 5% contamination by dry CPC “G” grade is the same as that of sample Ceramicrete formulation #2 without 5% contamination by CPC “G” grade.

Case 4: Sample Ceramicrete formulation #3

The sample Ceramicrete formulation #3 with and without 5% contamination by dry CPC “G” grade underwent “flash setting” in the blender, and thus there was negligible fluid loss when the fluid-loss test was carried out at 1000 psi differential pressure and at room temperature.

From the above results it can be seen that fluid loss is less in the case of sample Ceramicrete formulation #2 with and without contamination by CPC “G” grade. Thus, in order to further minimize fluid loss, fluid loss control additives can be used effectively for oil well cementing applications on the ANS.

6.5 Uniaxial Compressive strength testing

6.5.1 Introduction

The crushing load that predicts the compressive strength of the set cement has been widely used for more than 40 years in establishing wait-on-cement time, i.e. to decide how long to wait for cement to set. It is important to know how strong the cement must be before drilling can begin, and to understand the strength development characteristics of the cement. It is generally accepted in the petroleum industry and by regulatory bodies that a compressive strength of 500 psi is adequate for most operations, and by using good cementing practices an operator should be able to drill out safely by adhering to this minimum strength requirement. It has been observed that the curing temperature has a significant influence on cement strength development (Smith, 1990).

6.5.2 Experimental Procedure

Uniaxial compressive strength testing was used to determine stress (psi) vs. compression displacement (inch) plot of a cement sample, which can be used to

determine the strength of the cement sample. This test involves compressing a cylindrical sample under a flat metal plate at a constant rate. Sample cylinders used in this test are generally 4 inches in length and 2 inch in diameter. The load on these cylindrical samples is increased until the sample undergoes fracturing under the applied force. While carrying out uniaxial compressive strength testing (Figure 38), it is necessary to ensure that both of the planes of the sample are parallel to the loading plate to ensure uniform loading. In this test, a hydraulic compression-testing device was used to provide a load at the rate of 0.2 mils/sec for the first 2000 psi and a reduced rate of 0.1 mils/sec for the next 2000 psi.

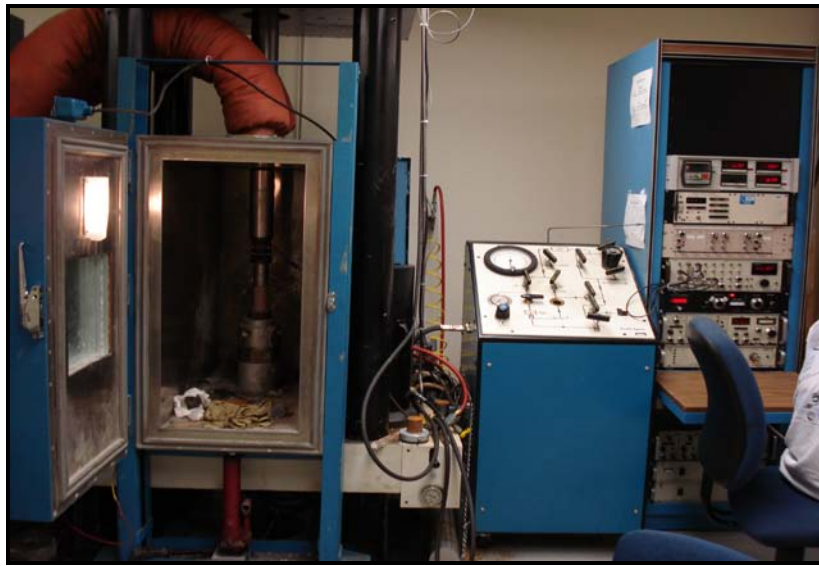


Figure 38: Compression Testing Data Measurement Setup

Ceramicrete sample after compression in uniaxial compressive strength testing, i.e. post-fracturing, is shown in Figure 39.



Figure 39: Ceramicrete Compression Samples (Post-Fracturing)

6.5.3 Results and Discussion

For uniaxial compressive strength testing, Ceramicrete slurry samples were produced by mixing the powder blend with water in a desktop mixer; slurries of these samples were poured into plastic cylinders each measuring 4 inches in height and 2 inches in diameter, which were kept in a refrigerator for curing at 32 degrees F for 24 hrs. It has been consistently observed that the compressive strength of Ceramicrete samples with and without contamination by 5% dry CPC “G” grade is the same. Stress vs. displacement data for different Ceramicrete formulations is shown in figures 40-45.

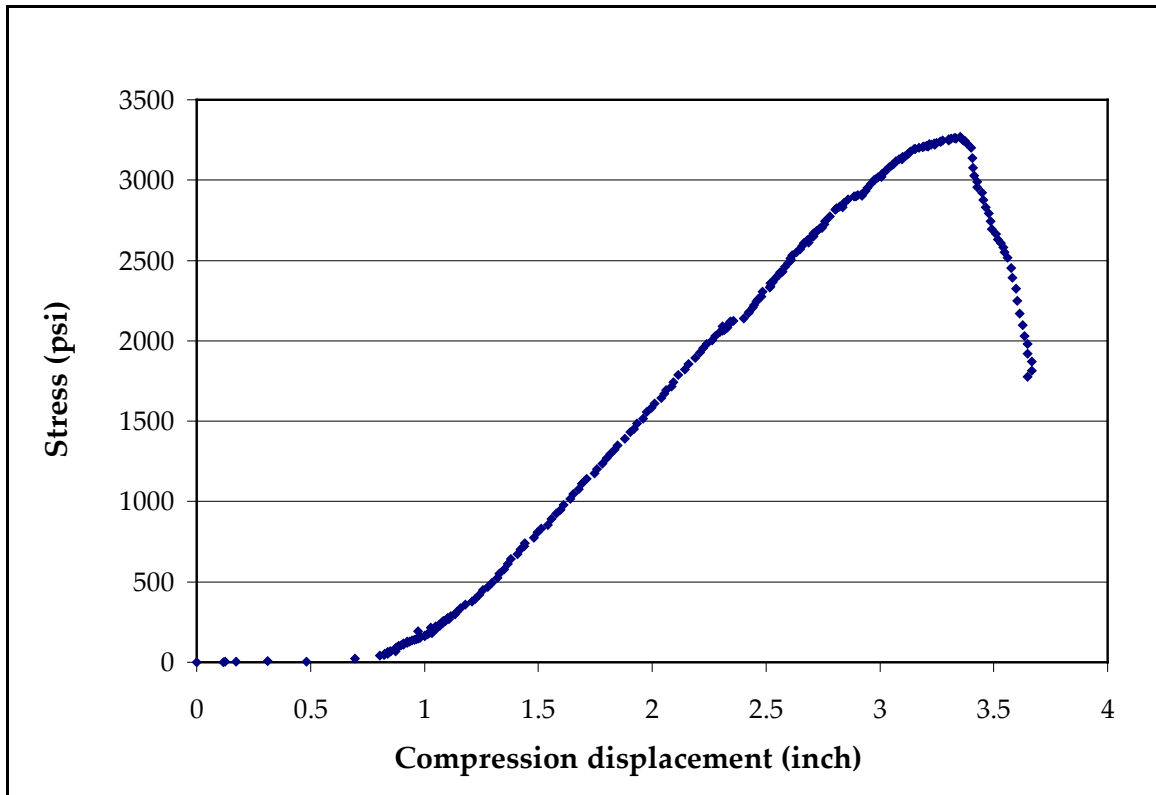


Figure 40: Compression Testing Data for Base Ceramicrete Sample Without 5% Contamination by Dry California Portland Cement "G" Grade at Room Temperature (Load rate : 37 lbs/sec).

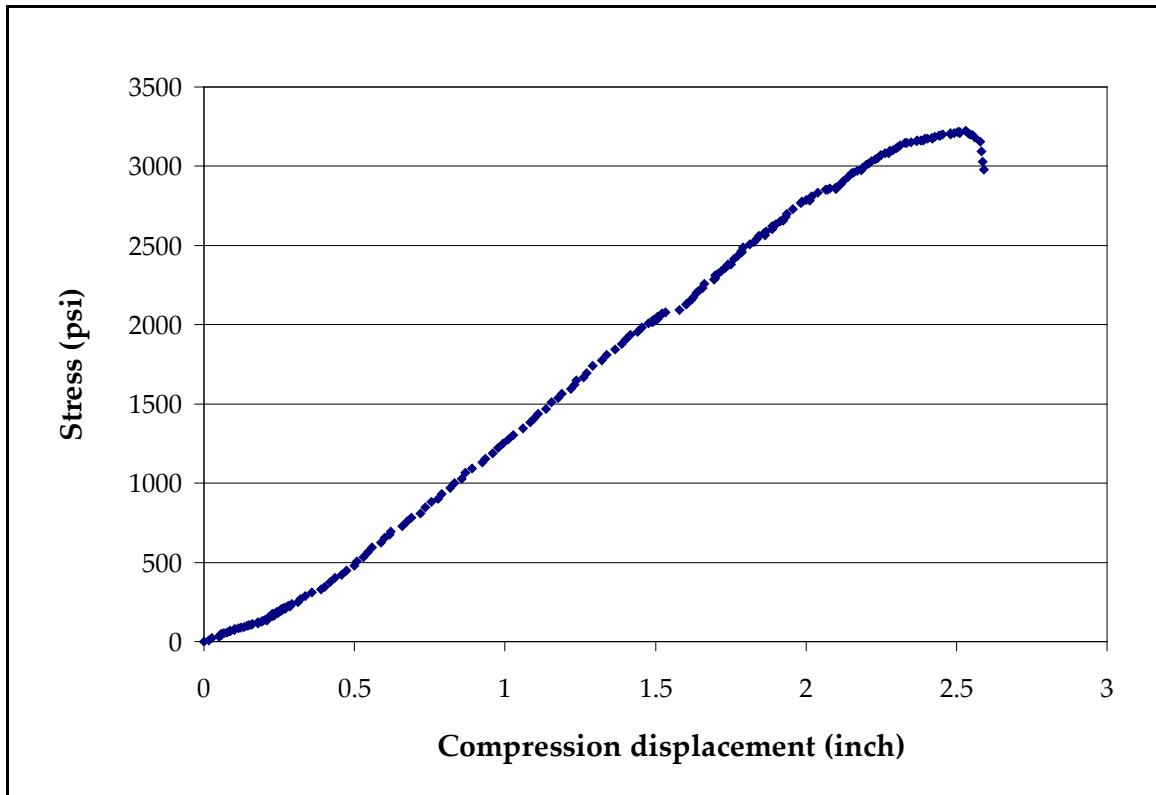


Figure 41: Compression Testing Data for Base Ceramicrete Sample with 5% Contamination by Dry California Portland Cement "G" Grade at Room Temperature (Load rate : 37 lbs/sec).



Figure 42: Compression Testing Data for Sample Ceramicrete Formulation #1 Without 5% Contamination by Dry California Portland Cement "G" Grade at Room Temperature (Load rate = 47.6 lbs/sec).

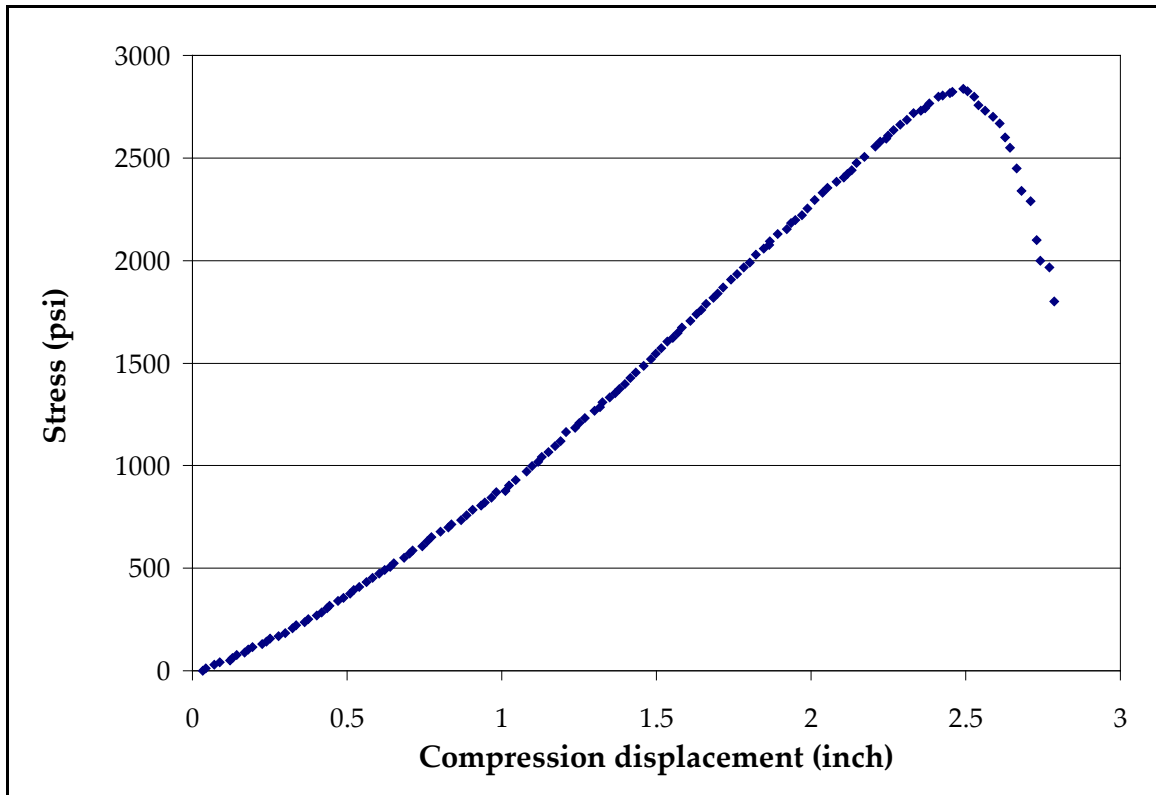


Figure 43: Compression Testing Data for Sample Ceramicrete Formulation #1 with 5% Contamination by Dry California Portland Cement “G” Grade at Room Temperature (Load rate = 47.7 lbs/sec)

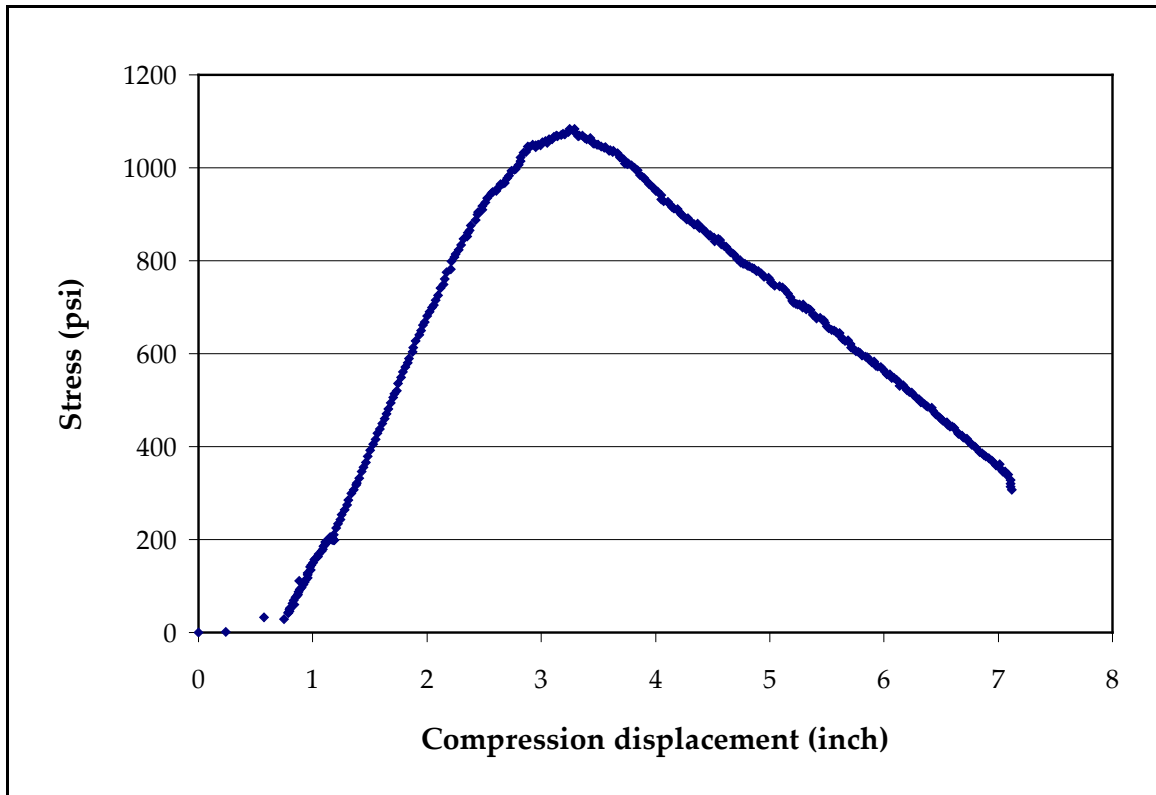


Figure 44: Compression Testing Data for Sample Ceramicrete Formulation #2 Without 5% Contamination by Dry California Portland Cement “G” Grade at Room Temperature (Load rate = 18.5 lbs/sec)



Figure 45: Compression Testing Data for Sample Ceramicrete Formulation #2 With 5% Contamination by Dry California Portland Cement “G” Grade at Room Temperature (Load rate = 18.23 lbs/sec)

The sample Ceramicrete formulation #3 developed cracks after setting and expansion at 32 degrees F; thus, sample Ceramicrete formulation #3 was not subjected to uniaxial compressive strength testing. The ultimate compressive strength before failure shows very little dependence on the Portland cement impurity that exists within the Ceramicrete slurry. From the Figures 40-45, it can be seen that as the percentage of MgO is reduced, the sample Ceramicrete formulation shows an increase in plastic deformation. The compressive strength of the base Ceramicrete formulation was found to be greater than that of the other Ceramicrete formulations.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

In normal field practices, when Ceramicrete is mixed with water in mixers it may become contaminated with leftover Portland cement. In order to identify the effect of Portland cement contamination, tests were conducted at BJ Services in Tomball, TX and at the University of Alaska Fairbanks with Ceramicrete formulations proposed by the Argonne National Laboratory, and the following conclusions can be drawn:

1. Experiments carried out at BJ Services, Tomball, TX have shown that a proposed Ceramicrete formulation with 5% contamination by set Portland cement has undergone “flash setting” with a final temperature of the slurry being in the range of 55 degrees F to 120 degrees F; these temperatures can cause the thawing of the permafrost zone around the wellbore to a certain extent.
2. A proposed Ceramicrete binder with 10% contamination by dry Portland cement has undergone setting in 3.5 hrs., with an increase in temperature. Simulations carried out using ABAQUS software have shown that Ceramicrete with 10% contamination by dry Portland cement can cause the thawing of permafrost zone around the wellbore after 3.5 hrs., i.e. the setting time, by as much as 9 cm. Thawing of the permafrost zone around the wellbore can cause casing collapse, which will eventually lead to a loss of well integrity.
3. However, the proposed Ceramicrete formulation with 5% dry Portland cement has other properties satisfying the characteristics of an ideal permafrost cement, except that it develops cracks after an expansion test at 40 degrees F; this behavior might be due to a concentration of MgO in the Ceramicrete that is too high or too low compared to the concentration of KH_2PO_4 .

From the tests conducted at the University of Alaska Fairbanks, it can be concluded that the recently-developed Ceramicrete formulation provides a novel and highly advantageous arctic cementing solution as stated below:

1. The newly-developed formulation of Ceramicrete binder: MgO (22.9%), KH_2PO_4 (28.5%), C-class fly ash (10.6%), Wollastonite (10.6%), and Boric Acid (0.1%) has shown slurry expansion without crack development.
2. In addition, this formulation does not flash set or show reduced strength in the presence of Portland cement impurities and its compressive strength is the same with and without contamination by 5% CPC “G” grade, i.e. 2800 psi.
3. A slurry with less fluid loss without fluid-loss additives does not lead to a temperature increase after setting, preventing the thawing of the permafrost around the wellbore when used as an oil-well cement on the ANS.

7.2 Recommendations

1. Additional research is still needed to develop strong characterizations of the newly-developed Ceramicrete formulation, i.e. the thickening time of the newly-developed Ceramicrete formulation slurry should be determined using a consistometer.
2. A fluid-loss program should be implemented to establish the ideal fraction of water that should be introduced into Ceramicrete slurry.
3. The behavior of a newly-developed Ceramicrete formulation should be analyzed for high-temperature oil well cementing operations as well as for interaction with downhole non-hydrocarbon chemicals.
4. In order to determine whether a newly developed Ceramicrete formulation is oilfield-worthy or not, it is important to carry out actual yard tests.

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