# INVESTIGATION OF THE AFFECTS OF BENTONITE IN

# CEMENT-BENTONITE GROUTS USED FOR MONITOR WELL

# COMPLETION

A Thesis

by

STEPHEN PATRICK HANEY

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| Chair of Committee, | Christopher Mathewson |
| Committee Members, | Peter Knappett |
| | Robert Lytton |
| Head of Department, | Rick Giardino |

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**ABSTRACT**


Bentonite is one of the most common additives to cement to form grouts for completion of monitor wells. Recent studies have indicated that these grouts may not be the most appropriate method for completing monitor wells, because of fractures that form during curing of the grouts. Within grouts examined with optical microscopy, a reaction halo is present around the fracture. Further microprobe examinations indicate a zonation of elements around the fractures. Studies on cement-bentonite grouts that are used for slurry walls have indicated that montmorillonite dissolution and the formation of secondary minerals can lead to fracturing of the cement-bentonite grouts. This study will examine cement-bentonite grouts, which were used in the optical microscopy and microprobe study, to determine if secondary minerals can be identified. The study used powdered x-ray diffraction to examine the minerals present within four differently prepared cement-bentonite grouts and one neat cement grout.

Three minerals were identified with x-ray diffraction in all mixtures of cement-bentonite grouts and the neat cement-grout. Those minerals were calcite, vaterite, and portlandite. The three minerals had variable intensities within each grout. There was one unidentified peak within the grouts that contained Aquagel[®]. Based on the results of the x-ray diffraction combined with the results of previous work, the unidentified peak was determined to be calcium silicate hydrate, which is a common secondary mineral formed from the dissolution of montmorillonite.

It was concluded that the variation in intensity of the identified minerals was likely the result of excessive or inadequate hydration depending on the mixing method. It was also concluded that the fracturing within these grouts is the result of the dissolution of montmorillonite and formation of the secondary minerals. Based upon these results, it is clear that the common practice of completing monitor wells with cement-bentonite grouts in most geologic conditions is inappropriate. It is recommended that cement-bentonite grouts should only be used to complete monitor wells that are in fractured hard rocks, because the fracturing of the grout will be similar to that of the local rock.

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**INTRODUCTION**

Bentonite is one of the most common additives to cement grouts. It is used when completing near surface monitor wells. The addition of bentonite to cement will cause the grout to have a lower slurry weight, increased slurry volume, lower viscosity, lower heat during settling, and lower cost over neat cement (Smith & Carter, 1966). These properties make cement-bentonite grouts a favored method for sealing the annular space of a monitor well.

Texas law is specific in the definition and construction of a completed monitor well when encountering contaminants. An excerpt from 16 Texas Administrative Code, Chapter 76 states the construction of a monitor well when a freshwater zone is below a contaminated zone as the following:

> "The annular space between the casing and the wall of the borehole shall be pressure grouted with positive displacement technique or the well is tremie pressured filled provided the annular space is three inches larger than the casing with cement or bentonite grout from an adequate depth below the undesirable water or constituent zone to the land surface to ensure the protection of groundwater. Bentonite grout may not be used if a water zone contains chlorides above one thousand five hundred (1,500) parts per million (milligrams per liter) or if hydrocarbons are present."

The Code also states the construction of a monitor well when a freshwater zone is above a contaminated zone as the following:

> "When undesirable water or constituents are encountered in a zone underlying a fresh water zone, the part of the wellbore opposite the undesirable water or constituent zone shall be filled with pressured cement or bentonite grout to a height that will prevent the entrance of the undesirable water or constituents into the water well. Bentonite grout may not be used if a water zone contains chlorides above one thousand five hundred (1,500) parts per million (milligrams per liter) or if hydrocarbons are present."

The Texas Administration Code defines cement as the following:

> "A neat portland or construction cement mixture of not more than seven gallons of water per 94-pound sack of dry cement, or a cement slurry which contains cement along with bentonite, gypsum or other additives."

Based on this definition a cement-bentonite grout can be used in any aquifer condition and with any contaminant or contaminant amount present in the water bearing zone to complete a monitor well, because only bentonite grouts may not be used when chlorides concentration is above 1,500 parts per million or if hydrocarbons are present. The Texas Code has defined a completed monitor well as the following:

> "A monitoring well which allows water from a single water-producing zone to enter the well bore, but isolates the single water-producing zone from the surface and from all other water-bearing zones by proper casing and/or cementing procedures. Annular space positive displacement or pressure tremie tube grouting or cementing (sealing) method shall be used when encountering undesirable water or constituents above or below the zone to be monitored or if the monitoring well is greater than twenty (20) feet in total depth. The single water-producing zone shall not include more than one continuous water-producing unit unless a qualified geologist or a groundwater hydrologist has determined that all the units screened or sampled by the well are interconnected naturally."

The importance of this definition is that the water-bearing zone is isolated from the surface and from all the other water-bearing zones, unless the zones are naturally connected. Several precursor studies have demonstrated that cement-bentonite grouts used for monitor well completion are not meeting the definition of the Texas Administrative Code for a completed monitor well, because of fracturing of the grout. Fracturing of the grout would allow water to flow from the surface and prevent isolation of the water bearing zone, which would allow for contact with other water-bearing zones that are not naturally connected.

**Project History**

  The study that started investigations into cement-bentonite grouts was a thesis by Wolde (1996). This thesis focused on proper monitor well completion, by examining the material properties for semi-rigid bentonite seals, pumpable bentonite grout seals, and cement based seals. The cement based seals that were examined include: neat cement, cement-bentonite grout, or sand-cement grout, and were load tested to examine the failure point. After curing, cement-bentonite grout and neat cement had significant macroscopic fracturing prior to load testing (Figure 1). Of all the different seals that were tested, it was noted that the cement-bentonite grout failed at the lowest shear strength. It was recommended the neat cement and cement-bentonite grouts, because of both the low shear strength and the fracturing present upon curing, should only be used to complete monitor wells in already fractured hard rock.



| Cement-Bentonite Grout | Neat Cement | Cement-Sand Grout |
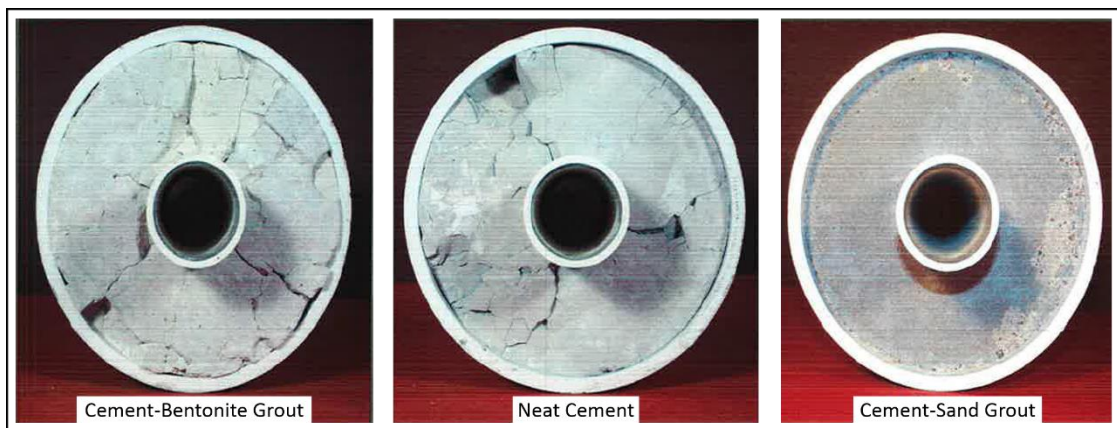
**Figure 1. Scale monitor well samples prepared with cement-bentonite grout, neat cement, and sand-cement grout. Macroscopic fractures are present in cement-bentonite and neat cement grouts shortly after curing (modifed from Weiss & Mathewson, 2005).**

The results and conclusions about cement-bentonite grouts by Wolde (1996) in his thesis prompted a study by Weiss and Mathewson (2005). This study prepared small scale grouts to determine why cement-bentonite grouts had a low shear strength, and examine fractures that developed upon curing. These small scale grouts were prepared with a variety of methods and bentonite sources. Along with the cement-bentonite grouts, a neat cement grout, containing no bentonite, was constructed for comparison to the cement-bentonite grouts. Grouts were mixed in the proper portions of cement to bentonite to water in a kitchen blender and then allowed to cure. In grouts where bentonite was prehydrated extra water was needed to get bentonite and cement to fully mix. After curing it was noticed that all methods of constructing cement-bentonite grouts had some form of fracturing associated with them. In the grout where bentonite was prehydrated there was an increased porosity as compared to the other grouts. Thin sections were prepared from each of the samples and it was noticed that all the samples with visible fractures had a reaction halo around all of the fractures. This indicated a potential chemical reaction occurring at or near the fracture zones. Figure 2 shows the cement-bentonite sample, where bentonite was prehydrated, floating in water, demonstrating the porosity of the mix and its high permeability. Also shown, is the thin section for this cement-bentonite grout in cross polarized light and the width of the reaction halo around the fracture.
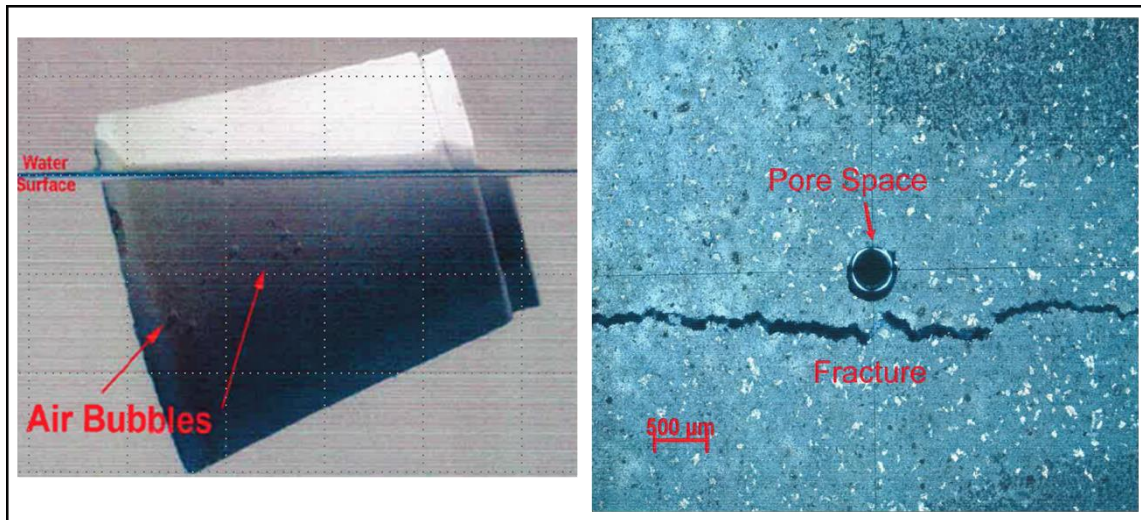
**Figure 2. Porosity in cement-bentonite grout where bentonite was prehydrated and cement and extra water were added, in both small scale sample and thin section under cross polarization (modified from Weiss & Mathewson, 2005).**

The presence of the reaction halos initiated an electron microprobe study by Mathewson and Ebrom (2011). Electron microprobe analysis found that there were two zones around the fractures. The first zone nearest the fractures was depleted in oxygen, but enriched in carbon, aluminum, calcium, sodium, sulfur, and silica (Figure 3). The second zone was enriched in oxygen, but depleted in all other elements. It was initially concluded that there was a similar reaction to the one that occurs is cement mixed with aggregates. This reaction is known to cause fracturing within these grouts and form the secondary mineral ettringite.
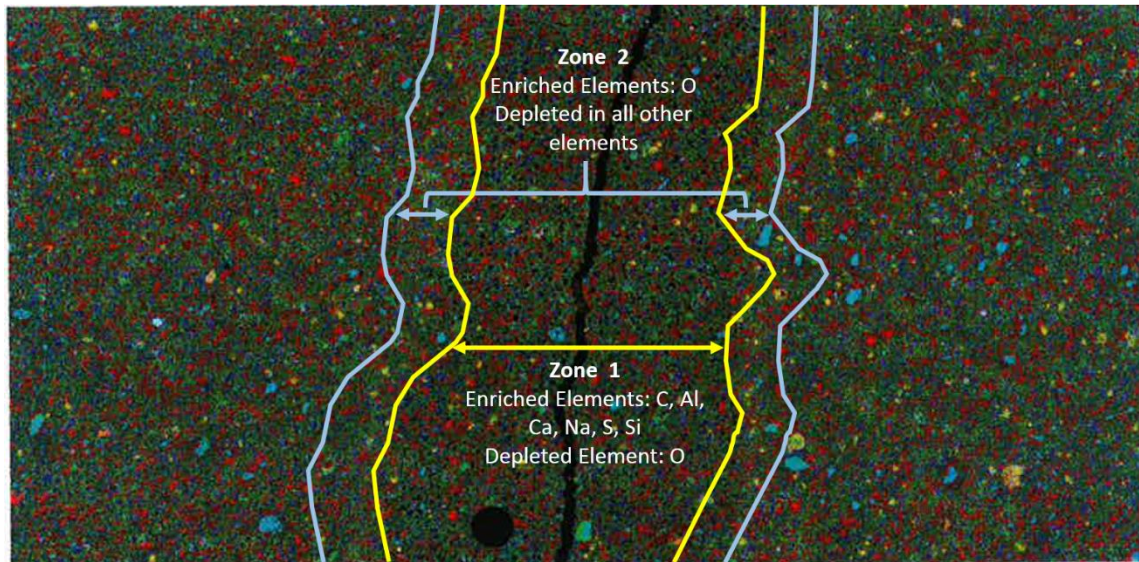
**Figure 3. Microprobe x-ray map of grout prepared by prehydrating cement and adding bentonite showing zonation of elements around fractures (Mathewson & Ebrom, 2011).**

**Secondary Mineral Formation in Cement-Bentonite Grouts**

From the reaction halo observed in the optical microscopy in Weiss and Mathewson (2005) and the element depletion observed in the microprobe investigation in Mathewson and Ebrom (2011), it is necessary to determine if the initial conclusion of secondary mineral formation is the cause of fracturing within these grouts. The information on fracturing or secondary mineral formation in cement-bentonite grouts when used for completing monitor wells is limited. However, several recent studies examine secondary mineral formation when cement and bentonite are mixed for use in cement-bentonite slurry walls that surround geologic repositories (Philip, 2001; Gates & Bouazza, 2010; Fernámdez, et al., 2006; Fernámdez, et al., 2010; Sánchez, et al., 2006; Savage, et al., 2002; Savage, et al., 2007). The use of cement-bentonite slurry in slurry walls serves a similar purpose to that of the grout in a monitor well and that is to prevent

contaminant migration. The difference between the slurry wall and a grout prepared for monitor well completion is the amount of bentonite used. The slurry will contains up to 30% percent bentonite in the slurry while a cement-bentonite grout typically contains around 8% bentonite (Garven & Hayles, 1999).

These studies have indicated that when bentonite is interacting with a hyperalkaline solution, such as cement, the result will be dissolution of the montmorillonite within the bentonite, formation of a secondary mineral, and fracturing of the grout. Cement-bentonite slurry wall studies typically combine bentonite with a hyperalkaline solution such as NaOH, $Ca(OH)_2$, and KOH in place of cement, and cure the samples at a higher temperature to encourage montmorillonite dissolution and secondary mineral formation (Gates & Bouazza, 2010; Fernámdez, et al., 2006; Fernámdez, et al., 2010; Sánchez, et al., 2006; Savage, et al., 2002; Savage, et al., 2007).

The dissolution of montmorillonite occurs in alkaline solutions such as cement, and from Savage et al. (2007) the stoichiometry for the dissolution of montmorillonite is as follows:

$$Na_{.33}Mg_{.33}Al_{1.67}Si_4O_{10}(OH)_2 + 4.68OH^- + 2H_2O \rightarrow$$

$$0.33Na^+ + 0.33Mg^{2+} + 1.67Al(OH)_4^- + 4HSiO_3^- \qquad (1)$$
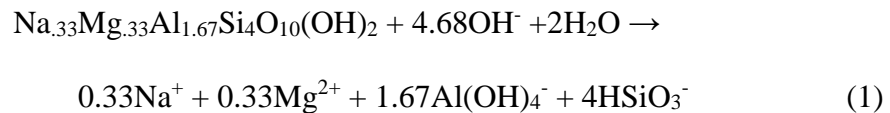
When interacting with the Ca and $OH^-$ produced when cement is hydrated, calcium silicate hydrates (C-S-H) can be formed by the following reaction from Savage (2007):

$$5Ca^{2+} + 6HSiO_3^- + 4OH^{--} + 5.5H_2O \rightarrow Ca_5Si_6H_{21}O_{27.5} \qquad (2)$$
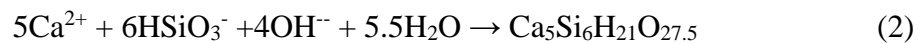
Potential secondary mineral formation can slow down or accelerate the dissolution of montmorillonite. From the studies using hyperalkaline solutions, a model was

developed for the interaction between cement and bentonite (Figure 4). The model

shows that the dissolution of montmorillonite can increase or decrease depending upon

the secondary minerals formed. As C-S-H forms, as a secondary mineral, this will

increase the amount of $OH^-$ consumed and lower the pH, which will decrease the

dissolution of montmorillonite. As zeolites form, as a secondary mineral, this will

increase the amount of $OH^-$ produced and further accelerate the dissolution of

montmorillonite (Savage, et al., 2007).
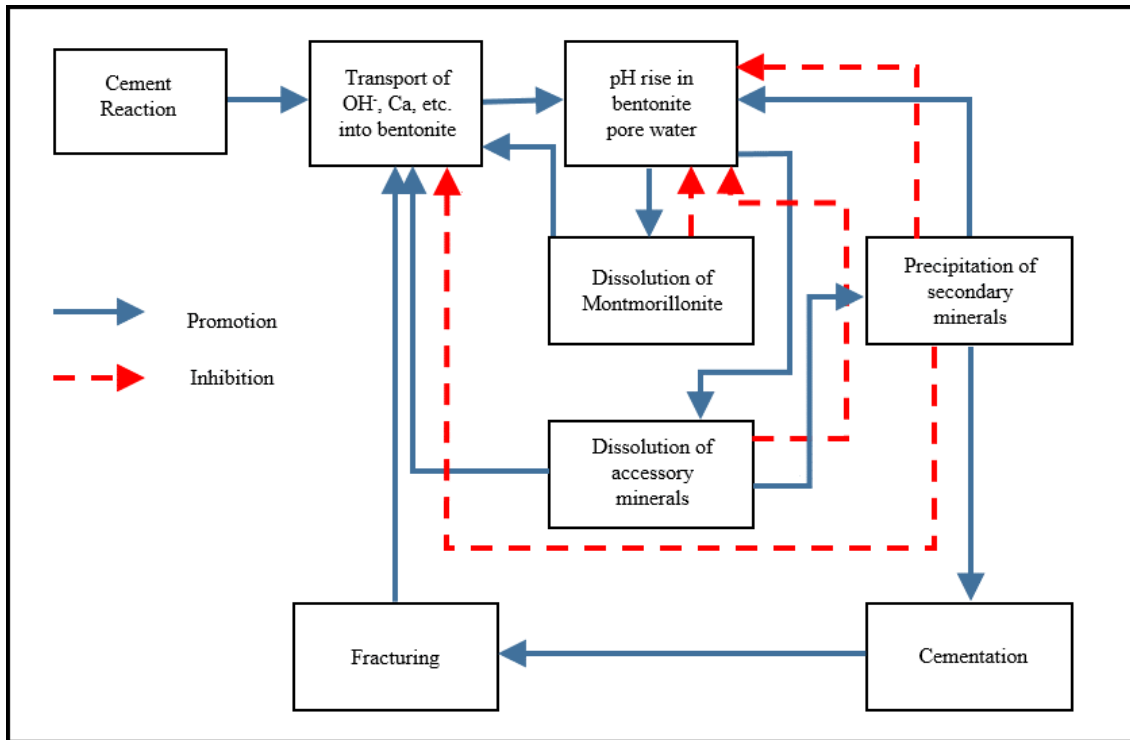


**Figure 4. Coupled linear reaction of bentonite and cement showing the dissolution of minerals and production of secondary minerals, can both promote or inhibit the pH rise within bentonite (modified from Savage, et al., 2007).**

**Objectives**

  This study will use XRD to examine several cement-bentonite grouts and one neat cement grout, and couple the XRD results with the results of Weiss and Mathewson (2005) and Mathewson and Ebrom (2011) to determine if secondary mineral formation is the cause of fracturing with these grouts. Based upon previous work on the cement-bentonite slurry walls the likely cause of secondary mineral formation will be from the dissolution of montmorillonite. The major difference between this study and that of cement-bentonite slurry wall studies is the sample preparation. The grouts that will be used for this study have been prepared to common standards for production of cement-bentonite grout for use in monitor wells, and will not be using a hyperalkaline solution such as NaOH, KOH, or CaOH or curing at elevated temperatures to promote secondary mineral growth. This study will use the same fractured cement-bentonite grouts that were examined with optical microscopy by Weiss and Mathewson (2005) and with the microprobe by Mathewson and Ebrom (2011). It is important to determine if montmorillonite dissolution and what secondary minerals are forming, so that recommendations can be made on how to properly complete a monitor well based on the local geology.

## PREVIOUS WORK

**Cement-Bentonite Grout Monitor Well Studies**

As previously stated in the project history, Wolde (1996) examined the proper completion for monitor wells based on geologic conditions. The materials that were examined were various forms of bentonite (chips, dried chips, pellets and dried pellets) and cement-bentonite grouts. The material properties that were examined were unidirectional swell behavior, reserve expansion, and shear strength and recoverability. Cement-bentonite grouts, neat-cement, sand-cement grouts, and concrete were also examined for shear strength. It was noted that there was significant fracturing in the cement-bentonite grout and neat-cement laboratory model monitor wells after curing and prior to testing of the shear strength. Cement-bentonite grouts and neat-cement had the lowest shear strength of the materials tested. The study concluded that, because of the fractures present at curing, cement-bentonite grouts and neat-cement should only be used to seal a monitor well annulus in high strength and already fractured rock, because the fracturing in the rock already contains migration pathways to the aquifer.

The presence of fracturing upon curing in the model monitor wells in Wolde (1996) study prompted the studies by Weiss and Mathewson (2005) and Mathewson and Ebrom (2011). In Weiss and Mathewson (2005), small scale samples were prepared using the different mixing methods but the same ratios of cement to bentonite to water. In grouts where bentonite was prehydrated first it was noticed that extra water was required to form a pumpable grout, which also resulted in an increased porosity within

the grout.  Fracturing occurred upon curing for all grouts independent of the mixing method.  Thin sections taken of all the grouts showed that there was a reaction halo present around the fractures indicating at that a chemical reaction was occurring at or near the fractures.  The presence of the reaction halos prompted a study by Mathewson and Ebrom (2011) to further analyze these samples using the electron microprobe.  Two zones that were enriched and depleted in different elements were present around the fractures.  The inner zone, closest to the fracture, was enriched in the elements C, Al, Ca, Na, S, and Si, but was depleted in O.  The outer zone was depleted in all elements but enriched in O.  It was initially concluded that there is a similar reaction occurring to the one that forms ettringite in grouts containing cement and aggregate.

A field study examining the performance of annular seals in in-service water and monitoring wells, Christman et al (2007), uses an ultrasonic probe to examine 35 wells in unconsolidated sediments.  The ultrasonic probe would generate two wave forms with the second wave form indicating the material composition on the outside of the well casing.  In the study, the sealant properties and the well construction and geologic conditions were taken into consideration.  It was concluded that wells constructed with cement-bentonite grouts appeared more susceptible to fracturing than those completed with only bentonite.

**Cement-Bentonite Slurry Wall Studies**

The work that has been done on the chemical reactions between cement and bentonite has typically been examined in their use in liner for geologic repositories. A slurry wall's design is a trench around a geologic repository with a cement-bentonite slurry with up to 30% percent bentonite in the slurry (Garven & Hayles, 1999). These studies typically assess the dissolution of montmorillonite when it is reacting with a hyperalkaline solution such as NaOH, $Ca(OH)_2$, and KOH.

Philip (2001) performed a study on cores from a single-phase cement-bentonite slurry wall and performed hydraulic tests on the cores. The study pulled out several cores from a cement-bentonite slurry wall that had been placed three years prior. The slurry wall was in good condition with no visible oxidation and the core recovery was considered to be good. The samples were dried after removal from the slurry wall, and the samples quickly degraded and were required to be confined to maintain structural integrity. Permeability was examined by loading the samples into a triaxial load cell using the constant flow rate values, and was determined to have a high permeability. The samples were further studied for diffusive and advective flux and modeling of the potential contaminant flow across the cement-bentonite slurry. It was determined that the main contaminant flow from the sample would be the result of advective flux.

Gates and Bouazza (2010) used four physical methods, XRD, diffuse reflectance infrared, x-ray absorption spectroscopy, and thermal gravimetric analysis, to examine the physical changes in bentonite when exposed to a hyperalkaline solution. The samples were prepared with bentonite mixed with a 1 M NaOH solution, and allowed to cure for

six weeks to six months. The samples that were placed in the alkaline solution were then compared to bentonite that had not been reacted with alkaline solutions. The sample treated with 1 M NaOH and allowed to cure for six months showed the greatest mineral alteration. In the XRD analysis, peaks representing hydrous calcium, hydrous silicate, calcium silicate hydrate, calcium-aluminum-silicate-hydrate were identified. It was concluded based off of the physical methods that there is strong evidence for dissolution of the montmorillonite within bentonite in the presence of hyperalkaline solutions. It was concluded that calcium silicate hydrate and calcium-aluminum-silicate-hydrate are direct results of the dissolution of montmorillonite. Other secondary mineral formation, such as hydrous carbonate, was likely the results of drying the sample for analysis. It was also concluded that the dissolution of montmorillonite could affect the performance of a barrier, but is dependent on several factors such as alkalinity, concentration, and temperature.

Sanchez, et al. (2006) examine the reaction kinetics of FEBEX bentonite with the interaction of hyperalkaline solutions, using 0.1 to 0.5 M NaOH. The samples were left to cure for 1 month to 18 months at a temperature range of 25°C to 250°C. The system was buffered initially by including an excess of portlandite to the mixture. After curing for the necessary amount of time, the aqueous and solid phases of the sample were separated. The solid phase was examined with XRD and SEM and the reaction kinetics were modeled. The results of the XRD showed the presence of zeolites and C-S-H from the dissolution of the montmorillonite. Also, the XRD analysis showed that portlandite was no longer present within the samples. It was noted that reactions to produce the

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secondary minerals like calcium silicate hydrate are OH$^-$ sinks, which will cause the pH to decrease. As more secondary minerals are produced this will prevent further dissolution of montmorillonite.

Fernandez, et al., (2006) examined secondary mineral formation in FEBEX bentonite, which is a Mg-rich form of bentonite, when interacting with $Ca(OH)_2$ and NaOH at a range of molar concentrations and temperatures in a load cell test. Ordinary portland cement was also examined in the load cell test. It was noticed that there was significant alteration of montmorillonite when the bentonite was interacted with NaOH. Modelling was used to further examine the significant alterations to montmorillonite when reacted with NaOH. The reactive-transport geochemical code PHREEQC, version 2 was used with NaOH at a concentration 0.25M and temperatures at 25° and 120°C. The $Ca(OH)_2$ had very little effect on the dissolution of montmorillonite that is within bentonite. The only mineral alteration that occurred was calcium silicate hydrates because of the Ca presence. NaOH showed that at low temperatures of 25°-60° C, the development of calcium silicate hydrates and brucite affected only about a millimeter into the bentonite. At higher temperatures of 120°C, the entire column of bentonite was affected by mineral alteration. The results of the modeling confirmed qualitatively what had been previous observed in other models and what was observed in the load cell tests with NaOH.

Fernadez, et al., (2010) used FEBEX bentonite and two synthetic alkaline solutions, which mirrored those of squeezed cement pore waters, to determine the geochemical constraints of the stability of zeolites and C-S-H. The samples were load

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cell tested for two years at a range of temperatures and the alkaline solutions were refreshed periodically. The results showed that zeolites formed at temperatures around 60°C. At higher temperatures than 60°C, C-S-H appeared to be in equilibrium with montmorillonite. At lower temperatures, C-S-H appeared to be metastable. The thermodynamic dissolution rates were calculated for montmorillonite and showed to be in good agreement with previous calculations.

Savage et al., (2002) simulated the interaction between hyperalkaline fluids and bentonite using a reaction-transport model. The development of secondary minerals was modeled by using an equilibrium constant for each mineral present within bentonite and changing the pore fluids. It was found that C-S-H forms closest to the cement-bentonite boundary, and zeolites and smectite clays formed as a secondary mineral further away. It was concluded that the hyperalkaline solutions would lead to an increased dissolution of silicates and aluminosilicates and could dissolute as much as 60% bentonite.

Savage et al., (2007) examined the results of several studies on secondary mineral development that involved both laboratory and natural environment testing. It was found that pH greatly affects the alteration of the minerals within bentonite, and the types of mineral alteration that occur can increase or decrease the pH. The most pH dependent mineral alteration is that of zeolite. The zeolites tend to form under lower pH. Thermodynamic control plays a role in the secondary mineral growth but is still poorly understood on how it affects bentonite alteration.

## METHODOLOGY

**Bentonite and Cement Mineral Composition**

Bentonite is a term used to describe a soil which is composed primarily of swelling clay minerals (Karnland, 2010). The most commonly used bentonite in the United States for drilling and engineering projects is Wyoming bentonite. Wyoming bentonite's mineralogical composition is montmorillonite (79%), plagioclase (9%), quartz (3%), mica (3%), K-feldspar (2%), carbonates (2%), and other minerals (2%) (Charpentiera et al, 2006). Montmorillonite is an aluminum phyllosilicate of the smectite group, in which all members of the group contain a layered structure and swelling properties. The structure of montmorillonite is 2:1 sheet silicate where octohedrally arranged cations are linked in between by oxygen to tetrahedrally aligned cations. Where the octahedral sheet has aluminum as the central atom, and the tetrahedral sheet has silicon as the central atom (Figure 5). The alignment and spacing between mineral layers will increase and the montmorillonite will become more hydrated, causing the mineral to swell as it is hydrated (Karnland, 2010).
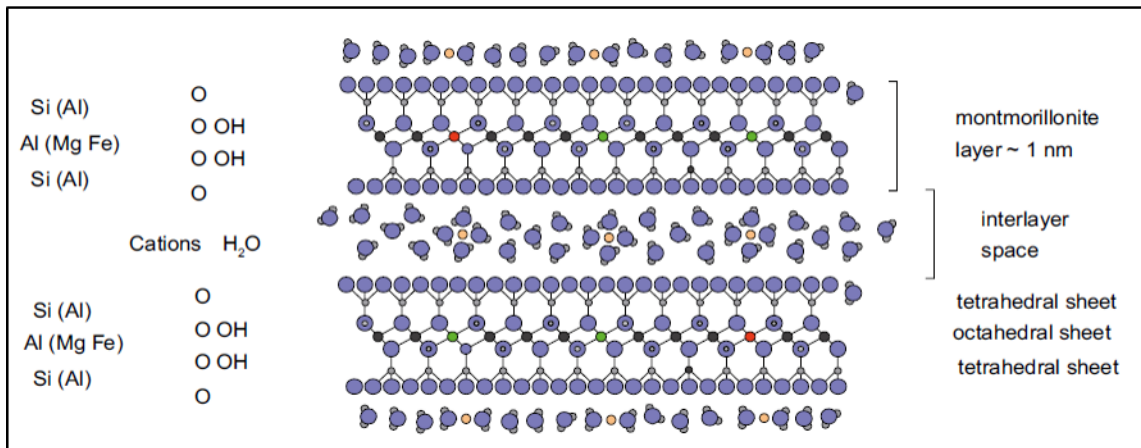
**Figure 5. Montmorillonite atomic structure (Karnland, 2010).**

Type I Portland cement is a hydraulic cement that is composed of fine grade

clinkers. Typically Type I Portland cement is composed of clinkers made up of

tricalcium silicate ($(CaO)_3SiO_5$) and dicalcium silicate ($(CaO)_2SiO_4$) that are usually

derived from the mixture calcareous material and a silica source. Other phases that

may be present in Type I Portland cement clinkers are tricalcium aluminate

($(CaO)_3Al_2O_3$) and tetracalcium aluminoferrite ($(CaO)_4Al_2O_3Fe_2O_3$). Gypsum

($CaSO_4 \cdot 2H_2O$) may also be present for controlling setting time and enhancing the

strength of the cement (Helmuth, et al., 1993).

**Cement-Bentonite Grout Mixing Methods**

There are four common methods for mixing cement with bentonite to create a

grout. The methods are: hydrating cement and adding bentonite, hydrating the

bentonite and adding cement, dry mixing bentonite and cement, and the Smith

Method. For all methods, except the Smith Method and prehydrating bentonite, the

minimum water needed to fully hydrate cement is 5.2 gallons of water for every 94

lbs of cement. For every 2% of bentonite added to the cement an extra 1.3 gallons of

water is needed. In the case of prehydrating bentonite, the cement will not fully

hydrate when added to the prehydrated bentonite. This results in an extra 10 to 20

gallons of water needed to fully hydrate the cement and form a pumpable grout. The

Smith Method is patent #3,227,213 filed in January 1966. In this method, the

bentonite is prehydrated before mixing with the Portland cement. In the Smith

Method, 1% of prehydrated bentonite is equal to 3.5 wt% of dry mix of Portland

cement. The Smith Method gets around the problem of needing extra water to form

a pumpable grout when bentonite is prehydrated by using less bentonite in the grout.


**Cement-Bentonite Grout Preparation and XRD Methods**

Based on previous studies on secondary mineral development and dissolution of

montmorillonite within cement and bentonite grouts, XRD was used to analyze the

samples. The samples are small scale cement-bentonite grouts and neat cement that

were prepared for the Weiss and Mathewson (2005) study on fracture development. The

grouts were prepared in all of the methods commonly used for mixing cement and

bentonite (prehydrate bentonite add cement, prehydrate cement add bentonite, dry mix

bentonite and cement, and the Smith Method), common ratios of cement to bentonite to

water based off of state regulations. State regulation differs for each state on the amount

of water required to hydrate cement.

For hydrating cement the Texas Administration Code defines cement as:

"A neat portland or construction cement mixture of not more than seven gallons of water per 94-pound sack of dry cement…"

In the grouts that were prepared for the Weiss and Mathewson (2005) the amount of water, though small scale samples, followed the ratio of 5.2 gallons of water per 94 lbs of cement, which is the amount of water required to fully hydrate a 94 lb. sack of Portland cement.

The bentonite used in these grouts are Aquagel® and Super Gel-X®, which are commercial Wyoming bentonites. Aquagel® is a sodium bentonite produced by Baroid International Trading, LLC., and Super Gel-X® is a sodium bentonite produced by CETCO Energy Services. State regulations also differ on the amount of bentonite, from 2% to 20% based on the total volume of solids, and the amount of water to fully hydrate the bentonite from a specific amount of water to just described as a pumpable slurry. For all of the grouts prepared for this study 8% bentonite based on the total volume of solids was used. These grouts were hydrated with 1.3 gallons of water per 2% bentonite, except for the grout where bentonite was prehydrated. In the grout where bentonite was prehydrated extra water was necessary to form a pumpable grout. In all the other cement-bentonite grouts a total of 10.4 gallons of water was necessary to hydrate both the cement and bentonite. Thin sections had been cut from the grouts for both the optical microscopy and microprobe analysis of the samples that were done in Weiss and Mathewson (2005) and Mathewson and Ebrom (2011), respectively.

Five grouts were selected from the grouts prepared for Weiss and Mathewson (2005) for analysis with XRD. The grouts were chosen based on mixing method and

type of bentonite used.  A sample of neat cement was included to compare the mineralogy to the cement-bentonite grouts.  The percentage of bentonite per grout, based on the total volume of solids, and the mixing method for each sample are listed below:

- Aquagel®, bentonite was prehydrated and cement was added in.

- Aquagel®, cement was prehydrated and bentonite was added in.

- Aquagel®, cement and bentonite were dry mixed together and hydrated.

- Super Gel-X®, bentonite was prehydrated and cement was added in.

A sample using the Smith Method was not included for this XRD analysis, because it would contain less bentonite in it and would be more difficult to detect any secondary mineral formation.

Powdered XRD analysis was performed in a Rigaku XRD computerized powder diffractometer over a °2θ CuKα range of 2°-60° using a 0.3° step to get the full range of minerals present within the grouts.  Peaks were analyzed using the Rigaku software associated with the XRD system and compared to the °2θ present in the Joint Committee of Powdered Diffraction Standards (JCPDS) for mineral identification.  If secondary minerals are present in the samples, they will be compared to those that were present in slurry wall studies.

# RESULTS AND DISCUSSIONS

**Neat Cement Grout**

Figure 6 shows the XRD diffractogram for the grout containing neat cement. There are no unidentified peaks in the XRD diffractogram. The following minerals are identified within the grout: calcite ($CaCO_3$), vaterite ($CaCO_3$), and portlandite ($Ca(OH)_2$).
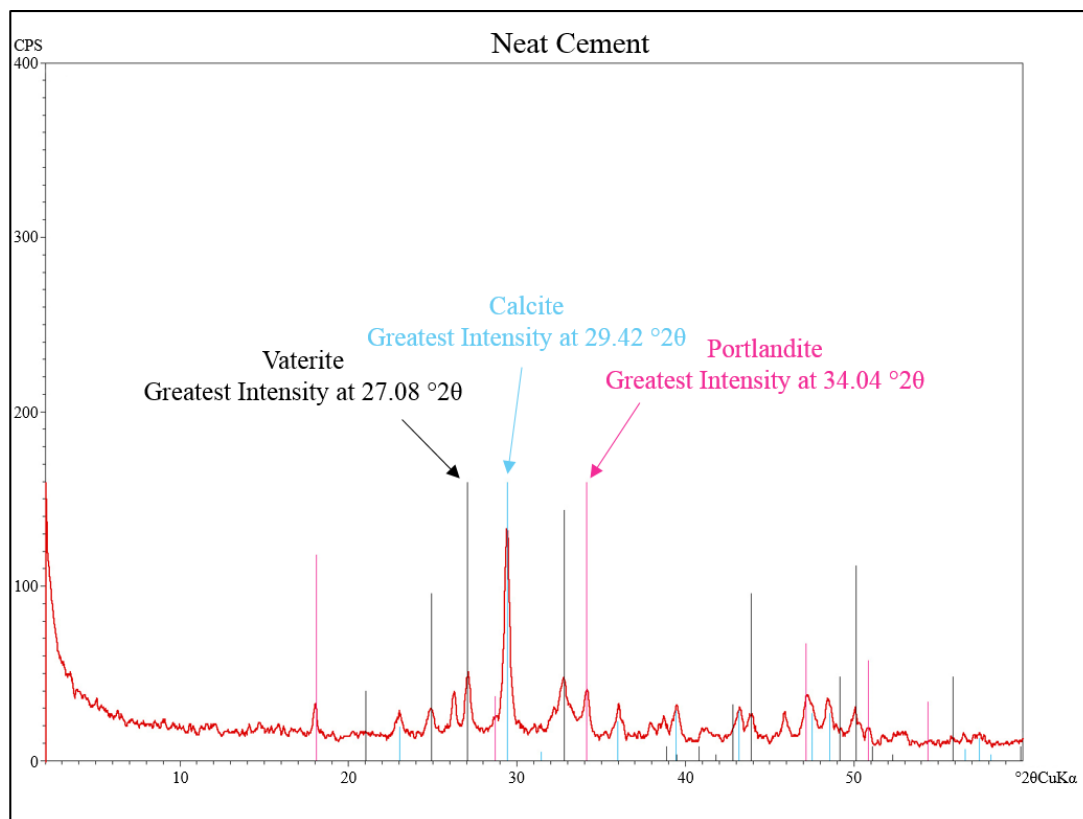


**Figure 6. XRD diffractogram for neat cement grout showing the minerals present (calcite, vaterite, and portlandite) and the °2θ for the greatest intensity associated with each mineral.**

In the neat cement grout, the greatest relative intensity for each identified minerals

occurs at the following °2θ, 29.42 for calcite, 27.08 for vaterite, and 34.04 for

portlandite. These intensities correspond to the Miller Indices of hkl(104) for calcite,

hkl(112) for vaterite, and hkl(101) for portlandite, and are all primary peaks for

identifying these minerals.


**Prehydrate Bentonite and Add Cement Grouts**

Figure 7 shows the XRD diffractogram for the grout containing Super Gel-X®,

where bentonite was prehydrated and cement was added in. The following minerals are

identified within the grout: calcite ($CaCO_3$), vaterite ($CaCO_3$), and portlandite

($Ca(OH)_2$). In the Super Gel-X® grout, the greatest relative intensity for each identified

minerals occurs at the following °2θ, 29.42 for calcite and 27.02 for vaterite. For

portlandite the counts are equal at °2θ of 18.05 and 34.13. The intensities correspond to

the Miller Indices of hkl(104) for calcite, hkl(112) for vaterite, and hkl(101) and

hkl(001) for portlandite. These Miller Indices correspond to the primary peaks for

mineral identification for calcite and vaterite. For portlandite, the Miller indices

correspond to the primary and secondary peak for mineral identification. There are no

identifiable montmorillonite peaks, and there are no unidentified peaks within the grout.

Figure 8 shows the XRD diffractograms for the grouts containing Aquagel®

where bentonite was prehydrate and cement was added in. The following minerals are

identified within the grout: calcite ($CaCO_3$), vaterite ($CaCO_3$), and portlandite ($Ca(OH)_2$)

**Figure 7. XRD diffractogram for Super Gel-X® grout, where bentonite was prehydrated, showing the minerals present (calcite, vaterite, and portlandite) and the °2θ for the greatest intensity associated with each mineral.**

In the Aquagel® prehydrate bentonite add cement grout, the greatest relative intensity for each identified minerals occurs at the following °2θ, 29.42 for calcite, 26.99 for vaterite, and 18.02 for portlandite. These intensities correspond to the Miller Indices of hkl(104) for calcite, hkl(112) for vaterite, and hkl(101) for portlandite. The Miller Indices correspond to the primary peaks for mineral identification for calcite and vaterite, but for portlandite the Miller Index corresponds to a secondary peak for mineral identification. There are no identifiable montmorillonite peaks, and there is one unidentified peak that occurs at approximately 32.24 °2θ
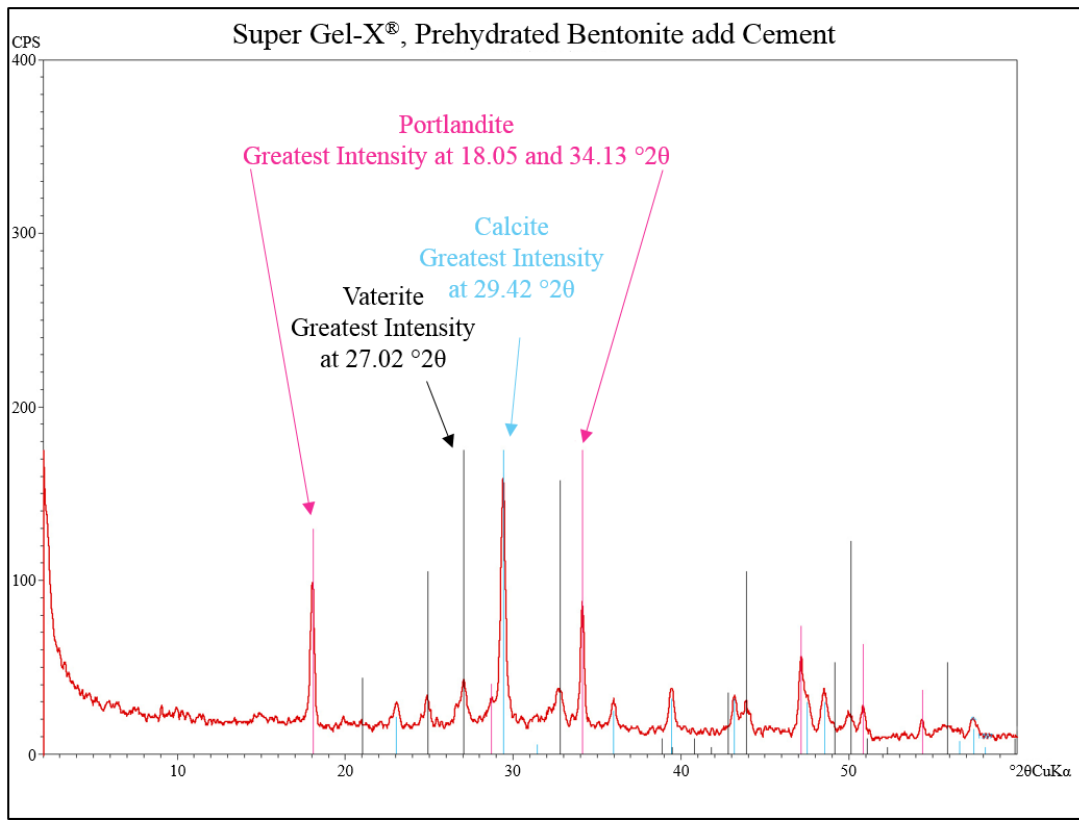
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**Figure 8. XRD diffractogram for Aquagel® grout, where bentonite was prehydrated, showing the minerals present (calcite, vaterite, and portlandite) and the °2θ for the greatest intensity associated with each mineral.**

*Effects of Excess Hydration on Cement-Bentonite Grouts*

Portlandite's greatest intensities occur with the hkl(101) peak or hkl(001) peak, which are the primary and secondary peak for mineral identification for portlandite. In grouts where bentonite was prehydrated first these two peaks are of almost equal intensity in all the Aquagel® grout, and are equal intensity in the Super Gel-X® grout. The intensity of these peaks are increased in both intensity and how well defined the peak is when compared to the XRD diffractogram for the grout containing neat cement.

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This difference in intensity in the grouts where bentonite was prehydrated and cement was added and the grout containing only neat cement indicate that there is a greater degree of crystallization of portlandite within the prehydrated bentonite grouts. Stepkowska et al., (2003) investigated the formation of portlandite and calcite polymorphs as a result of varying degrees of hydration in ordinary Portland cement. In this study it was concluded that an increased hydration would increase the production of portlandite and calcite polymorphs. The hydration comes from the extra water necessary to fully hydrate the cement within these grouts to form a pumpable grout. This increase in water will cause more complete crystal growth for portlandite and increase the intensity of the reflection of the primary and secondary peaks.

**Dry-Mix Cement and Bentonite Grout**

Figure 9 shows the XRD diffractograms for the grouts containing Aquagel® where cement and bentonite were dry mixed together. The following minerals are identified in all three grouts: calcite ($CaCO_3$), vaterite ($CaCO_3$), and portlandite ($Ca(OH)_2$). In the Aquagel® dry mix bentonite and cement, the greatest relative intensity for each identified minerals occurs at the following °2θ, 29.45 for calcite, 32.87 for vaterite, and 34.10 for portlandite. These intensities correspond to the Miller Indices of hkl(104) for calcite, hkl(114) for vaterite, and hkl(101) for portlandite. The Miller Indices correspond to the primary peaks for mineral identification for calcite and portlandite, but for vaterite the Miller Index corresponds to a secondary peak for mineral

identification.  There are no identifiable montmorillonite peaks, and there is one

unidentified peak that occurs at approximately 32.18 °2θ.



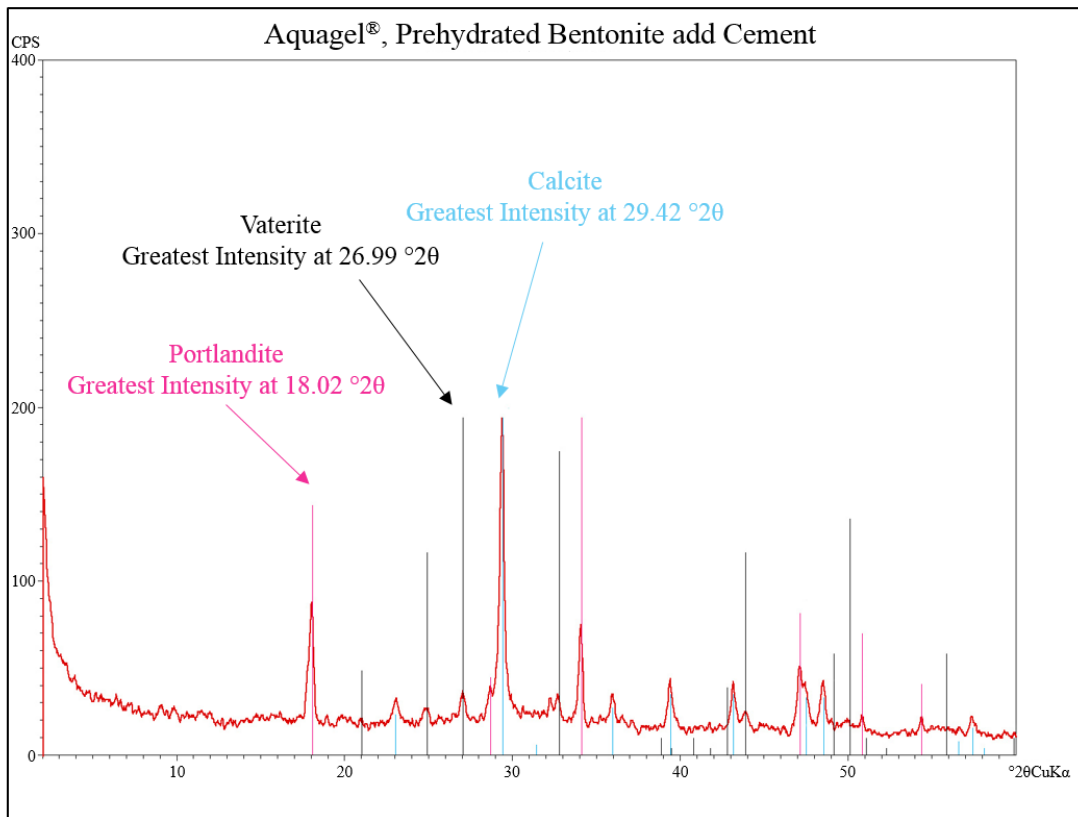**Figure 9.  XRD diffractogram for Aquagel grout, where bentonite and cement were dry mixed, showing the minerals present (calcite, vaterite, and portlandite) and the °2θ for the greatest intensity associated with each mineral.**

*Effects of Inadequate Hydration of Cement*

Calcite has the greatest intensity, compared to all other grouts, in the grout where

cement and bentonite were dry mixed together before hydrating.  Also when comparing

the vaterite peak in the dry mix cement and bentonite grout and the neat cement grouts,

there is a shift in the intensity peak with the greatest intensity from the primary peak for

mineral identification at hkl(112) in the neat cement grout to the secondary peak for

mineral identification at hkl(114). Vaterite is a polymorph of calcite that forms from the

hydration of calcite that is present when Portland cement is hydrated (Stepkowska, et al.,

2003). The increased intensity in calcite is likely because calcite and the lack of

intensity for vaterite, is likely caused by the inadequate hydration of cement because of

bentonite absorbing additional water. The lack of hydration limits the crystallization of

vaterite, which leads to a the shift in the peak to the secondary peak and a weaker

intensity when compared to neat cement


**Prehydrate Cement and Add Bentonite Grout**

Figure 10 shows the XRD diffractograms for the grouts containing Aquagel[®]

where cement was prehydrated and bentonite was added in. The following minerals are

identified in all three grouts: calcite ($CaCO_3$), vaterite ($CaCO_3$), and portlandite

($Ca(OH)_2$). In the 8% Aquagel ® prehydrate cement add bentonite grout, the greatest

relative intensity for each identified minerals occurs at the following °2θ, 29.42 for

calcite, 27.08 for vaterite, and 34.22 for portlandite. These intensities correspond to the

Miller Indices of hkl(104) for calcite, hkl(112) for vaterite, and hkl(101) for portlandite,

and are all primary peaks for identifying these minerals. The similarites between this

grout and the neat cement in peak location and relative intensity of the peak, is likely

caused by the hydration of cement prior to adding the bentonite and no extra water being

required. There are no identifiable montmorillonite peaks, and there is one unidentified
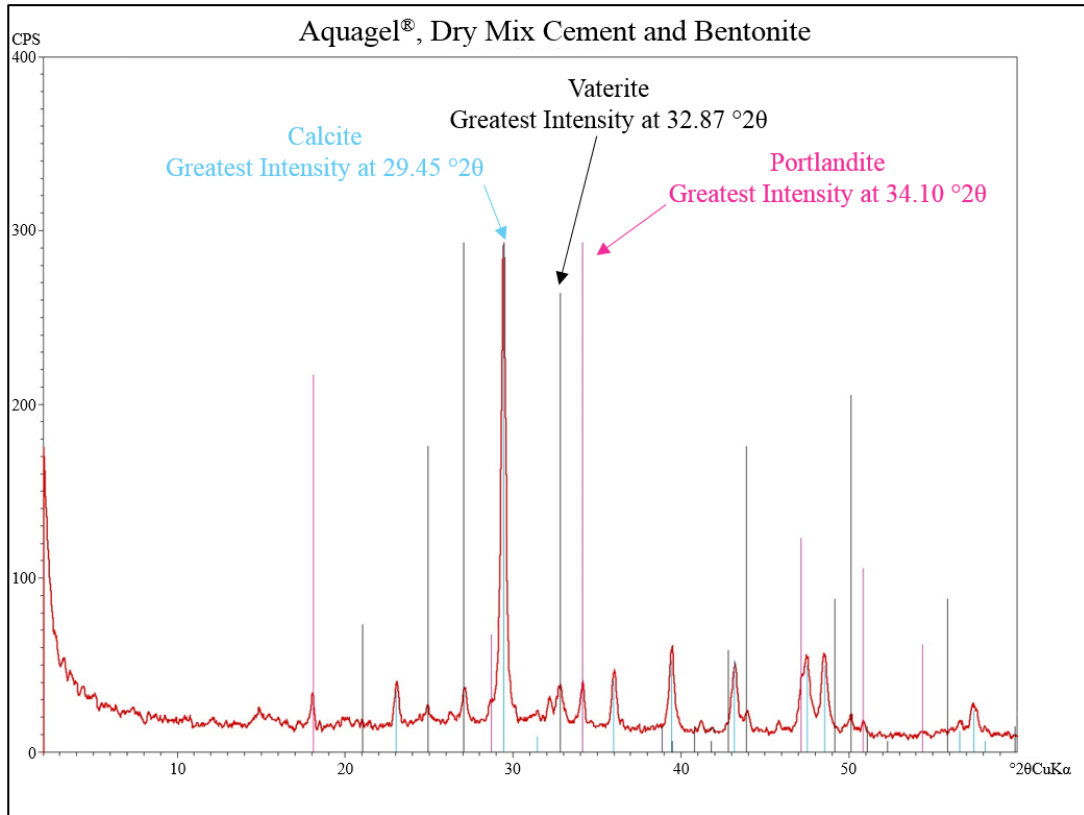
peak that occurs at approximately 32.21 °2θ.
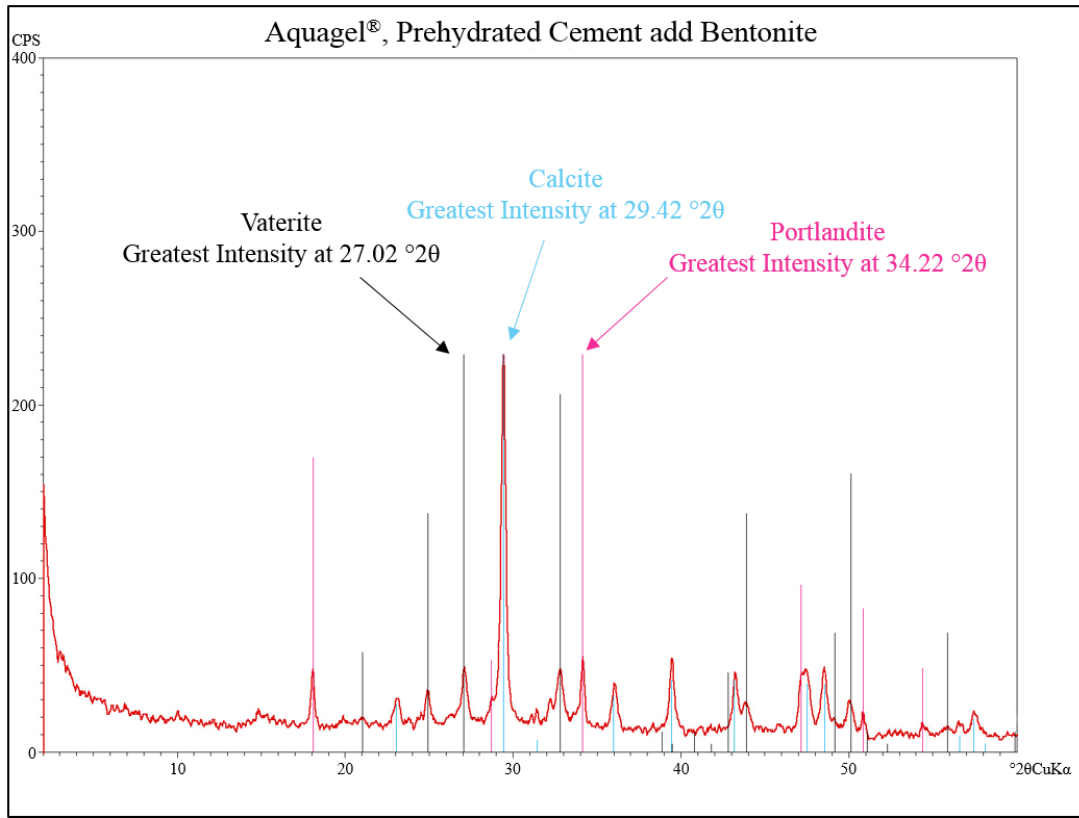
**Figure 10. XRD diffractogram for Aquagel® grout, where cement was prehydrated, showing the minerals present (calcite, vaterite, and portlandite) and the °2θ for the greatest intensity associated with each mineral.**

**Secondary Mineral Formation**

From Weiss and Mathewson (2005), a reaction halo is present around the fractures that were examined in thin section. This halo indicates that there is a chemical reaction occurring at or around the fractures within these cement-bentonite grouts. The goal of the XRD was to determine what minerals were present within these cement-bentonite grouts, with a focus on investigating if mineral formation was the cause of the fracture. Previous works on cement-bentonite slurry walls commonly find that the

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dissolution of the montmorillonite and the formation of calcium silicate hydrate (C-S-H) and zeolite minerals will cause fracturing of cement-bentonite grouts.

From the XRD results, there are no directly identifiable C-S-H or zeolite minerals within the cement-bentonite grouts, but there is also no indication of montmorillonite or other minerals associated with bentonite. Within the grouts containing Aquagel®, there is an unidentified peak, which is not present in the Super Gel-X® or Neat Cement grouts, at approximately 32.2 °2θ. This peak is not clearly defined because of its proximity to a portlandite peak, and has a relatively weak intensity (Figure 10). Based off of Gates and Bouzza (2010), this potentially correlates to a secondary °2θ for C-S-H. Identification of C-S-H in these cement-bentonite grouts from the XRD solely is not possible because the primary peak for C-S-H is shared with the hkl(104) peak for calcite, which occurs at approximately 29.4 °2θ.

For identification and explanation of this peak, it is necessary to include the results of Weiss and Mathewson (2005) and Mathewson and Ebrom (2011). From Savage, et al., (2007) as secondary minerals begin to crystallize, these minerals will begin to fracture a cement-bentonite slurry wall. The reaction halo identified in the optical microscopy study performed by Weiss and Mathewson (2005) are present in conjunction with the fractures in the thin sections. This gives evidence that the unidentified peak represents a potential secondary mineral had started crystallizing to form the fractures. The microprobe x-ray maps show that the zone near the fractures is enriched in the following elements: Ca, Na, Si, C, Al, and S (Figure 12).

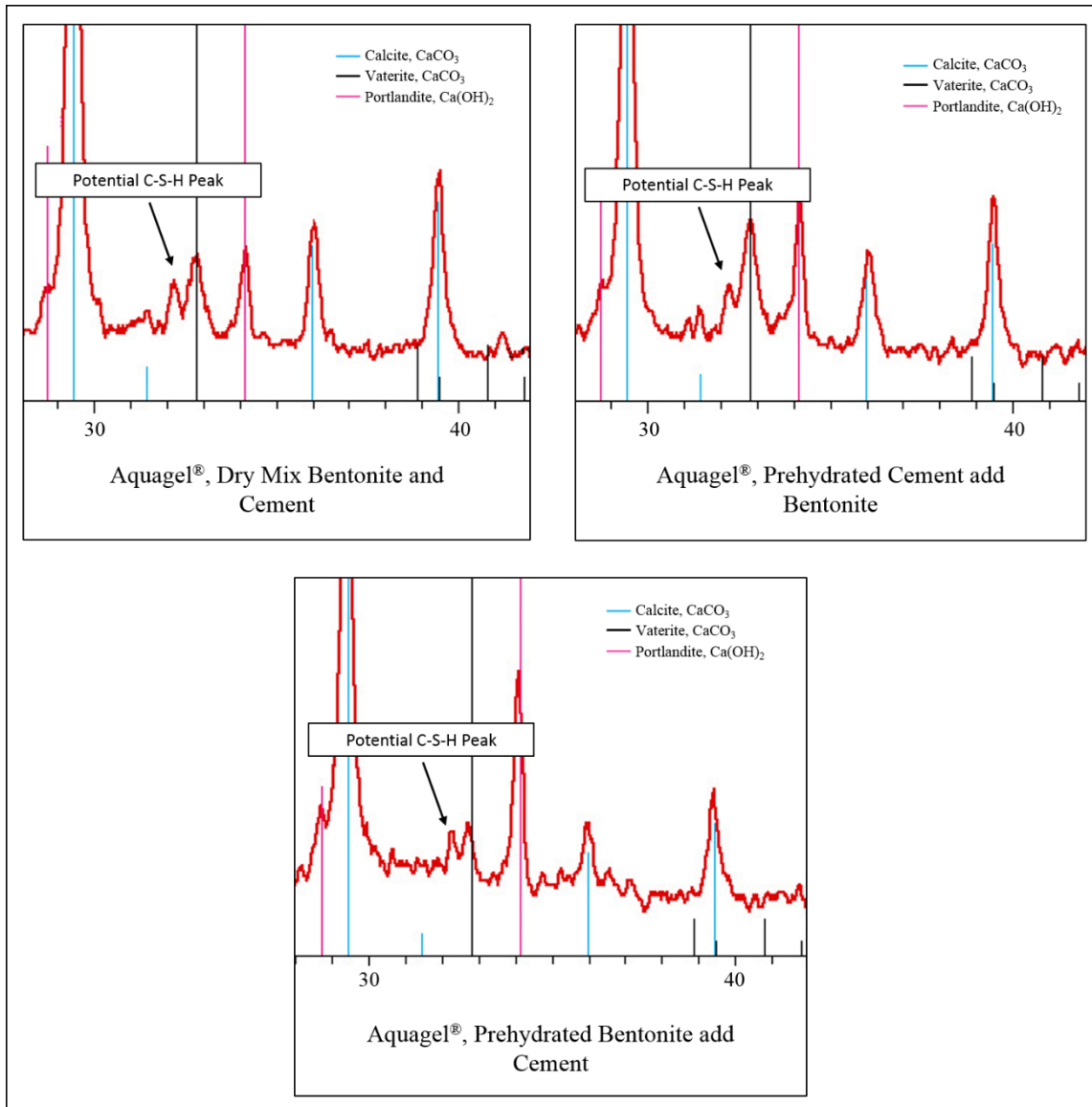**Figure 11. Potential C-S-H peak that occurs at approximately 32.2 °2θ in grouts that contain Aquagel®.**

Out of the three elements found in the zone, three are elements that make up montmorillonite. These elements are Na, Si and Al (Mathewson and Ebrom, 2011). Savage, et al., (2007) has stated when bentonite is mixed with cement, Ca and OH$^-$ transport into the pore space of bentonite, which could explain the Ca present in the

microprobe x-ray map (Mathewson and Ebrom,2011).  The common C-S-H mineral

which forms as a result of montmorillonite dissolution is tobermorite that has the

chemical formula of $Ca_5Si_6H_{21}O_{27.5}$ (Savage, et al., 2007).  Within the zone depleted of

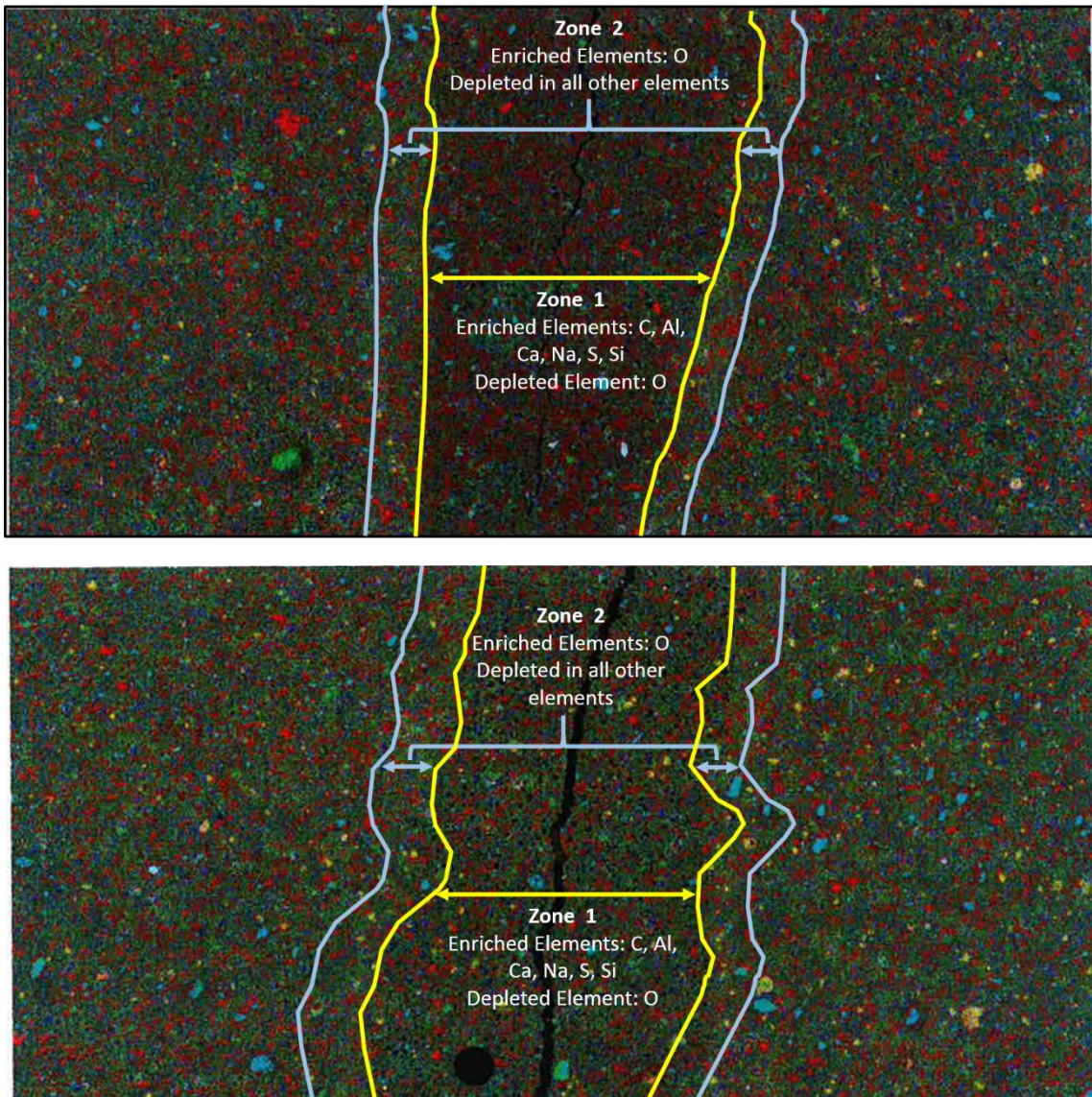oxygen, all the elements necessary to form tobermorite, except for oxygen, are present.



**Figure 12.  Microprobe x-ray maps showing zonation of element around fractures in grout containing dry mixed bentonite (top) and the grout containing prehydrated cement and bentonite (bottom) ( Mathewson & Ebrom, 2011).**

Based off of this information, it can be assumed that the unidentified peak within Aquagel® grouts is likely a peak for C-S-H, because of the weak peak this would suggest that C-S-H is present is poorly crystallized or it is amorphous.  Because of both the lack of a C-S-H peak at approximately 32.2 °2θ and the lack of montmorillonite in the Super Gel-X® grout, it can be assumed that if C-S-H is present it is not crystallized and is completely amorphous.

Fernandez, et al., (2006) demonstrated that in a load cell test that C-S-H will form at the boundaries between cement and bentonite.  What is likely being observed in the reaction halo in the thin sections and the zonation of elements microprobe x-ray maps, are the dissolution of montmorillonite and the formation of C-S-H at a boundary between the zone enriched in oxygen and the zone depleted in oxygen.  These events give indications that boundaries have formed between cement and bentonite when mixed together for the grouts, and do not form a homogenous mixture between the two materials.

# CONCLUSIONS

**XRD Investigation Conclusions**

Based upon the fractures observed in cement-bentonite grouts prepared for completion of monitor wells in Wolde (1996), several investigations have gone on to determine the cause of these fractures.  The optical microscopy investigation revealed the presence of reaction halos around the fractures, and the microprobe showed a zonation of elements present around the fractures.  The results of both optical microscopy and microprobe analysis indicated a chemical reaction occurring around the fractures of the grouts, and concluded a secondary mineral forming was the cause of fractures (Weiss & Mathewson, 2005 and Mathewson & Ebrom, 2011).  This study focused on the XRD analysis of these fractured cement-bentonite grouts and neat cement to identify secondary minerals that could be the cause of the fracture development.  Calcite, vaterite, and portlandite, minerals common to hydrated cement, are present in all grouts, and have not been indicated as a cause of fracturing for neat cement or cement bentonite grouts.  These minerals vary in intensity in the cement-bentonite grouts when compared to neat cement.  These intensity variations indicate the degree of crystallization of the minerals present, and are based on how well hydrated the cement was when the grout was prepared.

The most commonly reported cause of fracturing when cement is reacted with bentonite is the dissolution of montmorillonite and the formation of secondary minerals such as calcium silicate hydrate and zeolites (Gates & Bouazza, 2010; Fernámdez, et al.,

2006; Fernámdez, et al., 2010; Sánchez, et al., 2006; Savage, et al., 2002; Savage,

et al., 2007).  Within these cement-bentonite grouts, montmorillonite is not identified

from the XRD results, indicating that dissolution may be occurring.  There is a

secondary peak which is potentially associated with calcium silicate hydrate in all of the

cement-bentonite grouts that contain Aquagel [®]. The presence of calcium silicate hydrate

cannot be directly confirmed from the XRD, because the primary peak for this mineral

shares the same primary peak as calcite.

The results of optical microscopy study in Weiss and Mathewson (2005) and the

results of the microprobe analysis in Mathewson and Ebrom (2011) combined with the

results of this XRD analysis, it can be concluded that montmorillonite dissolution is

occurring within these grouts and forming poorly crystallized and amorphous calcium

silicate hydrate and is the cause of the fracturing within these grouts.  This mineral is

likely forming at boundaries between cement and bentonite when the grouts are initially

prepared.  A secondary peak for calcium silicate hydrate cannot be identified in the grout

containing Super Gel-X[®], but it can be assumed because of the lack of montmorillonite

that calcium silicate hydrate is not crystallized and purely amorphous within this grout.

It can also be concluded that the lack of montmorillonite in any grout containing

bentonite that this dissolution begins to occur almost instantly once cement and

bentonite have been mixed together, and that this reaction will continue to occur until

montmorillonite is no longer present or equilibrium is reached between the two

materials.  Based on the work of Savage et al., (2002) this reaction can cause complete

montmorillonite dissolution in grouts containing as much as 60% bentonite by weight of

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total volume before reaching equilibrium.  With the amounts of bentonite commonly used in grouts for completing monitor wells, montmorillonite will likely be completely dissoluted prior to curing of the grout.

**Recommendations for Monitor Well Completion**

Based on the conclusions of this study and the current Texas Administration Code for monitor well completion, it is important to recognize that this code may not be sufficient in describing the appropriate use for cement-bentonite grouts, because of the fracturing that results from the dissolution of montmorillonite.

Wolde (1996) originally concluded that cement-bentonite grouts should only be used in already fractured hard rock.  Hard rock is defined as brittle rock materials containing faults, fractures, bedding planes, or any other high permeability unit.  This original conclusion still holds true, because the fractures that develop from the dissolution of montmorillonite will become part of the local fracture system.  The fractures already present within the rock do not prevent migration to the aquifer, and therefore it is unnecessary for the grout used to hold the monitor well in place to also prevent migration to the aquifer.

In a soft rock setting, Wolde (1996) concluded that cement-bentonite grouts and neat cement should not be used.  A soft rock setting is described as a shale sandstone clastic system that is plastic or ductile, which does not deform by fracturing.  In these settings the shales present above the aquifer make an impermeable seal above the aquifer preventing migration to it.  Therefore, the grout used to keep the monitor well in place

should also be impermeable and not allow migration from the surface to the aquifer. Bentonite granules, chips, pellets, or pumpable bentonite grout should be used instead, because of the fractures that develop within cement-bentonite grouts by the dissolution of montmorillonite would not form an impermeable barrier. Also, fluids traveling through this grout would allow the continued transfer of $Ca^{2+}$ and $OH^-$ into the pore space of the any bentonite that remains, which would result in further fracturing of the grout and creation of more migration pathways to the aquifer.

The construction of the monitor wells for both rock types would consist of: a gravel/sand filter at the aquifer and a top seal immediately about the filter. The purpose of the top seal is to seal all backfill materials from the filter and the aquifer. The type of material chosen for the seal is dependent on aquifer saturation. If the aquifer is not saturated bentonite granules can be used for the top seal, but if the aquifer is saturated then bentonite chips should be used instead. After the top seal, in the hard rock setting sand-cement, neat cement or cement- bentonite grouts can be used followed by surface infiltration control and surface protection. In the soft rock setting after the top seal bentonite chips, pellets, or pumpable bentonite grout should be used followed by surface infiltration control and surface protection (Figure 13).
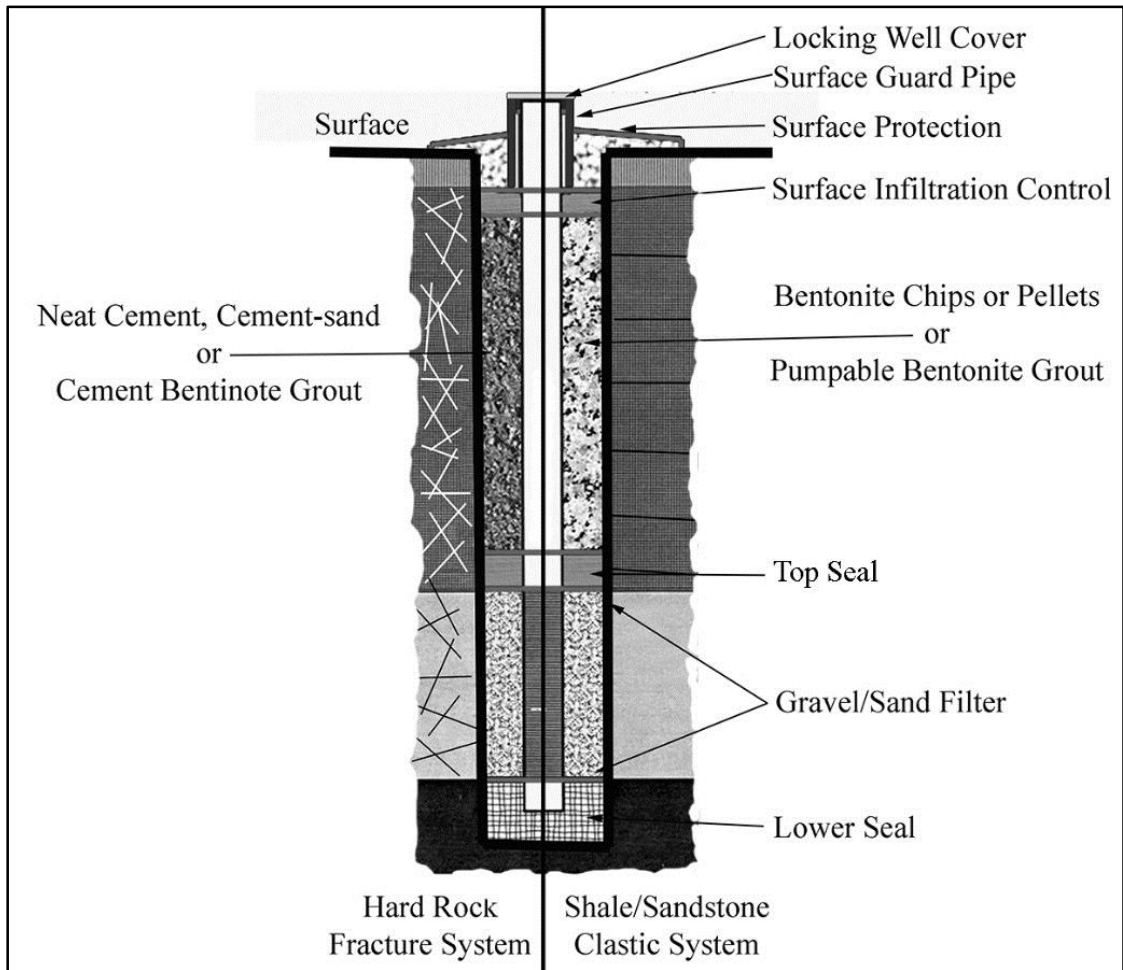
**Figure 13. Diagram showing the proper completion of a monitor well dependent on rock type. Hard rock fracture system is on the left side of the monitor well diagram and soft rock setting composed of sandstones and shales on the right side of the monitor well diagram.**

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