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**EXAMINATION OF SILICA REMOVAL WITH SOLIDS
RECYCLE FOR REVERSE OSMOSIS PRETREATMENT**

by

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BACHELOR OF SCIENCE, MANAGEMENT

THESIS

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EXAMINATION OF SILICA REMOVAL WITH SOLIDS RECYCLE FOR REVERSE OSMOSIS PRETREATMENT

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ABSTRACT

Water treatment methods serve to remove harmful constituents from ground and surface waters prior to municipal distribution by exploiting the physical and chemical properties of those constituents. Properties can include size, charge, or solubility. Silica (SiO_2) is difficult to remove during water treatment because it can exist in ground and surface waters as various dissolved and particulate species, all of which are defined by different properties. Silica speciation is dependent on variables like pH, temperature, concentration, and ionic composition.

Consumption of silica as it exists in drinking water is not dangerous to humans or animals, but it can form damaging scales on the surfaces of industrial equipment and reverse osmosis membranes. For this reason, the subject of silica removal has been the focus of many studies; yet, there remains much to be learned. This thesis aimed to study the complex issue of silica removal as a pretreatment step to RO. A review of the literature indicated that silica is most commonly removed during a lime softening process but that removal is tied mostly to the presence of magnesium. Furthermore, studies have shown that removal is best when the chemical softening process is operated at a pH of 10

or above. Magnesium hydroxide precipitates in this higher pH range thereby removing silica via a co-precipitation or adsorption mechanism.

This project explored the relationship between magnesium concentration, pH, and silica removal in two phases. Phase 1 included 21 jar tests that studied silica removal within a pH range of 7 to 12 and with different concentrations of dissolved magnesium chloride ($MgCl_2$) and freshly precipitated magnesium hydroxide ($Mg(OH)_2$); freshly precipitated ferric hydroxide ($Fe(OH)_3$) was also studied in one test. Phase 2 flow-through experimentation consisted of 5 tests that were conducted in a system operating around a pH of 9.5 or 10 with solids recirculation. $Mg(OH)_2$ and $Fe(OH)_2$ were tested in Phase 2.

The concentrations of dissolved $MgCl_2$ and freshly precipitated (also referred to as preformed) $Mg(OH)_2$ used in Phase 1 were 100, 200, 600, 1,000, 1,200, and 10,000 mg/L as Mg^{2+}. The concentration of freshly precipitated (also referred to as preformed) $Fe(OH)_3$ used in Phase 1 was 2,300 mg/L as Fe^{3+}. In Phase 2, preformed $Mg(OH)_2$ concentrations were 0.5, 1, and 3 mg/L as Mg^{2+} and preformed $Fe(OH)_3$ concentrations were 1.15 and 2.3 mg/L as Fe^{3+}.

Phase 1 demonstrated that in tests were no calcium was present, preformed $Mg(OH)_2$ solids removed more silica than $Mg(OH)_2$ solids that precipitated during tests with dissolved $MgCl_2$. This result suggested that adsorption was a more dominant removal mechanism than co-precipitation. The first 11 tests with $MgCl_2$ and $Mg(OH)_2$ were compared on the basis of initial pH, but it was determined that final pH would offer a more accurate comparison.

The jar testing completed during Phase 1 served two purposes, the first of which was to explore the question of which mechanism – adsorption or co-precipitation – is more dominant in silica removal. The second goal was to establish some ideal operating parameters (i.e., magnesium concentration, pH, hydraulic residence time) to be used during phase two of the project. The flow-through experimentation phase looked at silica removal over an extended period of time within a system that recirculated solids.

Results showed that freshly precipitated magnesium hydroxide solids achieve significant silica removal in the pH range of 9.5 to 10, despite the common assertion that good removal can only be achieved at a pH greater than 10. Furthermore, findings from Phase 1 suggested that adsorption was the more dominant removal mechanism during the softening process. Phase 2 results supported findings of Phase 1, and demonstrated that freshly precipitated $Mg(OH)_2$ solids were good silica adsorbents but that silica removal was limited by adsorption capacity of the solids present in the system. Phase 2 results also supported the hypothesis that increased solids recycle in a system will enhance silica removal.

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CHAPTER 1: INTRODUCTION

The purpose of water treatment is to remove harmful or problematic constituents from ground and surface waters prior to its consumption, industrial supply, or other use. Similarly in wastewater treatment, certain organic and inorganic compounds must be removed before water may be discharged to the environment. In some circumstances, non-hazardous constituents can be problematic; the compound silica, or SiO_2, falls into this latter category. Silica in drinking water is not harmful to humans or animals, but it will cause scaling of industrial equipment and reverse osmosis membranes (Al-Mutaz and Al-Anezi 2004; Al-Rehaili 2003; Badruzzaman et al. 2011; Batchelor et al. 1991; Chao and Westerhoff 2002; Chen et al. 2006; Cheng et al. 2009; Chuang et al. 2006; Den and Wang 2008; Kimura et al. 2013; Koo et al. 2001; Milne et al. 2014; Neofotistou and Demadis 2004; Ning 2002; Sanciolo et al. 2014; Semiat et al. 2003; Sheikholeslami and Bright 2002; Sheikholeslami et al. 2001), which results in decreased process efficiency and significant monetary losses.

In industrial applications, silica scales can form on turbines, boilers, heat exchangers, and transfer pipes. Silica scaling is also problematic in water treatment methods that utilize membranes. For instance, silica scaling on nanofiltration (NF) and reverse osmosis (RO) membranes can be an issue when treating brackish groundwater for municipal distribution or in treating wastewater from some manufacturing processes. Silica scaling decreases the flux and increases the frequency with which membranes must be cleaned or replaced, both of which are expensive and result in higher operation and maintenance costs for companies that employ membrane treatment.

In cooling towers, nonvolatile compounds like silica become concentrated and inorganic scaling can occur on the surfaces of heat exchangers if the concentration exceeds the solubility limit; the scaling results in a loss of heat transfer efficiency (Batchelor et al. 1991). With regards to steam generating installations, silica may form scales on turbine blades which will cause excessive equipment wear (ASTM International 2010). Municipal water treatment, microelectronics production, ultrapure water generation, and mining and natural gas operations are other examples of industries that rely on single- or multi-pass reverse osmosis treatment (Milne et al. 2014; Ning 2002); membrane fouling due to silica or other compounds is often a concern for these industries.

Research on silica has demonstrated its troublesome nature and there is opportunity to expand on the subject of how it may be removed from water. Most commonly, silica is removed using a water softening process. Water softening serves to principally remove Mg^{2+} and Ca^{2+}. During water softening, silica might be captured during precipitation of calcium carbonate or magnesium hydroxide compounds or it can adsorb to the surface of existing or newly formed solids. Other treatment methods employed to remove silica include ion exchange, distillation, reverse osmosis, and coagulation with filtration (ASTM International 2010; Cheng et al. 2009; Chuang et al. 2006). To varying degrees, these methods can be effective in removing both soluble and insoluble silica from water; but, as mentioned above, the chemical and physical properties of silica make it difficult to remove. Chemical and physical properties can include charge, size, solubility volatility, and polarity. Not only is there room for

improvement in the efficiency of silica removal processes, but there is a genuine need to more thoroughly understand the mechanism by which silica is extracted from water.

Studies have shown that silica removal by precipitation processes is dependent on the presence of magnesium in the water and less on calcium (Al-Mutaz and Al-Anezi 2004; Chao and Westerhoff 2002; Chen et al. 2006; Cob et al. 2014; GE Water & Process Technologies n.d.; Sheikholeslami et al. 2001; Sheikholeslami and Bright 2002). As such, this research focused on silica removal by magnesium precipitation. To more fully understand the role of magnesium in silica removal, the project was broken up into two phases:

- Phase 1: Jar Testing

- Phase 2: Flow-Through Experimentation with Solids Recycle

The jar testing completed during Phase 1 served two purposes, the first of which was to explore the question of which mechanism – adsorption or co-precipitation – is more dominant in silica removal. The second goal was to establish operating parameters – i.e., magnesium concentration, pH, hydraulic residence time – that would be applied to Phase 2 testing. The question of how solids recycle might influence silica removal is a subject that has received little attention. As such, the flow-through experimentation in Phase 2 was aimed at examining silica removal over an extended period of time within a system that recirculated solids.

The main hypothesis of this work was that silica removal via adsorption or chemical co-precipitation would be enhanced within a system that recirculated a high concentration of solids. There is no consensus in the literature as to which mechanism, adsorption or co-precipitation, is more dominant; however, the one conjecture that could

be made was that both mechanisms would likely play *some* role in silica removal, regardless of which was more dominant.

Objectives

In summation, the research objectives of Phases 1 and 2 of this project were to:

- Explore the removal of silica by a chemical softening process that utilized solids recycle with a high solids concentration.

- Establish optimum operating parameters for the softening process.

- Gain further insight into adsorption and/or co-precipitation as the mechanism for silica removal.

CHAPTER 2: BACKGROUND AND LITERATURE REVIEW

The subject of silica removal has been the focus of many studies because silica scales can damage reverse osmosis membranes and industrial equipment. In spite of the considerable effort that has been made to understand the causes of silica scaling and to develop effective methods of scale mitigation, it remains a complex subject. The background and literature review presented in this chapter are intended to shed light on the problem of silica removal in water treatment.

Silica Chemistry

The term silica refers to the compound SiO_2, or silicon dioxide. Silica is ubiquitous in nature. It composes a significant portion of the earth's crust and is even found in the tissues of living organisms. Silica is found in most surface waters, wells, and deep aquifers owning to the degradation of silica containing rocks and minerals. Silica can exist in different crystalline and amorphous phases, and solubility varies depending on phase (Iler 1979). In crystalline form, silica is generally found as quartz (SiO_2) or cristobalite (SiO_2) and has a very low solubility (Sheikholeslami and Tan 1999). According to Sheikholeslami et al. (2001), silica in an amorphous phase has the highest solubility, especially at ambient temperatures and a pH less than 8. Furthermore, variables like temperature, pH, salt concentration, silica concentration, and pressure can influence the solubility of silica (Den and Wang 2008; Hermosilla et al. 2012; Koo et al. 2001; Sheikholeslami et al. 2001).

This thesis is concerned with the presence of dissolved, amorphous silica species in water. In an aquatic environment, the existence of silica is further complicated by its

speciation and its removal from water can be tricky owing to its chemical and physical properties.

Silica Speciation

In water, silica can refer to both dissolved and suspended forms and it is found in surface and ground waters in concentrations generally ranging from $1 - 30$ mg/L but depending on the water source can exceed concentrations of 100 mg/L (Al-Rehaili 2003; APHA et al. 1995; ASTM International 2010; Koo et al. 2001; Neofotistou and Demadis 2004). The aqueous chemistry of silica is complex. Silica may be found in water as suspended particulates, colloidal or polymeric matter, hydroxides, silicate ions, and acids (Al-Rehaili 2003; APHA et al. 1995). Silicates, which are made up of a silicon-oxygen anion bonded with a metal cation, may also be found in ground and surface waters. Exact speciation depends on factors like concentration, temperature, pH, TDS, alkalinity, and presence of multivalent ions (Al-Rehaili 2003; Den and Wang 2008; Hermosilla et al. 2012; Koo et al. 2001; Sheikholeslami et al. 2001). There is occasionally some confusion with regards to the terminology of silica species (Sheikholeslami et al. 2001). Silica in water is generally referred to as H_4SiO_4, which is an oversimplification because multiple species of silica – monomeric, polymeric, colloidal, particulate, and ionic – can exist in water at any given time (Milne et al. 2014). The following is an overview of silica species found in natural waters.

Monomeric Silica

In water, dissolved silica typically exists as silicic acid, $Si(OH)_4$, and metasilicic acid, H_2SiO_3 (Bremere et al. 2000; Sheikholeslami et al. 2001). It is also referred to as reactive silica, orthosilicic acid, monosilicic acid, dissolved silica, or monomeric silica. In

natural waters at a neutral pH and temperature around 25°C, monomeric silica will dominate until a concentration of around 2 x 10^{-3} M, at which point it will begin to polymerize and eventually form polymeric silica (Iler 1979; Ning 2010; Sheikholeslami and Tan 1999).

Polymeric Silica

Polymeric silica, also called polysilicic acid, includes dimers, trimers, and oligomers of monomeric silica. It is less reactive than monomeric silica and thought to be unstable and relatively transient in nature (Milne et al. 2014; Ning 2010). It is typically less than 5nm in diameter (Sheikholeslami and Tan 1999) and as it grows colloidal silica is formed.

Colloidal Silica

Colloidal silica, which is soluble and sometimes designated as unreactive silica, is characterized as large polymeric structures (Bremere et al. 2000); thus, colloidal silica has the general formula $n\text{SiO}_2 \cdot n\text{H}_2\text{O}$. The most commonly used definition states that silica colloids are 5 nm in size or greater (Iler 1979; Milne et al. 2014), but smaller than particulate silica, as described below. Because of its small size, filtration is not effective in removing colloidal silica from suspension (Ning 2002).

Particulate Silica

Particulate silica is larger in size than colloidal silica. It is unreactive and insoluble. It is commonly defined as silica that can be captured on a filter; however, there is no accepted definition of the size of particulate silica, though some characterize it as being larger than 45 μm, as that is the typical filter sized used to remove it from solution for characterization as dissolved or particulate (Milne et al. 2014). Particulate silica can

form in super silica-saturated solutions by means of agglomeration or crystal growth (Milne et al. 2014).

Iler (1979) describes the progression of particulate silica formation in three stages: (1) Monomeric polymerization that results in particle formation, (2) Growth of particles, and (3) Particles that have linked together to form chains and then networks within a liquid, resulting in gel formation.

Ionic Silica

Silica ions are released into water when silicic acid undergoes deprotonation according to the following equation:

$$H_4SiO_4 \leftrightarrow H^+ + H_3SiO_4^-; \ pK_a = 9.83 \ at \ 25°C \tag{1}$$
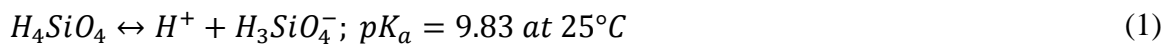
Sheikholeslami et al. (2001) demonstrated that silica polymerization is most likely to occur between a pH of 5.5 and 9.5. Above 9.5, monosilicic acid begins to dissociate and become more soluble, at which point silicate ions like $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ dominate in solution.

Visual MINTEQ v. 3.0 – a program used to model chemical equilibrium, speciation, solubility, and reactions in natural waters (KTH 2013) – was used to model the solubility of monosilicic acid, which is presented in Figure 2-1.
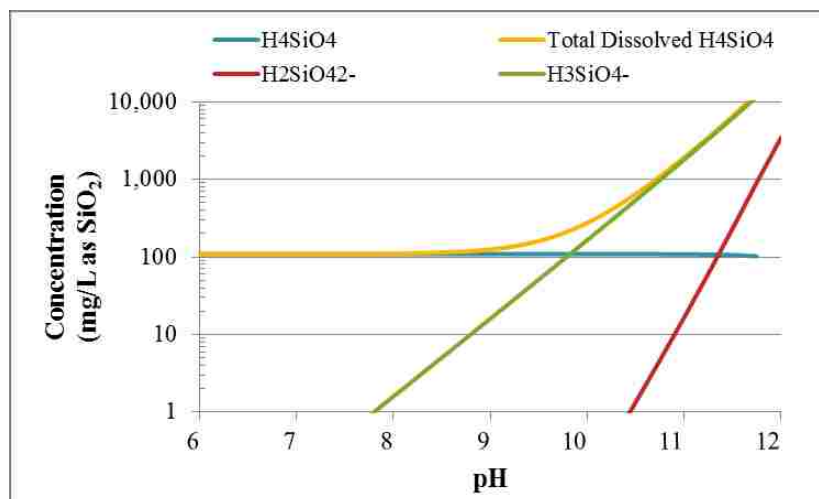
Figure 2-1: Solubility of Monomeric Silica Between pH Values of 6 and 12 Modeled in Visual MINTEQ

Ionic silica is easier to remove from water that uncharged species of silica. Charged species, for instance, can be removed by ion exchange or by adsorption if there is a high affinity between the surface of the adsorbent and the charged particles.

Silica Scaling

The problem of silica scaling on RO membranes and industrial equipment is ultimately an expensive one. Silica scales cannot easily be removed and require cleaning with corrosive acids and chemicals (Milne et al. 2014; Neofotistou and Demadis 2004). RO is commonly employed to desalinate brackish groundwater or brackish water from mining and natural gas operations (Badruzzaman et al. 2011; Milne et al. 2014). It is also used to treat water used in microelectronics production and ultrapure water generation (Ning 2002). These applications often rely on multi-stage RO treatment and it is in the later stages where silica fouling can become a significant problem because the concentrations are highest (Badruzzaman et al. 2011).

In RO treatment, membrane fouling can occur when certain compounds – particularly those containing silica, carbonate, calcium, magnesium, sulfate, strontium,

barium and phosphate – become increasingly concentrated and exceed their respective solubility limits, resulting in precipitation of solids that accumulate on the membrane surface (Abdel-Wahab and Batchelor 2006; Badruzzaman et al. 2011; Milne et al. 2014). In the long term, fouling will deteriorate a membrane, ultimately necessitating its replacement. In the short term, membrane fouling decreases RO system flux and recovery (Badruzzaman et al. 2011).

Water with high concentrations of silica may require its removal prior to RO treatment (Al-Rehaili 2003; Koo et al. 2001). During RO treatment silica becomes highly concentrated and can quickly exceed its solubility limit resulting in precipitation of solids that may form deposits on the membrane; it is for this reason that scaling is a more significant problem during multi-stage RO treatment. Membrane fouling can also occur when aluminum or iron ions react with dissolved silica to form sparingly soluble aluminum or iron silicates (Bremere et al. 2000). High concentrations of aluminum and iron may occur when dissolved Al or Fe is present in the feed water, either naturally or as a residual concentration from upstream coagulation/flocculation processes. Cob et al. (2012) found that for a range of RO recoveries, silica and aluminosilicate scaling occurred during a second stage RO process. Their treatment process included cation exchange (CIEX) followed by nanofiltration and then RO.

It has been said that effective silica scale mitigation is one of biggest issues in desalination (Sheikholeslami and Zhou 2000). Many explanations have been proposed for the cause of silica fouling (Badruzzaman et al. 2011).

1. In highly silica-saturated waters, extensive polymerization occurs and leads to formation of sub-micron colloidal silica that accumulates on the

membrane surface (Semiat et al. 2003). In waters with low silica concentrations, the authors suggest that membrane deposition occurs primarily because of monomeric silica species. Batch tests by Sheikholeslami and Tan (1999) demonstrated this idea that polymerization increases as silica concentration increases. They found that polymerization occurred in supersaturated conditions and resulted in formation of porous colloidal silica deposits on the membrane surface.

2. During filtration or RO, amorphous silica becomes concentrated. Silica polymers and colloids begin to build up on the membrane surface owing to concentration polarization (Bremere et al. 2000).

3. Koo et al. (2001), Sheikholeslami and Zhou (2000), and Sheikholeslami et al. (2001) demonstrated that increased concentrations of hardness – Ca and Mg – facilitate silica polymerization and, thus, colloidal silica formation and membrane fouling. Both studies also suggest that magnesium has a greater effect on polymerization than calcium. Magnesium catalyzes polymerization by decreasing the solubility of silica at a neutral pH range (Sheikholeslami and Zhou 2000).

4. Colloidal silica in solution accumulates on membrane surfaces and forms a porous film on the surface (Sheikholeslami and Tan 1999). Colloidal silica deposits are argued to be one of the most deleterious membrane foulants that form in industrial process waters (Neofotistou and Demadis 2004).

5. Monosilicic and polysilicic acid may react with metal hydroxides in the water to form silicates that are deposited on the membrane surface

(Sheikholeslami et al. 2001; Sheikholeslami and Tan 1999). Unlike porous colloidal silica deposits, Sheikholeslami and Tan (1999) point out, the monosilicic acid forms a film that is more glasslike.

6. Dissolved metals react with dissolved silica to form silicates with very low solubilities (Gabelich et al. 2005).

7. Den and Wang (2008) presume that silica scaling either happens when monomeric silica is first deposited on the membrane surface and is subsequently polymerized or when silica colloids accumulate on the membrane.

Common Silica Treatment Methods

Because silica scale can be extremely difficult and costly to remove from RO membranes (Milne et al. 2014; Neofotistou and Demadis 2004; Sheikholeslami et al. 2001), silica should ideally be removed during pretreatment. Removal of bivalent ions – which can form insoluble scaling salts and foul RO and NF membranes – during pretreatment is a relatively easy feat; however, any silica or metal silicates that remain will ultimately limit recovery (Cob et al. 2012). Certain RO pretreatment methods like micro- or ultrafiltration, use of antiscalants, or chemical cleaning serve to reduce fouling (Badruzzaman et al. 2011). Antiscalants – which work by disrupting or distorting crystal formation – are generally unsuccessful in prohibiting colloidal silica formation because of the amorphous structure of silica in water (Neofotistou and Demadis 2004). Milne et al. (2014) outline three common methods to reduce membrane fouling potential: (1) removal of hardness followed by RO operation at a high pH, (2) RO operation at a low pH, and (3) silica reduction by a pretreatment or intermittent treatment stage. The first

method is effective because, as was already discussed, silica solubility increases with pH largely owing to the formation of charged species. In the absence of hardness, silica is less likely to polymerize and form scales on the RO membrane surface. The second method is effective because it has been shown by Iler (1979) that silica solubility at a pH of 2 is around 150 mg/L (Milne et al. 2014). The third method is effective because if there are lower concentrations of silica in the feed water, there is reduced silica polymerization as silica concentrates during treatment.

In a study that investigated inhibition of silica formation by means of different antiscalants, Neofotistou and Demadis (2004) found that the formation of silica scale is likely to occur at a pH less than 8.5; they also determined that magnesium silicate scale occurs when the pH exceeds 8.5 and there is a high magnesium concentration. These results correspond with those of the Sheikholeslami et al. (2001) study that concluded silica polymerization is greatest at a pH below 9.5; however, at a pH greater than 9.5, silicates are likely to form if ample Ca and Mg hardness is present. The polymerization of silica leads to formation of colloidal silica and, thus, an increase in membrane fouling potential. Formation of calcium and magnesium silicates can also increase fouling potential.

Methods to remove silica include chemical softening, adsorption, co-precipitation, ion exchange, distillation, reverse osmosis, and coagulation with filtration. The effectiveness of each process depends upon that process's ability to exploit physical and chemical properties of the constituent in question. In the case of silica, this is not straightforward and efforts to improve silica removal are ongoing.

Lime Softening

The most common method for silica removal is water softening, particularly lime softening, the goal of which is to eliminate water hardness primarily due to the presence of Mg^{2+} and Ca^{2+} ions (Sheikholeslami et al. 2001). During lime softening, hydrated lime – $Ca(OH)_2$ – is added to hard water to precipitate $CaCO_3$ and $Mg(OH)_2$, which are then removed by sedimentation or filtration (Al-Mutaz and Al-Anezi 2004; GE Water & Process Technologies n.d.). These magnesium and calcium compounds are removed prior to RO treatment to minimize membrane fouling. Sometimes soda ash, Na_2CO_3, is added in conjunction with lime if the dissolved CO_2 concentration is not sufficient for $CaCO_3$ precipitation (GE Water & Process Technologies n.d.). Al-Mutaz and Al-Anezi (2004) list the main objectives of lime-soda ash softening as:

1. Removal of CO_2

2. Removal of hardness due to carbonate species

3. Removal of non-carbonate calcium hardness – i.e., $CaSO_4$ or $CaCl_2$

4. Removal of non-carbonate magnesium hardness – i.e., $MgCl_2$ or $MgSO_4$

According to the GE Water & Process Technologies *Handbook of Industrial Water Treatment* (n.d.), cold lime softening is carried out at room temperatures while warm and hot lime softening are operated at temperatures of 49-60°C and 108-116°C, respectively. GE (n.d.) reports that the hot lime process not only ensures removal of hardness but reduction of silica, as well. Even at ambient temperatures, though, it has been demonstrated that lime softening is effective in reducing silica. When $CaCO_3$ and $Mg(OH)_2$ precipitate during lime softening, soluble and insoluble silica can be removed when particles are trapped by precipitated solids or adsorb to the surfaces of precipitated solids (Al-Mutaz and Al-Anezi 2004). Sheikholeslami et al. (2001) claim the

precipitation of magnesium hydroxide during the lime softening process is the driver for silica removal because silica adsorbs to the surface of the magnesium solids. Since silica removal is dependent upon water hardness, there must be ample hardness present to sufficiently reduce silica during treatment; otherwise, chemicals must be added. Although lime softening can effectively remove silica from water, there are some drawbacks to consider with regards to chemical usage and waste produced. For instance, if chemicals must be added to increase water hardness, not only does this necessitate the purchase of extra chemicals but there is ultimately more solid waste production. The issue of sludge disposal is often an important concern in chemical softening processes (Chao and Westerhoff 2002).

There has been considerable research focused on silica removal via chemical softening and even more specifically on lime softening (Abdel-Wahab and Batchelor 2006; Al-Mutaz and Al-Anezi 2004; Al-Rehaili 2003; Batchelor et al. 1991; Chao and Westerhoff 2002; Chen et al. 2006; Masarwa et al. 1997; Sheikholeslami and Bright 2002; Sheikholeslami et al. 2001; Tarquin 2005). With the exception of Tarquin (2005), all of these studies also evaluated the effects of removal by lime in conjunction with other compounds like soda ash, sodium aluminate, ferric chloride, alum, or various polymers. Al-Rehaili (2003) found that it was necessary to add precipitation aids – aluminum compounds, iron compounds, or polymers – during a lime-soda ash treatment process to achieve adequate removal, which was defined as silica residual of less than 18 mg/L.

Batchelor et al. (1991) conducted a study that focused on an ultra-high lime (UHL) treatment process for silica removal from recycled cooling water. UHL works by maintaining a very high pH and a high calcium concentration and silica is removed as a

calcium silicate precipitate. Their process was two-stage. During the first stage, excess amounts of lime were added to increase the pH to around 11 or 12. Silica, magnesium, and some sulfate, they reported, were removed during this stage – the silica removed was in the form of CaH_2SiO_4 or MgH_2SiO_4. The second stage involved addition of carbon dioxide and soda ash to remove calcium as $CaCO_3$. The authors cite the importance of stoichiometry in the UHL process; to precipitate CaH_2SiO_4, the calcium to silica molar ratio should be 1.0.

The Batchelor et al. (1991) study is the only one in this review that incorporated solids recycle with high solids concentration. Results demonstrated that good silica removal was affected by pH, temperature, hydraulic retention time, and solids retention time. Furthermore, the authors concluded that suspended solids concentration was the best parameter on which to gauge what kind of silica removal would be achieved. Even though high pH was determined to be a necessary factor, the researchers indicated that ample solids (reactor solids greater than 1000 mg/L at 25°C or 400 mg/L at 35°C and 45°C) must also be present to facilitate precipitation kinetics necessary to generate calcium silicate and thereby remove silica. Lastly, they found that lime doses of 0.5 g/L – 6.7 mM $Ca(OH)_2$ – or less were sufficient in operation of the UHL process.

Research by Tarquin (2005) on silica removal from RO brine was based on two different concepts. The first concept utilized a two-step membrane process of nanofiltration – to remove hardness – followed by RO to concentrate silica. The idea was that silica would be less likely to precipitate, even though highly saturated, in the absence of hardness. The second method of silica removal explored lime treatment of different nanofiltration and RO waste and permeate streams followed by RO. Results showed that

precipitation of silica from brine with high silica concentrations can be influenced by the presence of calcium hardness. Alkalinity, too, can impact silica removal when lime is added.

Masarwa et al. (1997) studied a Compact Accelerated Precipitation Softening (CAPS) process that employed both lime and sodium hydroxide as softening compounds. They supplemented the lime softening with $AlCl_3$ and $ZnCl_2$ to explore the effect on silica removal and found that on a molar basis, aluminum was more effective; however, the silica removal came at the expense of removal of calcium hardness.

Chen et al. (2006) offered a comparison between a lime-soda ash softening process to remove silica to one that utilized coagulation in addition to softening. Their research led them to the conclusion that magnesium is more effective in removing silica than calcium. Removal ratios were determined to be 0.044 mg SiO_2/mg $Mg(OH)_2(s)$ and 0.027 mg SiO_2/mg $CaCO_3(s)$. They also found that softening and coagulation were effective silica treatment techniques.

Al-Rehaili (2003) noted that silica removal during lime softening may be enhanced by the addition of coagulants like ferric chloride and aluminum salts but that removal is dependent on the amounts of iron and aluminum precipitates that form. The interest in understanding the role of coagulants in silica removal is a common theme in some of the literature and to varying degrees of significance, it has been found that coagulants aid in silica removal during the softening process (Al-Rehaili 2003; Chen et al. 2006).

One conclusion that may be drawn from the studies on lime softening is that calcium alone is not responsible for silica removal. Silica reduction seems to be

dependent on the formation of magnesium hydroxide and is enhanced by the inclusion of an aluminum or iron compound.

Non-Softening Methods

Various studies on removal by coagulation have been conducted (Chen et al.2006; Cheng et al. 2009; Chuang et al. 2006; Davis et al. 2002; Gabelich et al. 2005; Hermosilla et al. 2012). Hermosilla et al. (2012) evaluated removal during RO pretreatment by coagulation with different polyaluminum chlorides (PACls) and $FeCl_3$. Research by Chuang et al. (2006) considered removal of colloidal silica using coagulation and filtration processes and compared the effectiveness of alum, Al_2O_3, and polyaluminum chloride (PACl) in silica removal from waters of an industrial park. Alum, or aluminum sulfate, is a common coagulant used in RO treatment but in the presence of silica can lead to the problem of membrane fouling when dissolved aluminum and silica react to form aluminum silicates (Gabelich et al. 2005). The researchers studied the effects of using metal chelating agents to limit formation of aluminum silicates and, thus, reduce fouling potential. Of the various silica adsorption techniques, Milne et al. (2014) reports that adsorption onto aluminum compound seems to be the most effective. Iron compounds, while a good silica adsorbent, can form an unwanted hard, glass-like scale. Other methods that have been studied include in-line coagulation/ultrafiltration (Cheng et al. 2009) electrocoagulation pretreatment (Den and Wang 2008). Table 2-1 presents an overview of the silica removal methods that were evaluated in the literature reviewed for this thesis.

Table 2-1: Summary of Previous Studies on Silica Removal Methods

Process	Removal Compound	Molecular Formula	Notes on Silica Removal	Reference
Ultra-High Lime with Aluminum (UHLA)	Dry Lime Dry Sodium Aluminate	$Ca(OH)_2$ $NaAlO_2$	Two initial Si concentrations of 1.5 mM and 3.0 mM (or about 3.2 and 6.4 mM as SiO_2, respectively) were tested. The $NaAlO_2$ dose was 50% of the $Ca(OH)_2$ dose. Results showed that silica removal increased as the molar ratio of lime dose to intial [Si] increased and also as pH increased. For an intial Si concentration of 1.5 mM with a ratio of 1 mol $Ca(OH)_2$/mol intial Si and a pH of 11.6, silica removal was about 40%. Removal increased to just under 80% for a ratio of 2 mol lime/mol Si and appoximate pH of 11.8 and then increased to almost 100% for a ratio of 4 mol lime/mol Si and pH of 12. For an initial [Si] of 3.0 mM at a ratio of 0.5 $Ca(OH)_2$/inital Si and pH around 11.7, almost 40% Si removal was acheived. Removal increased to about 65%, 95%, and 100% for the following respective ratios and pH values: 1 mol lime/mol Si and pH of 11.9, 2 mol lime/mol Si and pH of 12, and 3 mol lime/mol Si at a pH of 12.2. Calcium silicate and calcium aluminosilicate were determined to be the only critical calcium compounds that precipitated in the system.	Abdel-Wahab and Batchelor 2006
Chemical Softening	Lime Soda Ash Sodium Aluminate	$Ca(OH)_2$ Na_2CO_3 $NaAlO_2$	Removal was studied over a pH range of 8.2 and 10.8 and found to be best above a pH of 10. In tests with both lime and soda ash operated at an average pH of 8.9 and an average silica concentration of 16 ppm, average silica removal was around 44%. In tests that included only lime, an average silica concentration of 10.6 ppm, and an average pH of 9.9, a removal of roughly 60.5% was observed.	Al-Mutaz and Al-Anezi 2004
Chemical Softening	Lime Soda Ash Alum Caustic Soda Sodium Aluminate Ferric Chloride Polymer	$Ca(OH)_2$ Na_2CO_3 $Al_2(SO_4)_3$ $NaOH$ $NaAlO_2$ $FeCl_3$ Various	The goal was to reduce silica to a level below 18 mg/L in two different source waters with intial silica concentrations of 23.4 mg/L (Water 1) and 34.6 mg/L (Water 2). 27% was the highest removal achieved for Water 1 using a combination of 110 mg/L lime, 120 mg/L soda ash, and 15 mg/L sodium aluminate. The highest removal for Water 2 was 58% using a 180 mg/L dose of caustic soda alone. The second highest level of removal was 51% using a combination of 120 mg/L lime, 350 mg/L soda ash, 50 mg/L alum, and 0.1 mg/L polymer.	Al-Rehaili 2003
Ultra-High Lime (UHL) Softening	Lime	$Ca(OH)_2$	For continuous flow experiments, the authors concluded that typically a lime dose greater than 0.5 g/L (or 6.7 mM) was required for silica removal.	Batchelor et al. 1991
Chemical Softening	Lime Soda Ash Ferric Chloride Ferric Sulfate Aluminate Salt	$Ca(OH)_2$ Na_2CO_3 $FeCl_3$ $Fe_2(SO_4)_2$ $Na_2Al_2O_4$	Silica removal was not the primary target in this study; removal of hardness was also evaluated. The highest level of Si removal (48%) was achieved using a 528 mg/L lime dose and 148 mg/L soda ash dose. In experiments with iron, removal was not found to be significant until a dose of 40 mg/L or more was added.	Chao and Westerhoff 2002
Chemical Softening and Coagulation	Lime Soda Ash Polyaluminum Chloride (PACl)	$Ca(OH)_2$ Na_2CO_3 -	Higher pH (> 9.9) was determined to be more effective for silica removal because of presence of $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ increased electrostatic attraction between silicate ions and calcium and magnesium solids. Removal ratios were statistically determined to be 0.044 mg SiO_2/mg $Mg(OH)_2(s)$ and 0.027 mg SiO_2/mg $CaCO_3(s)$. Softening was found to remove about 80% silica, while coagulation was found to remove only 40%.	Chen et al. 2006

In-line Coagulation and Ultrafiltration	Alum	Al_2O_3	A maximum of 65% silica removal was achieved with an alum dose of 30 mg/L as Al_2O_3 at a pH of 7.1. The average initial silica concentration was 30 mg/L; thus, at the highest level of removal, 1.1 mol SiO_2 was removed per mol Al_2O_3.	Cheng et al. 2009
Coagulation and Flocculation	Polyaluminum Chloride (PACl) Alum Polyacrylic Acid (PAA)	- Al_2O_3 -	The range of coagulant dosage was 30-150 mg/L Al_2O_3 and removal capacity was found to be 0.135 mg SiO_2/mg Al_2O_3. Coagulation and flocculation experiments were carried out at a pH of 7.5. Colloidal silica removal was found to increase as Al_2O_3 dosages increased for alum and PACl. For alum, colloidal silica was 9.3% for a 30 mg/L Al_2O_3 dose and 43.9% for a 150 mg/L Al_2O_3 dose. Colloidal silica removal by PACl at the afformentioned 30 and 150 mg/L Al_2O_3 doses was 27.2% and 65.9%, respectively.	Chuang et al. 2006
Cation Exchange (CIEX), Nanofiltration (NF), Reverse Osmosis (RO)	-	-	This study looked at removal or reduction of Ca^{2+}, Ba^{2+}, and Mg^{2+} during pretreatment with CIEX in order to limit the potential for RO membrane fouling due to salt formation. The primary culprits of RO membrane fouling in this study were determined using SEM-EDX analysis and found to be Si, Al, Fe, and O. In order to maintain RO recovery above 94%, it was concluded that silica must either be removed during pretreatment or must remain in solution during the RO process.	Cob et al. 2012
Precipitation with Fe^{3+}, Al^{3+}, and Silica Gel	-	-	Removal of silica via precipitation with $Fe(OH)_3$, $Al(OH)_3$, and silica gel was evaluated in this study and precipitation with $Al(OH)_3$ was found to be the most effective. The initial silica concentration in the synthetic water was 200 mg/L. Fe^{3+} doses of 100 and 200 mg/L were tested at a pH of 8.5 and silica removal was observed over a 6 hour period. Based on the results presented by the authors, removal by the 200 mg/L dose appears to be higher than the 100 mg/L dose at 30 minutes and 1 hour, but was still only around 10%. At 6 hours, both doses had achieved removal of around 35%, (maximum removal). Based on their numbers, for 100 and 200 mg/L Fe doses, an estimated 0.56 mol SiO_2 and 0.28 mol SiO_2 was removed per mol Fe, respectively; thus, removal did not increase with Fe dose. Removal with Al^{3+} was much more efficient and occured quickly. At a pH of 8.5 with a 400 mg/L Al dose, almost all silica was removed within ten minutes. 99.9% removal was achieved by 1 hour. For 200 and 300 mg/L Al doses, roughly 95% and 99% removal, respectively, was achieved by 1 hour.	Cob et al. 2014
Electrocoagulation	-	-	The optimum conditions for silica removal were determined to be a hydraulic residence time of 30 minutes with a current intensity of 0.5 A. Up to 80% removal of silica in water containing SiO_2 concentrations between 80 mg/L and 200 mg/L were observed under the optimum conditions.	Den and Wang 2008
Coagulation Pretreatment	Polyaluminum Chlorides (PACls) Ferric Chloride	- $FeCl_3$	At a pH of 10.5, high basicity PACls at a dose of 2500 mg/L achieved roughly 100% silica removal. FeCl3 doses of 2000, 3000, 6000, and 3500 mg/L were tested at pH values of 5.5, 8.6, 10.5, and 5.5, respectively. Silica removal rates were between 17-32%.	Hermosilla et al. 2012

Compact Accelerated Precipitation Softening (CAPS) Lime Process with	Lime Caustic Soda Aluminum Chloride Zinc Chloride	$Ca(OH)_2$ $NaOH$ $AlCl_3$ $ZnCl_2$	Al was found to be better than Zn in the removal of silica. A 10 ppm dose in conjunction with 2-3 mM lime removed more than 50% Si; however, Si was found to be removed at the expense of Ca removal.	Masarwa et al. 1997
Chemical Softening	Lime Soda Ash Sodium Aluminate	$Ca(OH)_2$ Na_2CO_3 $NaAlO_2$	Results showed that silica polymerization (and, therefore, potential for membrane fouling) can be reduced by operating desalination processes above a pH of 9.5. Additionally, silica removal of about 50% was achieved with a NaAlO2 dose of 20-21.7 mg/L. A lime dose of 150 mg/L at a pH of 10.2 was found to remove 67% silica.	Sheikholeslami et al. 2001
Precipitation and Coagulation	Lime Soda Ash Caustic Soda Alum Ferric Chloride	$Ca(OH)_2$ Na_2CO_3 $NaOH$ $Al_2(SO_4)_3$ $FeCl_3$	An optimum NaOH dose was found to be 200 mg/L and removed 91% silica. It was presumed that removal was achieved via coprecipitation with precipitated insoluble metal hydroxides. The most effective lime and soda ash combination for silica and hardness removal was 150 mg/L $Ca(OH)_2$ and 450 mg/L $Na2CO_3$. Silica removal with these doses was 68%. Alum doses of 0-25 mg/L were tested. Lower doses achieved silica removal above 90% at a pH above roughly 10.8. Removal decreased for the 20 and 25 mg/L doses to about 90% and 80%, respectively; it was argued that the decrease in removal corresponded to a lower pH range of 10.6-10.7. Removal by Fe largely followed the same trend. Roughly 90% removal was achieved for doses between 10 and 25 mg/L $FeCl_3$ at a pH of around 10.7. Lower silica removal was achieved at lower pH values.	Sheikholeslami and Bright 2002
Chemical Softening	Lime	$Ca(OH)_2$	It was shown that a higher initial silica concentration corresponded to a higher rate of silica removal by lime. For example, an initial silica concentration of 250 mg/L corresponded to about 0.38 mg SiO_2 removed per mg lime. An initial silica concentration of 150 mg/L corresponded to 0.17 mg SiO_2 removed per mg lime. The reason for this, it is explained, is that silica becomes more unstable in highly silica-saturated solutions.	Tarquin 2005

Role of Adsorption and Co-precipitation in Silica Removal

An understanding of the mechanism – adsorption or co-precipitation – by which silica is removed from water may suggest improvements in silica removal by precipitation processes. For the purposes of this project, adsorption is defined as the adherence of silica to surfaces of preformed compounds while co-precipitation is defined as removal of silica that becomes trapped in solids as they precipitate, or that precipitate with ions in solution to form metal silicates.

The literature suggests that both adsorption and co-precipitation may play a role in silica removal and that one may be more dominant than the other depending on what

salt or metal is being introduced to the water; however, there does not seem to be any agreement as to which is the principal driver for removal. Although existing research addresses the topic of adsorption or co-precipitation as removal mechanisms, it has not been the main focus of any study. Furthermore, none of the literature reviewed herein employed specific methods to differentiate removal by adsorption and co-precipitation.

The Batchelor et al. (1991) study that focused on UHL treatment points to references that call out both adsorption and co-precipitation as responsible for removal. The GE Water & Process Technologies *Handbook of Industrial Water Treatment* (n.d.) reports that silica removal during a hot lime softening process is a result of silica adsorption to the surfaces of precipitated magnesium hydroxide. In the event of inadequate $Mg(OH)_2$ concentration, compounds like magnesium oxide, magnesium hydroxide, magnesium sulfate, magnesium carbonate, or dolomitic lime may be added during treatment (Al-Rehaili 2003; Batchelor et al. 1991; GE Water & Process Technologies n.d.).

Sheikholeslami and Bright (2002) surmise that silica may be removed by co-precipitation with soluble metals or by adsorption with insoluble hydroxides added to water. The authors found that alumina serves as a good adsorbent for silica but that magnesium hydroxide is most commonly used. For instance, using $Mg(OH)_2$ as an adsorbent requires a high pH, a hot process, and sludge recirculation. Silica will adsorb to the surface of insoluble magnesium compounds like $Mg(OH)_2$ or $MgCO_3$ and might also be removed by co-precipitation with $Mg(OH)_2$. Although the chemistry of silica removal by $Mg(OH)_2$ is unclear, the authors indicate that adsorption is likely the dominant removal mechanism. Sheikholeslami et al. (2001) similarly state that silica adsorbs to the

surfaces of precipitated magnesium solids. Cob et al. (2014) assert that silica is removed by co-precipitation with $Mg(OH)_2$ while Chen et al. (2006) determined adsorption to precipitated $Fe(OH)_3$, $Al(OH)_3$, of $Mg(OH)_2$ solids at a high pH to be the dominant removal mechanism. Additionally Chen et al. (2006) asserted that adsorption was more dominant than chemical reaction – in the case of their study, chemical reaction meant formation of $Mg_2SiO_4(s)$ – because it was shown that higher Mg concentrations forced precipitation of $Mg(OH)_2$ at a lower pH (around 9.4) and that $Mg_2SiO_4(s)$, which generally forms at a pH above 12, never had a chance to precipitate. XRD analysis was used to verify that no $Mg_2SiO_4(s)$ was formed, and therefore that no chemical reaction took place. Bremere et al. (2000) indicate that silica polymers adsorb to the surfaces of these polyvalent metal ions like Al^{3+} and Fe^{3+}.

Al-Mutaz and Al-Anezi (2004) studied silica removal at a treatment plant using a combination of lime and soda ash at varying concentrations and found that silica is removed during lime softening in one of two ways: (1) silica becomes trapped in the flocs of magnesium hydroxide that precipitate, or (2) silica adsorbs to the surface of precipitated magnesium hydroxide. Furthermore, they point out that calcium and magnesium silicates form during softening operations at higher pH. They studied removal over a pH range of 8.2 and 10.8 and found that silica removal by adsorption to magnesium hydroxide solids was optimized at a pH greater than 10.

In a series of tests utilizing both lime and soda ash with an average pH of 8.9 (measured in the reactor) and an average silica concentration of 16 ppm, Al-Mutaz and Al-Anezi (2004) achieved an average silica removal rate of about 44%. In a second series of tests that included only lime, an average silica concentration of 10.6 ppm, and an

average pH of 9.9, a higher removal rate of roughly 60.5% was observed. From the results, they concluded that silica removal was better in the absence of sodium aluminate and that silica adsorbed to the surfaces of precipitated magnesium hydroxide solids. It is unclear how the authors differentiated silica adsorption to magnesium solids from adsorption to calcium solids, but because they stated that magnesium hydroxide solubility drops severely as pH increases to above 9.5, it is assumed that they based their conclusion on the fact that their average pH was around 10. They also cited other research that claims magnesium is the most common removal agent, which likely also led them to their conclusion.

It would seem that with regards to magnesium, both adsorption and co-precipitation serve as mechanisms for removal of silica. Furthermore, based on the literature (Al-Rehaili 2003; Batchelor et al. 1991; Chen et al. 2006; GE Water & Process Technologies n.d.; Sheikholeslami et al. 2001), the conclusion could be drawn that adsorption is the more dominant mechanism, but it is entirely dependent either on the precipitation of magnesium hydroxide in solution or on the addition of magnesium hydroxide solids. Removal by aluminum and iron compounds appears to be driven by adsorption. It would be beneficial to gain a more complete understanding of the roles of adsorption and co-precipitation in silica removal to streamline removal techniques.

Relationship Between pH and Silica Removal

Although silica speciation and solubility are affected by a number of factors, it is evident that pH is one of the most critical. Studies cited by Batchelor et al. (1991) suggest the optimal pH for silica removal is in the range of 10.5 or 11. Sheikholeslami et al. (2001) explain that a pH of 10 to 11 is ideal for silica removal via adsorption onto

Mg(OH)$_2$ precipitates. Kotz et al. (2006) indicate that a pH of around 11 is optimal for precipitation of Mg(OH)$_2$. Chao and Westerhoff (2002) found that silica removal was tied to magnesium removal, which in turn was dependent on pH. Furthermore, it was observed that higher removal was achieved at a pH around 11.

There are two main explanations for more effective removal at higher pH.

1. Recall the deprotonation of silicic acid, represented by equation (1). At a pH higher than the pK$_a$ value, monosilicic acid begins to dissociate to form H$_3$SiO$_4^-$; thus, at higher operational pHs, electrostatic attraction facilitates removal (Chao and Westerhoff 2002).

2. It has been established that silica removal is tied to the presence of magnesium hydroxide, which is generally precipitated during the lime softening process. Literature often reports that Mg(OH)$_2$ begins to precipitate at a pH around 10.5 or 11; but, precipitation is tied to pH *and* to Mg^{2+} and OH$^-$ concentrations. Modeling of Mg(OH)$_2$ precipitation is presented in Chapter 3.

CHAPTER 3: EXPERIMENTAL METHODS

This project was carried out in two phases. The first phase involved 21 jar tests that explored silica removal by precipitated and preformed magnesium hydroxide ($Mg(OH)_2$), brucite (crystalline $Mg(OH)_2$), and ferric hydroxide ($Fe(OH)_3$) over a range of pH values. The experimental set-up allowed for numerous jar tests. Information gleaned from Phase 1 was used to establish the experimental operating parameters employed in Phase 2, which entailed longer time scale tests to study the effect of magnesium hydroxide and ferric hydroxide solids recycle on silica removal.

Phase 1: Jar Testing

During Phase 1, 21 jar tests were completed and the main objectives were:

- Explore adsorption and co-precipitation as mechanisms for silica removal by compounds of dissolved $MgCl_2$ (used to precipitate $Mg(OH)_2$), preformed $Mg(OH)_2$, aged $Mg(OH)_2$, brucite, and preformed $Fe(OH)_3$

- Study the influence of pH on silica removal

- Test the effect of magnesium concentration on silica removal

- Establish operating parameters for Phase 2 including pH, magnesium concentration, iron concentration, and HRT

Initially, the project only considered silica removal by various magnesium compounds; however, as the project evolved it was determined that an additional compound – ferric hydroxide – should also be tested. In addition to ferric hydroxide, several magnesium compounds were used in the jar testing phase and include: dissolved magnesium chloride; freshly precipitated, amorphous magnesium hydroxide (also referred to as preformed magnesium hydroxide in this paper); brucite; and aged magnesium hydroxide. The

concentrations of these compounds were varied during jar testing, as was pH. Additional

Phase 1 variables included batch water composition and silica concentration.

Testing Compounds

Dissolved Magnesium Chloride

Dissolved magnesium chloride was used during Phase 1 to investigate silica

removal via co-precipitation. The idea behind co-precipitation as a removal mechanism

was that magnesium hydroxide would begin to precipitate as its solubility limit was

exceeded and as it did so, silica would be captured and removed. It should be noted that

when $Mg(OH)_2$ precipitates in the solution, the SiO_2 might be removed by precipitating

with the $Mg(OH)_2$ or by adsorbing to the $Mg(OH)_2$ solids after they precipitate. This

project did not use any analytical methods that would distinguish between the removal

mechanisms after $MgCl_2$ was added. Although either mechanism could take place when

$Mg(OH)_2$ precipitates in solution, only adsorption can occur when the preformed

$Mg(OH)_2$ are added; thus, the additional methods provide a way to distinguish whether

adsorption occurs.

A 100,000 mg/L as Mg^{2+} magnesium chloride stock solution was prepared using

high purity grade $MgCl_2$ from AMRESCO. The dissolved magnesium concentrations

tested during Phase 1 varied between 200 and 10,000 mg/L as Mg^{2+}. The $MgCl_2$ solution

strength was determined using a simple mass balance, which demonstrated that for a 1L

jar test, 2mL of the 100,000 mg/L $MgCl_2$ solution was equivalent to 200 mg/L $MgCl_2$ as

Mg^{2+}. Similarly, 100mL of the $MgCl_2$ solution was equivalent to 10,000 mg/L $MgCl_2$ as

Mg^{2+}. The mass balance is shown in equation 3.1:

$$c_1 v_1 = c_2 v_2 \qquad (3.1)$$

where: $c_1 = concentration\ of\ stock\ solution$; i.e., 100,000 mg/L MgCl₂ as Mg²⁺

$v_1 = volume\ of\ solution\ to\ be\ added\ to\ jar$; i.e., 2 mL

$c_2 = desired\ testing\ concentration$; i.e., 200 mg/L MgCl₂ as Mg²⁺

$v_2 = volume\ of\ jar$; i.e., 1L

Amorphous Magnesium Hydroxide

Preformed magnesium hydroxide was used to test silica removal via adsorption, which was defined as the adherence of silica to the surfaces of preformed Mg(OH)₂ solids. Freshly precipitated, amorphous magnesium hydroxide was generated in the lab and added directly to the jars during testing. It was assumed that adsorption was the dominant mechanism for any silica removal achieved during these tests.

The preformed Mg(OH)₂ solids were made by combining the 100,000 mg/L MgCl₂ as Mg²⁺ stock solution with a 164,560 mg/L NaOH solution, which was prepared using ACS grade sodium hydroxide from EMD Millipore. The MgCl₂ and NaOH solutions were equivalent on a molar basis; thus, based on equation 3.2, the preformed magnesium hydroxide could be prepared by mixing one part MgCl₂ solution with two parts NaOH solution.

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2(s) + 2NaCl \tag{3.2}$$

By equation 3.1, 10mL of MgCl₂ solution was equivalent to 1,000 mg/L MgCl₂ as Mg²⁺. The same methodology was applied in preparing magnesium hydroxide. 1,000 mg/L Mg(OH)₂ as Mg²⁺, for example, was made by mixing 10mL MgCl₂ solution with 20mL NaOH solution. The assumption was made that the magnesium chloride and sodium hydroxide underwent complete reactions to precipitate magnesium hydroxide

solids. The preformed magnesium hydroxide concentrations tested during Phase 1 varied between 200 and 10,000 mg/L as Mg^{2+}.

Brucite

Brucite is a mineral form of magnesium hydroxide and has the molecular formula $Mg(OH)_2$. It was presumed to have a more crystalline structure than that of the freshly precipitated $Mg(OH)_2$ created in the lab; thus, jar tests with brucite were intended to offer a comparison between the two compounds as silica adsorbents. There was also a question of whether the lower solubility of brucite would allow it to remain in solid form (i.e., not dissolve) at lower concentration than freshly precipitated $Mg(OH)_2$, and whether this would prove to be advantageous in silica removal.

Powdered brucite of over 95% purity was obtained from Garrison Minerals. It was indicated on the product information sheet that the brucite powder may contain less than 1.6% SiO_2. To determine the exact amount of reactive silica present in the brucite, 100 and 1,000 mg/L brucite solutions where made in the lab using nanopure water and reactive silica was measured using a Hach DR/890 Colorimeter. The percent of reactive silica in the 100 mg/L sample was 0.4% and in the 1,000 mg/L sample was 0.04%.

During jar testing, brucite concentrations of 100 and 1,000 mg/L were used.

Aged Magnesium Hydroxide

The idea to test aged magnesium hydroxide as an agent for silica removal was conceived after completing some tests with freshly precipitated $Mg(OH)_2$ and brucite. The primary goal was to determine if the same level of silica removal could be achieved as with preformed $Mg(OH)_2$ without dissolving at lower pH ranges.

Aged Mg(OH)$_2$ was prepared by making a batch of freshly precipitated magnesium hydroxide, as described above, and drying it in a 105°F oven for a total of 44 hours. The Mg(OH)$_2$ was briefly removed from the oven every 8 to 12 hours and mixed. After the Mg(OH)$_2$ was removed from the oven and cooled, it was ground into a fine powder. A concentration of 1,000 mg/L aged Mg(OH)$_2$ was tested during Phase 1.

Ferric Hydroxide

Freshly precipitated ferric hydroxide solids were tested during Phase 1 to determine if they would effectively supplement magnesium hydroxide solids during the silica removal process. Compared with Mg(OH)$_2$ at a lower pH range between 7 and 9, Fe(OH)$_3$ is virtually insoluble; thus, it was postulated that silica removal could be achieved by magnesium hydroxide at a lower pH if there were other more insoluble solids present that could offer additional adsorption surface area.

In a procedure similar to the one used to make preformed magnesium hydroxide, freshly precipitated ferric hydroxide, Fe(OH)$_3$, was prepared by mixing a Fe^{3+} solution with a solution of NaOH. The Fe^{3+} solution was prepared such that it would be equivalent to Mg(OH)$_2$ on a molar basis. For example, 1,000 mg/L Mg(OH)$_2$ as Mg^{2+} is equal to 0.0411 mol/L Mg^{2+}, the molar equivalent of which is 2,297.9 mg/L Fe^{3+}. For simplicity, this was rounded up to 2,300 mg/L Fe^{3+}. Guaranteed Reagent (GR) grade Fe$_2$(SO$_4$)$_3$ with 72% assay from EMD Millipore was used to prepare the 2,300 mg/L Fe^{3+} stock solution. A 128,910 mg/L NaOH solution was prepared using ACS grade sodium hydroxide from EMD Millipore. The strength of the solution was such that it could be combined with the Fe^{3+} stock solution on a 1-to-1 basis to produce Fe(OH)$_3$. Furthermore, 38mL of each solution would produce 2,300 mg/L Fe(OH)$_3$ as Fe^{3+}; this was the only Fe(OH)$_3$

concentration tested for Phase 1. The assumption was made that the $Fe_2(SO_4)_3$ and

sodium hydroxide solutions underwent complete disproportionation to precipitate pure

ferric hydroxide solids with no SO_4^{2-} or Na^+ present.

Batch Water Composition

Multiple batches of synthetic water were prepared for jar tests. Chemicals used in

the batch water include: GR ACS grade sodium bicarbonate ($NaHCO_3$) from EMD

Millipore, ACS grade sodium sulfate (Na_2SO_4) from J.T. Baker, ACS grade calcium

chloride dehydrate ($CaCl_2 \cdot 2H_2O$) from EMD Millipore, ACS grade sodium chloride

(NaCl) from Macron Fine Chemicals, laboratory grade 42° Baumé (°Be) sodium silicate

(Na_2SiO_3) solution from Columbus Chemical Industries (CCI), and reagent grade Sodium

Metasilicate Nonahydrate ($Na_2SiO_3 \cdot 9H_2O$) from Sigma-Aldrich. Table 3-1 outlines the

different batch water compositions.

Table 3-1: Synthetic Water Composition Used in Jar Tests

Batch A	Deionized Water 2,600 mg/L $NaHCO_3$ 1,485 mg/L Na_2SO_4 1,600 mg/L $CaCl_2 \cdot 2H_2O$ Approx. 75 mg/L Na_2SiO_3 as SiO_2	Exp. No. 1-4	Average Batch Water pH = 6.7
Batch B	Deionized Water 2,600 mg/L $NaHCO_3$ 1,485 mg/L Na_2SO_4 636 mg/L NaCl Approx. 60 mg/L $Na_2SiO_3 \cdot 9H_2O$ as SiO_2	Exp. No. 5-6	Average Batch Water pH = 8.9
Batch C	Deionized Water 2,338 mg/L NaCl Approx. 75 mg/L $Na_2SiO_3 \cdot 9H_2O$ as SiO_2	Exp. No. 7-16, 19-21	Average Batch Water pH = 10.96
Batch D	Deionized Water 11,688 mg/L NaCl Approx. 75 mg/L $Na_2SiO_3 \cdot 9H_2O$ as SiO_2	Exp. No. 7-13, 15-16, 17-18	Average Batch Water pH = 10.86

Batch A was designed to mimic an ionic composition of naturally existing water

that had been concentrated by multi-pass RO. The 42° Baumé (°Be) Na_2SiO_3 solution

was used to introduce silica to the water. The Baumé scale is used to measure the density of liquids. The Baumé of water, for instance, is 0. The desired total silica concentration was 75 mg/L; however, the exact amount of Na_2SiO_3 in the 42° Be solution was unknown and estimated to be 36% by weight. As a result, batch water silica concentration was approximate.

For Batch B, NaCl was substituted for $CaCl_2 \cdot 2H_2O$ on a molar basis. It was found during Exp. No. 1-4 that at a pH above 8 or so, calcium carbonate was precipitating out of solution. Although precipitation of calcium carbonate was more representative of what would be seen during a full scale softening process, it was an undesirable occurrence during jar testing because it interfered with the project's focus on silica removal by magnesium. To minimize potential silica removal by compounds other than magnesium, it was determined that $CaCl_2 \cdot 2H_2O$ should be omitted from the batch water. It was also decided that for the preparation of Batch B, the 42° Be Na_2SiO_3 should be replaced with $Na_2SiO_3 \cdot 9H_2O$. The $Na_2SiO_3 \cdot 9H_2O$, with over 98% purity, allowed for greater control over silica concentration in the water.

Batch C and Batch D were simplified even further and contained only NaCl and $Na_2SiO_3 \cdot 9H_2O$. Simplifying the batch water composition allowed for a more thorough investigation of magnesium (or iron) as the agent for silica removal. Batch C contained a lower NaCl concentration of 2,338 mg/L (or 40 mM) while Batch D contained a higher concentration of 11,688 mg/L (or 200 mM); the purpose of creating two different batch waters was to determine if the ionic strength influenced silica removal.

The type of silica compound and concentration added affected the batch water pH. This is why average batch water pH varies in Table 3-1.

Jar Test Process

Magnesium Concentration and pH

Magnesium concentration and pH were the most important variables in this project and the question of how they each affect silica removal was a chief focus. Much of the literature reported that pH must be sufficiently high – i.e., between 10.5 and 12.0 – to achieve significant silica removal. Calcium carbonate has a low solubility limit and can begin to precipitate at a pH > 6.3, but several studies have theorized that silica removal is tied to the presence or formation of magnesium hydroxide in solution, and not necessarily to $CaCO_3$ (Al-Mutaz and Al-Anezi 2004; Chao and Westerhoff 2002; Chen et al. 2006; Cob et al. 2014; GE Water & Process Technologies n.d.; Sheikholeslami et al. 2001; Sheikholeslami and Bright 2002). Magnesium hydroxide precipitates at pH values around 11, which is why existing research cites these values as being necessary for silica removal (Al-Mutaz and Al-Anezi 2004; Sheikholeslami et al. 2001).

This project examined silica removal at pHs in the range of 7 to 12. The magnesium concentrations employed during jar testing were in the range of 200 to 10,000 mg/L as Mg^{2+}, which was generally much higher than concentrations reported in the literature. The initial hypothesis was that a higher magnesium concentration would achieve greater silica removal. As for pH, it was theorized that results would coincide with those in the literature – namely, that silica removal by magnesium was dependent on a higher pH.

Experiments No. 1-11

Experiments 1-11 compared silica removal by dissolved $MgCl_2$ (via precipitation of $Mg(OH)_2$ during testing) and preformed $Mg(OH)_2$. For these tests, a pH adjustment

was made prior to the addition of the magnesium compound using laboratory grade 2N

HCl from VWR. For each test, the magnesium compound was quickly added to the jar

during a 3-5 minute rapid mix (200-250 rpm) period. Rapid mixing was followed by 20

minutes of slow mix at 35 rpm and then 30-45 minutes of settling time. Samples were

collected using a 60 mL syringe and filtered through Pall Corporation Type A/E Glass

Fiber Filters with a 1 μm pore size.

Figures 3-1, 3-2, 3-3, and 3-4 depict the magnesium concentrations and initial pH

values used in jar tests 1-11.

Figure 3-1: Diagram of Setup for Jar Tests Using Dissolved MgCl$_2$ and Preformed Mg(OH)$_2$ at Mg Doses of 200, 600, and 1,000 mg/L and Initial pH Values of 7 and 11 (Experiments No. 1-4)
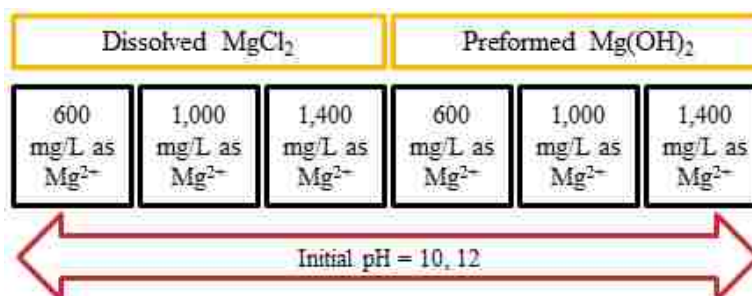
Figure 3-2: Diagram of Setup for Jar Tests Using Dissolved MgCl$_2$ and Preformed Mg(OH)$_2$ at Mg Doses of 600, 1,000, and 1,400 mg/L and Initial pH Values of 10 and 12 (Experiments No. 5-6)
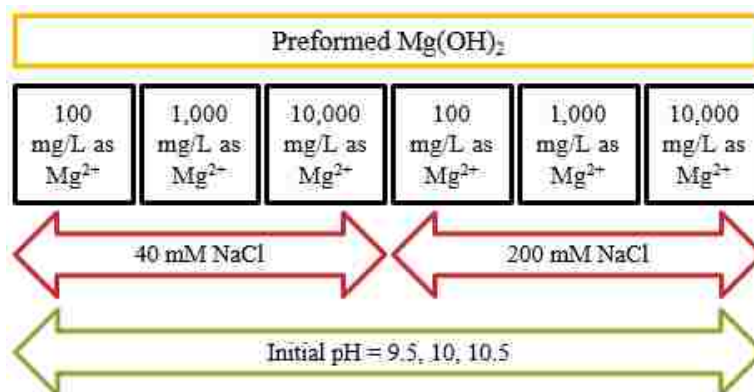
Figure 3-3: Diagram of Setup for Jar Tests Using Preformed Mg(OH)$_2$ at Mg Doses of 100, 1,000, and 10,000 mg/L, Initial pH Values of 9.5 to 10.5, and Using Batch Waters C and D (Experiments No. 7-9)
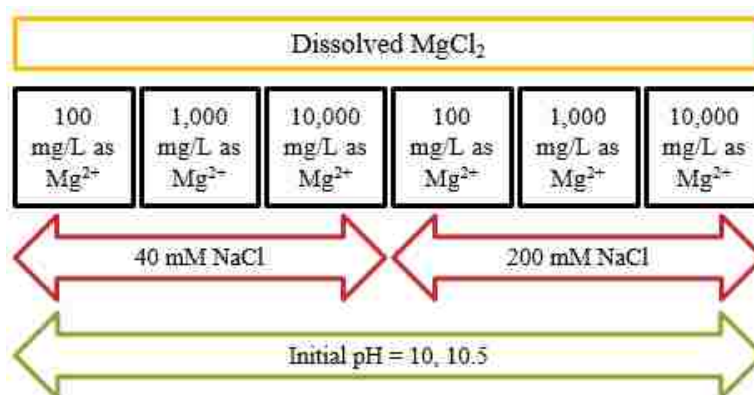
Figure 3-4: Diagram of Setup for Jar Tests Using Dissolved MgCl$_2$ at Mg Doses of 100, 1,000, and 10,000 mg/L, Initial pH Values of 10 to 10.5, and Using Batch Waters C and D (Experiments No. 10-11)

Visual MINTEQ was used to guide the selection of pH and magnesium concentration for experiments No. 7-11. A simple analysis was conducted that showed the solubility of active Mg(OH)$_2$ over a range of pH values and magnesium concentrations (refer to Figure 3-5). The Visual MINTEQ database does not indicate what is meant by "Active Mg(OH)$_2$", but Benjamin (1983) defines "Active" as meaning that the compound has available sorption sites. The model (Figure 3-5) shows that as pH increases, the solubility of magnesium hydroxide decreases. For experiments No. 7-11, magnesium concentrations of 100, 1,000, and 10,000 mg/L as Mg^{2+} were

selected to ensure silica removal was evaluated over an encompassing range. Experiments No. 7-9, which tested preformed $Mg(OH)_2$, had initial pH values of 9.5, 10, and 10.5. Based on the literature review, these might be considered fairly low values for removal by magnesium. Experiments No. 10-11 used dissolved $MgCl_2$ and initial pH values of 10 and 10.5. Based on the Visual MINTEQ analysis, it was not likely that $Mg(OH)_2$ would precipitate at a low pH of 9.5 during the $MgCl_2$ experiments; therefore, it was not deemed necessary to conduct such a test.
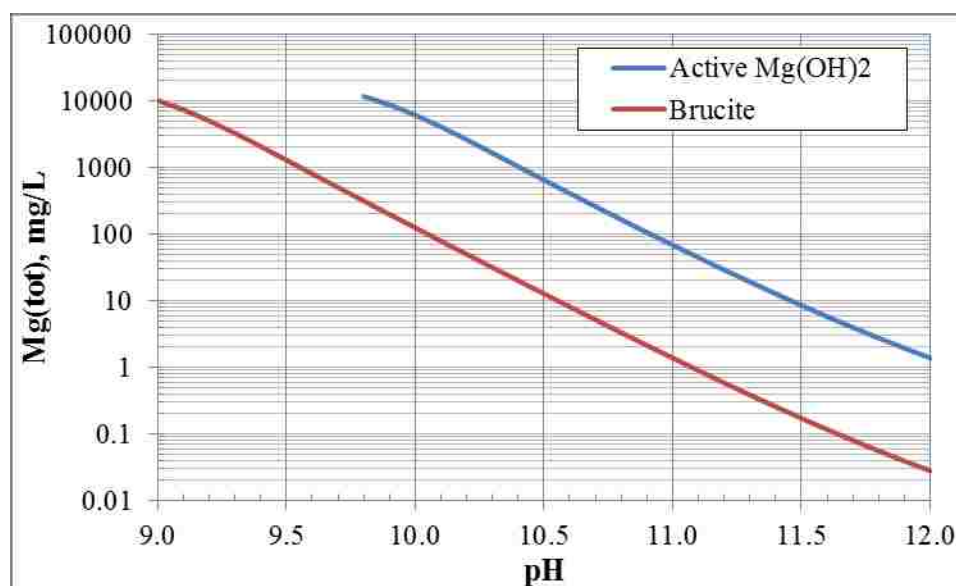
Figure 3-5: Saturation Concentration of Mg^{2+} in Equilibrium with Active $Mg(OH)_2$ and Brucite, Based on Modeling with Visual MINTEQ

Experiments No. 12-14

Experiments 12 and 13 tested the magnesium hydroxide mineral brucite, while experiment 14 used aged magnesium hydroxide. For these tests, pH adjustment was made prior to the addition of the magnesium compound using 2N HCl. The brucite and aged $Mg(OH)_2$ were in powdered form; thus, the appropriate amount was weighed out prior to each jar test. The powder was quickly added to the jar during a 3-5 minute rapid mix (200-250 rpm) period. Rapid mixing was followed by 20 minutes of slow mix at 35 rpm

and then 30 minutes of settling time. Samples were collected using a 60 mL syringe and

filtered through Pall Corporation Type A/E Glass Fiber Filters with a 1 µm pore size.

Figures 3-6 and 3-7 depict the concentrations and initial pHs used in jar tests 12-

14.

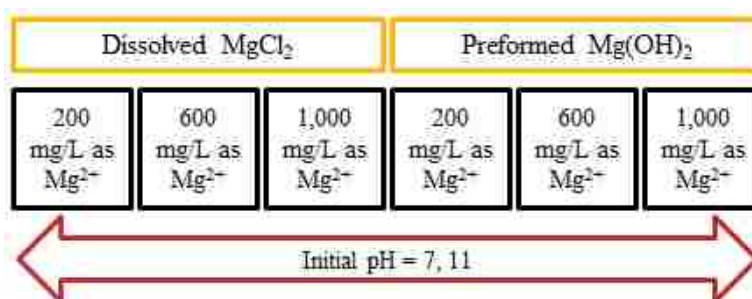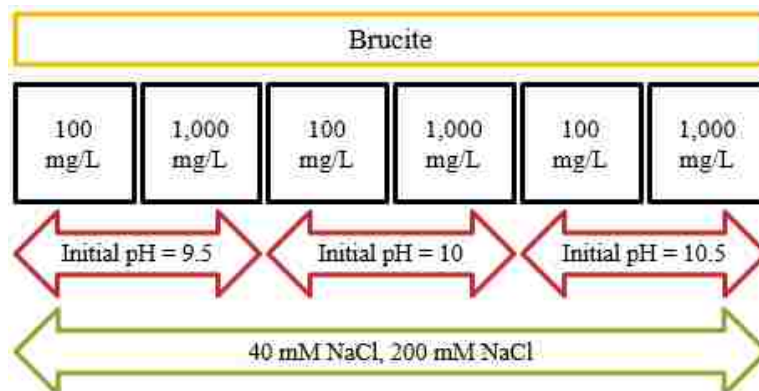**Figure 3-6: Diagram of Setup for Jar Tests Using Powdered Brucite at Doses of 100 and 1,000 mg/L (as Mg(OH)$_2$), Initial pH Values of 9.5 to 10.5, and Using Batch Waters C and D (Experiments No. 12-13)**
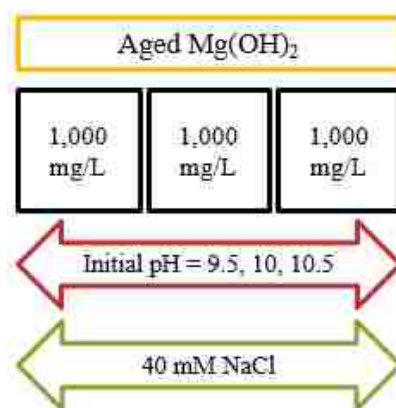
Figure 3-7: Diagram of Setup for Jar Tests Using Powdered Aged Mg(OH)$_2$ at a Dose of 1,000 mg/L (as Mg(OH)$_2$), Initial pH Values of 9.5 to 10.5, and Using Batch Water C (Experiment No. 14)

Experiments No. 15-17

Experiments 15-17 compared silica removal by dissolved $MgCl_2$ (via precipitation of $Mg(OH)_2$ during testing) and preformed $Mg(OH)_2$; however, unlike previous experiments which used initial pH as a basis for comparison, these tests aimed for a comparison based on final pH. The decision to run experiments 15-17 was made after analyzing results of the first fourteen experiments. It was conjectured that a comparison based on final pH would offer a more accurate picture of removal efficiency by preformed $Mg(OH)_2$ solids and $Mg(OH)_2$ precipitated in solution using dissolved $MgCl_2$, the idea being that initial pH adjustments were made prior to the addition of a magnesium compound and that by adding these compounds a second pH change was occurring almost immediately meaning the $MgCl_2$ tests and $Mg(OH)_2$ tests were not operating at the same pH.

Each of these experiments included only two jar tests. First, a test with 1,000 mg/L $MgCl_2$ as Mg^{2+} was completed at a pH of around 9.5 or 10. Then, a second jar test with 1,000 mg/L $Mg(OH)_2$ as Mg^{2+} was operated to mimic the pH trends of the first test as closely as possible. The operational and final pH varied slightly for the three experiments. Initial parameters are outlined in Table 3-2 below. Because final pH was not a predetermined value (it was dictated by each $MgCl_2$ jar test), a more thorough discussion of the pH fluctuations during experiments 15-17 has been reserved for Chapter 4: Results.

Table 3-2: Initial pH Conditions in Experiments No. 15-17 Using Dissolved $MgCl_2$ and Preformed $Mg(OH)_2$

	Jar 1	Jar 2
	1,000 mg/L $MgCl_2$ as Mg^{2+}	1,000 mg/L $Mg(OH)_2$ as Mg^{2+}
Exp. No. 15		
Batch Water C – pH	10.91	10.92
Pre-Test pH	9.71†	10.9*
Exp. No. 16		

Batch Water C – pH	10.75	10.80
Pre-Test pH	9.50[†]	10.80[*]
Exp. No. 17		
Batch Water D – pH	10.72	10.74
Pre-Test pH	10.04[†]	1.66[†]

[†] pH reduced with 12N HCl
[*] No pH adjustment made

At the beginning of each jar test, after pH adjustments were made, the magnesium compound was quickly added to the jar during a 3-5 minute rapid mix (200-250 rpm) period. Rapid mixing was followed by 20 minutes of slow mix at 35 rpm and then 30 minutes of settling time. pH readings were taken periodically during each test and pH adjustments were made to the $Mg(OH)_2$ jar as necessary using GR ACS grade 12N HCl from EMD Millipore. Samples were collected using a 60 mL syringe and filtered through Pall Corporation Type A/E Glass Fiber Filters with a 1 μm pore size.

Experiments No. 18-20

Experiments 18-20 were performed to estimate the hydraulic residence time (HRT) needed in the design of the Phase 2 flow-through system (this is discussed in greater detail on pages 38-39). Each experiment was 120 minutes long and used 1,000 mg/L $Mg(OH)_2$ as Mg^{2+}, but there were slight variations to operational pH. pH readings were taken at 2, 5, 10, 20, 40, 60, 90, and 120 minutes. Samples were also collected at these intervals using a 60 mL syringe and filtered through Pall Corporation Type A/E Glass Fiber Filters with a 1 μm pore size.

Experiment No. 18 used 200 mM NaCl batch water and no pH adjustments were made before or during the test. Experiment No. 19 used 40 mM NaCl batch water and a pH reduction was made prior to $Mg(OH)_2$ addition using 12N HCl. No additional pH adjustments were made during the course of the test. Experiment No. 20 used 40 mM

NaCl batch water and a pH reduction was made prior to Mg(OH)$_2$ addition using 12N

HCl. pH adjustments were made periodically throughout the duration of the test.

Experiment No. 21

Experiment 21 investigated silica removal by freshly precipitated ferric

hydroxide. Upon conclusion and analysis of some of the Mg(OH)$_2$ test results, it was

decided that an additional compound should be studied as a removal agent. The ultimate

goal was to use this compound in conjunction with Mg(OH)$_2$ during Phase 2

experimentation. Both iron and aluminum compounds were considered as candidates for

jar testing because, as was discussed in Chapter 2, both have been cited as being effective

in removing silica.

To guide the selection process, Visual MINTEQ analysis was utilized. A

comparison of the solubilities of amorphous Al(OH)$_3$ and ferrihydrite (Fe(OH)$_3$) at

various pH values was completed. The results are shown in Figure 3-8. The analysis

showed that the iron compound was much less soluble and was, therefore, selected for

experimentation.
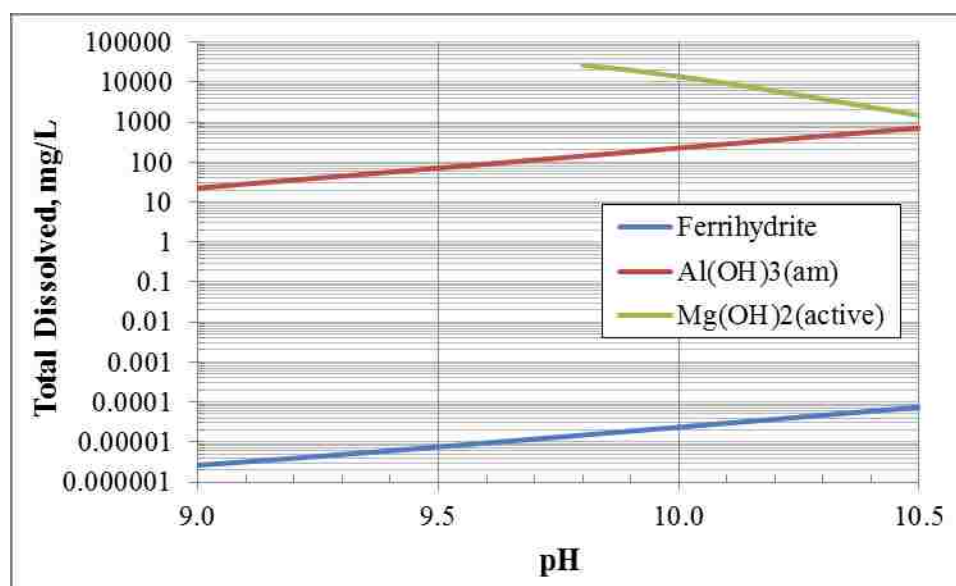
Figure 3-8: Saturation Concentrations of Fe^{3+}, Al^{3+}, and Mg^{2+} in Equilibrium with Ferrihydrite, Amorphous $Al(OH)_3$, and Active $Mg(OH)_2$, Respectively, Based on Modeling with Visual MINTEQ

The experiment was 120 minutes long and used 2,300 mg/L $Fe(OH)_3$ as Fe^{3+}, the molar equivalent of 1,000 mg/L $Mg(OH)_2$ as Mg^{2+}. pH readings were taken at 2, 5, 10, 20, 40, 60, 90, and 120 minutes. Samples were also collected at these intervals using a 60 mL syringe and filtered through Pall Corporation Type A/E Glass Fiber Filters with a 1 µm pore size. No pre-test pH changes were made; however, pH adjustments were made periodically during the course of the test using 3.2 mM NaOH.

Silica Measurement

Reactive silica was determined by the Molybdosilicate Method, Standard Method 4500-SiO_2 (APHA 1998), with color intensity measured using a Hach DR/890 Colorimeter. Total silica was measured by the University of New Mexico Geo/Analytical Chemistry Laboratory using the Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) Method, Standard Method 3120 (APHA 1998). ICP measures both reactive and colloidal silica; thus, Hach measurements were subtracted from ICP measurements to obtain information on colloidal silica content.

Phase 2: Flow-Through Experimentation

Phase 2 was designed to examine the impact of solids recycle on silica removal because little research has been done on this particular subject. Five tests, each 8 hours long, were conducted during Phase 2. Information gleaned during Phase 1 jar testing was used to establish some of the operating parameters during flow-through.

The main goals of Phase 2 were to:

- Establish whether or not the results of Phase 1 held up over a longer experimental period

- Study the effect of magnesium and iron solids recycle on silica removal

- Test the adsorption capacity of solids in the system

- Determine if silica removal could be achieved at a lower pH over an extended period of time

System Design

The system design considered three variables – flow (Q), volume (V), and hydraulic residence time (HRT or τ), all of which are related by the following equation:

$$\frac{V}{Q} = \tau \tag{3.3}$$

To determine HRT, three jar tests were conducted during Phase 1. Based on the results of these jar tests, an HRT of 20 minutes was selected. The flowrate into the system was chosen to be 0.1L/min; thus, based on equation 3.3, the system needed to be designed to hold a total volume of 2L. A rough schematic of the system is shown in Figure 3-9 and a photo of the completed system is provided in Figure 3-10.
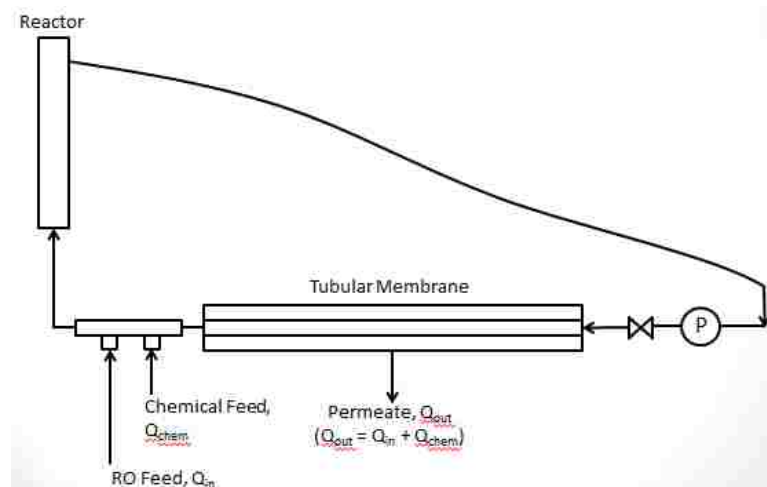
Figure 3-9: Flow-Through System Schematic

The system was designed around the desired volume, HRT, and flow rate but the actual values associated with the constructed system deviated slightly. The system specifications are shown in Table 3-3.

Table 3-3: Actual Phase 2 Design Specifications

Flow (Q_{in})	109 mL/min
HRT	24.8 min
Volume (V)	2.7L
Chemical Feed Flow (Q_{chem})	0-7 mL/min
System Recirculation Rate	4 gpm
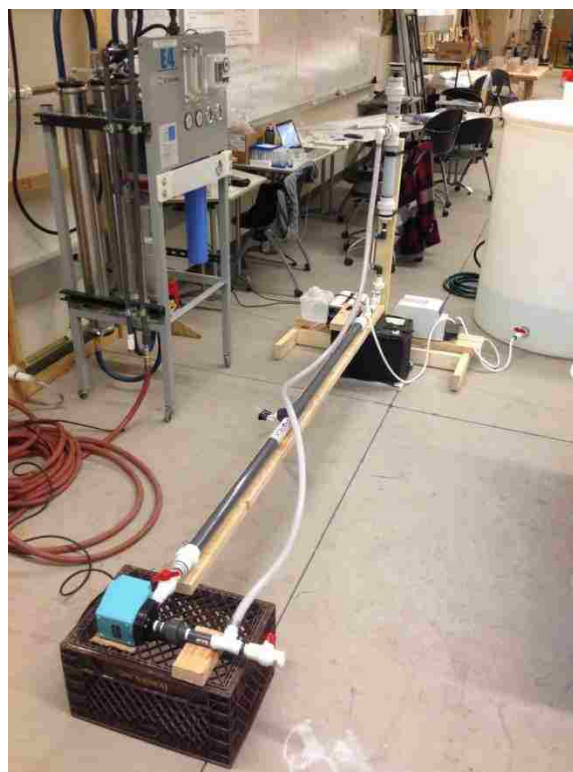
Figure 3-10: Constructed Flow-Through System Setup

Membrane Filter

The tubular membrane filter used in the flow-through system was provided by POREX® Filtration. The PVC membrane module was six feet in length and housed a

single tubular membrane with a 0.1 µm pore size. The diameter of the membrane was 0.5 inches, resulting in about 113 in^2 of membrane surface area. Based on the flow into the system, flux (J) was estimated to be around 89.6 $L/hr/m^2$ (Lmh). Of course, this number was based only on Q_{in}; a more accurate value for flux would need to be based on Q_{out}, a summation of the RO and chem feed rates. This will be discussed in greater detail in the results section.

Recirculating Pump

A Little Giant 3E-34N Dual Purpose Small Submersible Pump (see Figure 3-11 (a)) was used to recirculate solids and water through the system at a recirculation rate of roughly 4 gpm. A valve was affixed to the pump so that the recirculation rate could be adjusted as necessary (see Figure 3-11 (b)).

3-11 (a)   3-11 (b)

Figure 3-11: Little Giant Submersible Pump Used to Recirculate Solids in Flow-Through System

Feed Water

The feed water used during Phase 2 was reverse osmosis concentrate and was meant to mimic water that had passed through the first stage of a multi-state RO process.

Tap water was concentrated using a GE Osmonics RO Unit at a recovery rate of 60%,

resulting in a concentration factor of 2.5. The RO feed water was supplemented with

sodium chloride to achieve a total dissolved solids concentration closer to that of brackish

water with 5,000 mg/L TDS. 1.5 kg of ACS grade NaCl from EMD Millipore was added

to 100 gallons of RO concentrate. The composition of the RO feed water is shown in

Table 3-4. RO feed water was pumped into the system via laboratory feed pump.

Table 3-4: RO Feed Water Composition Used in Phase 2

Aluminum	0 mg/L
Barium	0.7 mg/L
Calcium	89.8 mg/L
Iron	0 mg/L
Magnesium	15.2 mg/L
Potassium	14.1 mg/L
Silica	141.9 mg/L
Strontium	1.0 mg/L
Zinc	0 mg/L

Chemical Addition

0.25M NaOH, prepared using nanopure water and ACS grade sodium hydroxide,

was used to make pH adjustments during each flow-through experiment. The NaOH was

added to the system via laboratory feed pump.

Flow-Through Process

Freshly precipitated $Mg(OH)_2$ and $Fe(OH)_3$ were the only compounds tested

during Phase 2; however, solids concentration and pH varied for each experiment (see

Table 3-5). Preparation of preformed $Fe(OH)_3$ followed the same process outlined under

Phase 1 methods. Preparation of $Mg(OH)_2$ also followed the same process except that a

stronger solution of NaOH (329,120 mg/L) was made so that $MgCl_2$ and NaOH could be

combined on a 1-to1 basis to achieve the desired $Mg(OH)_2$ concentration.

Table 3-5: Summary of Solids Concentrations and pH Used in Phase 2

	$Mg(OH)_2$ Conc.	$Fe(OH)_3$ Conc.	Desired pH
Experiment No. 22	1 g/L	-	10
Experiment No. 23	3 g/L	-	10
Experiment No. 24	3 g/L	-	9.5
Experiment No. 25	0.5 g/L	1.15 g/L	10
Experiment No. 26	-	2.30 g/L	10

Each experiment lasted 8 hours. Samples were taken from the permeate stream at the beginning of each test and then at regular intervals throughout the duration of the experiment. Both reactive silica and total silica measurements were taken using the Hach and ICP methods previously discussed.

Membrane Cleaning

A 1% citric acid solution was used to clean the flow-through system if membrane fouling was observed. A reduction in permeate flow was indicative of membrane fouling.

Sample Analysis

SEM

SEM images of preformed $Mg(OH)_2$ (dried at room temperature), aged $Mg(OH)_2$, and brucite were taken and analyzed in the SEM Laboratories at UNM's Institute of Meteoritics using a JEOL 5800LV Scanning Electron Microscope and Oxford Isis 300 Analytical System.

BET Surface Area Analysis

BET surface area analysis was performed for samples of preformed $Mg(OH)_2$ (dried at room temperature), aged $Mg(OH)_2$, and brucite. Analysis was done at the UNM Center for Micro-Engineering Materials (CMEM) laboratory using a Micromeritics Gemini 2360 Surface Area Analyzer.

XRD

X-ray diffraction (XRD) analysis of the samples of preformed $Mg(OH)_2$ (dried at room temperature), aged $Mg(OH)_2$, and brucite was completed at UNM's Center for Micro-Engineering Materials (CMEM) using a Philips Double and Triple Crystal Materials Research Diffraction (MRD) XRD System.

CHAPTER 4: EXPERIMENTAL RESULTS

The two phases of this project facilitated examination of silica removal by compounds of dissolved $MgCl_2$ (removal via co-precipitation with $Mg(OH)_2$ formed during softening) and $Mg(OH)_2$, brucite, and $Fe(OH)_3$ (removal via adsorption). A total of 26 experiments were completed – 21 jar tests and 5 flow-through experiments – that evaluated a range of magnesium concentrations (200 to 10,000 mg/L as Mg^{2+}), iron concentrations (1,150 to 2,300 mg/L as Fe^{3+}), and pHs (7 to 12) to understand the influence of these variables on silica removal.

<u>Phase 1: Jar Testing</u>

The purpose of Phase 1 was to perform small scale jar tests that investigated:

(1)   A comparison of silica removal by $Mg(OH)_2$ precipitated in solution and by preformed $Mg(OH)_2$ solids to understand co-precipitation and adsorption as removal mechanisms

(2)   The influence of pH on magnesium precipitation and silica removal

(3)   Silica removal by compounds of brucite and aged $Mg(OH)_2$ compared with freshly precipitated, amorphous $Mg(OH)_2$

(4)   The effect of high and low magnesium concentrations on silica removal

(5)   Reactive and colloidal silica removal

(6)   The feasibility of using $Fe(OH)_3$ as a supplemental compound to silica removal with $Mg(OH)_2$

(7)   Silica removal over time using preformed $Mg(OH)_2$ to determine a reasonable HRT for design of the flow-through system

Adsorption and Co-precipitation as Removal Mechanisms

The question of how silica is removed during chemical softening is important to improve the efficiency of the silica removal process. If it is known that silica is removed largely by adsorption to the surfaces of solids, then operators know that solids either have to be introduced during the softening process or that pH must be high enough to precipitate them. If co-precipitation is the main driver for removal, there are considerations with regards to pH and ionic composition that must be taken into account. There are also implications for waste management if high volumes of solids are generated during the removal process.

The literature seems to suggest that both mechanisms can play a part (Al-Mutaz and Al-Anezi 2004; Sheikholeslami and Bright 2002) but that adsorption may be the more dominant mechanism, whether it is adsorbing to the surfaces of solids introduced to the system or to solids that are precipitating out of solution during the softening process (Al-Rehaili 2003; Batchelor et al. 1991; Chen et al. 2006; GE Water & Process Technologies n.d.; Sheikholeslami et al. 2001).

This project sought to more thoroughly understand removal of silica via co-precipitation and adsorption during a series of jar tests that compared removal by $Mg(OH)_2$ precipitation in solution and by preformed $Mg(OH)_2$ solids. More specifically, dissolved $MgCl_2$ was used to study removal by co-precipitation, which meant that $Mg(OH)_2$ needed to be precipitated during the test. $MgCl_2$ concentrations of 200 to 10,000 mg/L as Mg^{2+} were studied over a range of pHs from 7 to 12. Preformed $Mg(OH)_2$ solids were used to study removal by adsorption. Although it was acknowledged that solids could also be precipitated during the course of these tests, it was assumed that adsorption would be the dominant removal mechanism. As was stated

in the methods section, this assumption seemed reasonable because the duration of each jar test was short. The results of experiments no. 1-11 offered insight into the nature of silica removal by co-precipitation and adsorption.

Experiments No. 1-4

The first four jar tests conducted for this project offered a comparison of the removal efficacy of preformed $Mg(OH)_2$ and $Mg(OH)_2$ precipitated during softening (using a dissolved $MgCl_2$) at initial pH values of 7 and 11. The magnesium concentrations used in these tests were 200, 600, and 1,000 mg/L as Mg^{2+}. An initial pH adjustment was made prior to the addition of the magnesium compound using either 2N HCl or 3.2M NaOH, depending on whether the pH needed to be increased or decreased to arrive at the desired value. No other pH adjustments were made during the course of each test. Figure 4-1 presents the results of the first four experiments in terms of percent reactive silica removed. Only reactive silica, measured by the colorimetric silicomolybdate method, was measured in these tests.
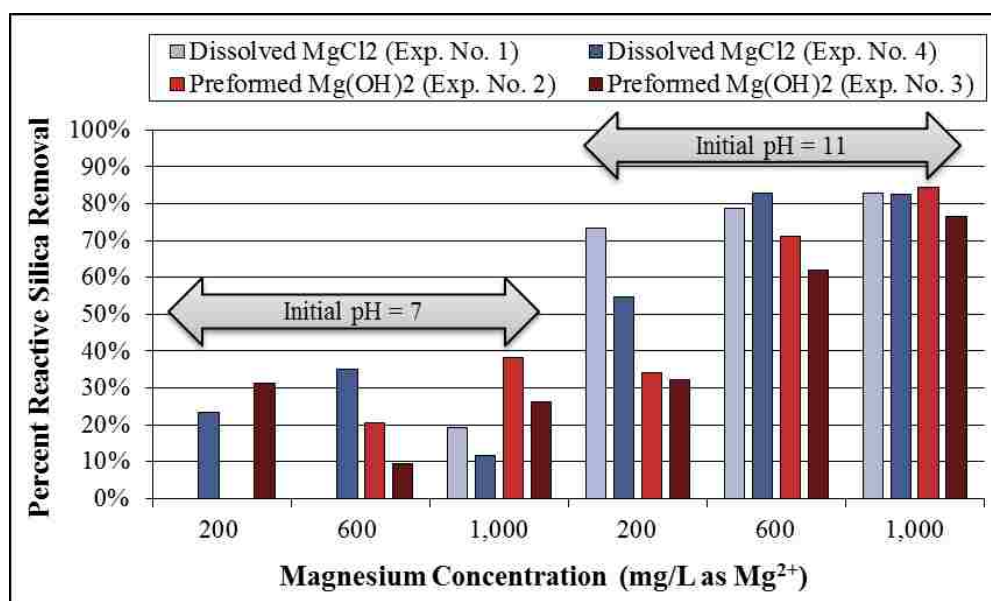
Figure 4-1: Reactive Silica Removal Observed in Jar Tests Using Dissolved MgCl₂ and Preformed Mg(OH)₂ at Mg Doses of 200, 600, and 1,000 mg/L and Initial pH Values of 7 and 11 (Experiments No. 1-4)

Because of reports in the literature that a high pH is required to remove silica (Al-Mutaz and Al-Anezi 2004; Sheikholeslami et al. 2001), it was not expected that high removal would be achieved at a pH of 7. The results confirmed that for both the dissolved and preformed compounds at all three magnesium concentrations, very little removal – 0 to 40% – was attained at the lower initial pH. Furthermore, there was no precipitation of solids in the three MgCl₂ jars because of the high solubility of Mg(OH)₂ at pH 7 (see Figure 3-5); without the formation of solids, silica could not be removed via co-precipitation. There were precipitates observed in the Mg(OH)₂ jars, but they were assumed to be the preformed magnesium solids introduced at the beginning of the test. It would have been reasonable to anticipate higher removal by preformed Mg(OH)₂ – since removal might be achieved by adsorption to the preformed solids – but results were on par with those of MgCl₂ tests, which is likely a result of dissolution of magnesium over time at such a low pH value (recall Figure 3-5).

The reactive silica removal rates were clearly higher at the initial pH of 11, especially for magnesium concentrations of 600 and 1,000 mg/L as Mg^{2+}. Silica removed during the dissolved MgCl₂ tests was between 50-85% of silica, suggesting that co-precipitation was more dominant. Mg(OH)2 only removed about 30% silica at the lowest magnesium concentration, but removal increased to between 60-80% at the two higher concentrations. Recall, though, that Batch Water A was used in these tests. It was noted in Chapter 3 that calcium carbonate, CaCO₃, was found to precipitate out of solution when the pH of the batch water was adjusted to anything higher than 8. In experiments no. 1-4, precipitation of CaCO₃ was observed to occur around pH 8.8; thus, it is not

possible to attribute all silica removal during the $MgCl_2$ tests to co-precipitation, nor is it possible to attribute all the silica removal during the $Mg(OH)_2$ tests to adsorption. A detailed SEM-EDS analysis of the settled solids would have been necessary to estimate the difference in removal by magnesium and calcium.

It should be noted that there was an error in making the preformed $Mg(OH)_2$ used in experiments no. 1-4 and 5-6 (discussed in the next section). Instead of combining $MgCl_2$ and NaOH solutions in a 1-to-2 ratio, which was the procedure outlined in the methods section, the solutions were mixed on a 1-to-1 basis. This means that there was less hydroxide available to react with the magnesium to form $Mg(OH)_2$, which would have reduced the solids in the system and impacted the effectiveness of removal by $Mg(OH)_2$ during these tests. Additionally, final pH was not measured in experiments no. 1-6. Because of the precipitation of calcium carbonate, the error in making the $Mg(OH)_2$ solids, and the unmeasured final pH value, these tests cannot be used to evaluate whether adsorption or co-precipitation is more important.

Experiments No. 5-6

Experiments no. 5-6 compared removal by dissolved $MgCl_2$ (via co-precipitation with $Mg(OH)_2$ formed in solution) with preformed $Mg(OH)_2$ at initial pH values of 10 and 12. The magnesium concentrations used in these tests were 600, 1,000, and 1,400 mg/L as Mg^{2+}. An initial pH adjustment was made prior to the addition of the magnesium compound using 3.2M NaOH. No other pH adjustments were made during the course of each test. Batch Water B was used in these tests, so no calcium was present. Figure 4-2 presents the results of experiments no. 5 and 6 in terms of percent reactive silica removed. As with the first four tests, only reactive silica was measured.
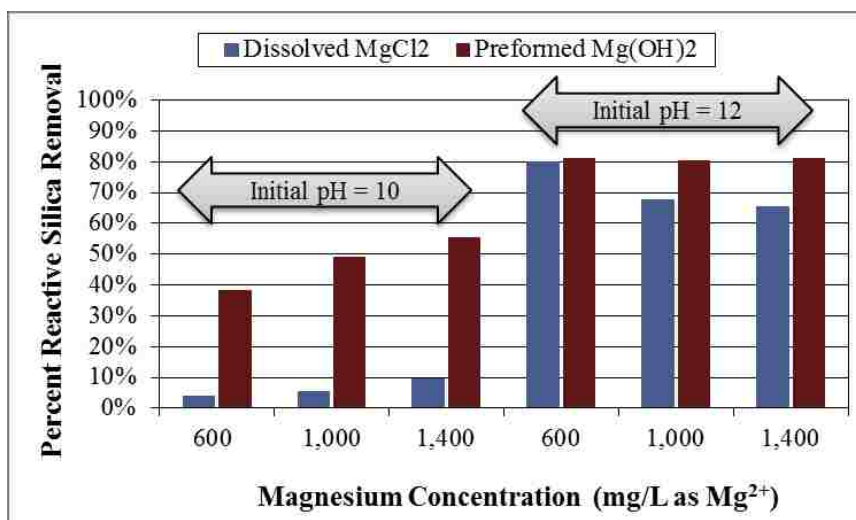
Figure 4-2: Reactive Silica Removal Observed in Jar Tests Using Dissolved MgCl₂ and Preformed Mg(OH)₂ at Mg Doses of 600, 1,000, and 1,400 mg/L and Initial pH Values of 10 and 12 (Experiments No. 5-6)

At an initial pH of 10, there was little removal – 0 to 10% – observed in the MgCl₂ jars. Based on the MgCl₂ results in experiments no. 1-4, we would have expected to see higher removal. The low numbers here likely demonstrate the influence of calcium carbonate on removal during the first four tests. Even at the higher magnesium concentrations for the MgCl₂ test, there was no precipitation of solids observed in any of the jars, which can be explained by Figure 3-5, which shows that the Mg^{2+} concentrations were below the $Mg(OH)_2$ solubility limit at a pH of 10 for experiments no. 5 and 6.

The $Mg(OH)_2$ results showed an interesting trend at an initial pH of 10. There was progressively higher removal as the concentration of magnesium increased suggesting that adsorption was driving removal but that silica reduction was limited by an adsorption capacity of the solids. The results influenced later tests that aimed to further explore removal at an even lower pH and higher magnesium concentration. A lower pH means fewer pH-adjusting chemicals are required, which is major benefit in a large scale softening process.

At the higher pH, removal by both compounds was fairly high, which was expected based on the literature. Silica removal by preformed $Mg(OH)_2$ was consistent at around 80% across all three concentrations, which could indicate adsorption was dominant. Removal by precipitated $Mg(OH)_2$ in the $MgCl_2$ tests was not as high as in experiments no. 1-4 but, again, this is likely explained by the presence of calcium carbonate in the first four tests and its role in removal.

Removal during $MgCl_2$ experiments no. 5-6 was high, 80%, for the lowest Mg^{2+} concentration but actually decreased to 68% and then 65% as concentration increased. This decrease in removal might be explained by the fact that a higher $MgCl_2$ dose corresponds to a greater decrease in pH, a result that is demonstrated in later tests (see experiments no. 7-11 and 15-17). If this was in fact the case, then the pH was not maintained at a high enough value to continue precipitating adequate $Mg(OH)_2$.

Experiments No. 7-11

Experiments no. 7-11 continued the exploration of silica removal via adsorption and co-precipitation. These tests were performed using Batch Waters C and D, which consisted only of NaCl in concentrations of 40 mM and 200 mM. The two different batch waters were used to examine whether or not ionic strength played a role in removal. The graphs presented in Figures 4-3 and 4-4 demonstrate that ionic strength was not a critical variable in these tests. The difference in removal by the two batch waters was virtually indistinguishable at each pH and magnesium concentration.

The purpose of these jar tests, in addition to exploring adsorption and co-precipitation, was to gain a better understanding of the relationship between pH, magnesium compound (dissolved or preformed), and magnesium concentration to

determine an optimal combination for silica removal. The magnesium concentrations used in these tests were selected with the aid of Figure 3-5, which summarizes the pH dependence of the solubility of $Mg(OH)_2$. At 100 mg/L Mg and between a pH of 9 and 10.5, $Mg(OH)_2$ is not expected to precipitate. Similarly for 1,000 mg/L Mg, $Mg(OH)_2$ is not expected to precipitate between a pH of 9.5 and 10; but at a pH of 10.5, Mg exceeds the saturation concentration and is expected to begin precipitating. For 10,000 mg/L Mg, precipitation is expected at a pH of 10 or greater.

Figure 4-3 shows the results of experiments no. 7-9, which tested $Mg(OH)_2$ over an initial pH range of 9.5-10.5. While it is clear that the 100 mg/L Mg^{2+} concentration did not achieve much removal, there was little difference between removal by concentrations of 1,000 and 10,000 mg/L. This might suggest that for the concentration of silica present in the water, 1,000 mg/L $Mg(OH)_2$ as Mg^{2+} provided ample surface area for adsorption. Furthermore, good removal was achieved at all three initial pH values for the two higher magnesium concentrations. The removal at 1,000 mg/L and initial pH of 10 was a little over 80%, which is quite a bit higher than the roughly 50% that was observed in experiments no. 5-6. The discrepancy might be explained by the difference in $Mg(OH)_2$ preparation. Recall that for experiments no 5 and 6, a 1-to1 ratio of $MgCl_2$ and NaOH solutions was used to generate $Mg(OH)_2$, when it should have been a 1-to-2 ratio, as was used in experiments no. 7-9. This suggests that not all of the Mg was precipitated in experiments no. 5-6. Presumably, with the correct $MgCl_2$ to NaOH ratio, all of the Mg was precipitated to make $Mg(OH)_2$ solids used in experiments no. 7-9, thereby supplying more surface area for silica adsorption.
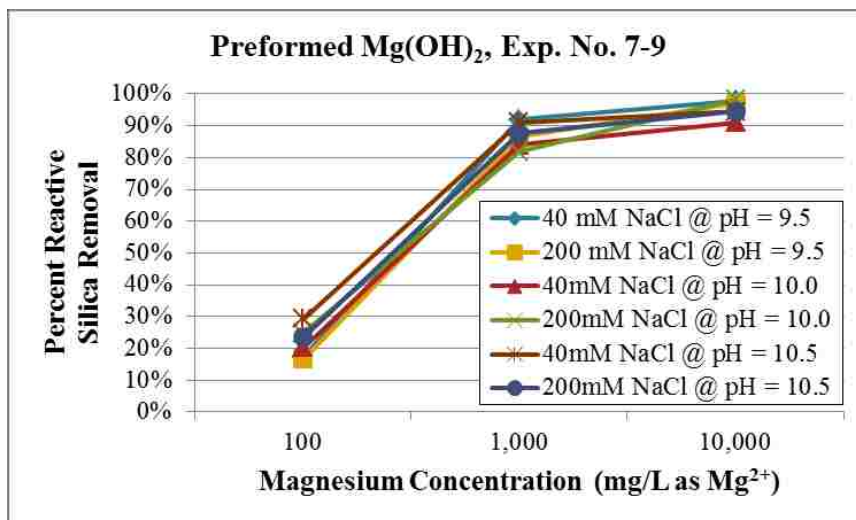
Figure 4-3: Silica Removal by Preformed Mg(OH)₂ at Mg Doses from 100 to 10,000 mg/L, Initial pH from 9.5 to 10.5, and Average Initial Reactive Silica Concentration of 63.9 mg/L (Experiments No. 7-9)

The results of experiments no. 10-11 are plotted in Figure 4-4. $MgCl_2$ was tested at initial pHs 10 and 10.5. A pH of 9.5 was not included as an experimental parameter because it was unlikely that solids would be precipitated at this pH, as demonstrated by the results of experiments no. 5 and 6 (refer to Figure 4-2). Removal during the $MgCl_2$ tests was worse than in those with preformed $Mg(OH)_2$. At an initial pH of 10 and magnesium concentration of 1,000 mg/L as Mg^{2+}, precipitated $Mg(OH)_2$ solids during the $MgCl_2$ test only achieved about 20% removal while preformed $Mg(OH)_2$ solids achieved closer to 80% removal. Removal in the $MgCl_2$ tests was better for a concentration of 10,000 mg/L as Mg^{2+} – between 60 and 70% – but was still less than the 90-100% removal observed during the preformed $Mg(OH)_2$ tests. Unlike the preformed $Mg(OH)_2$ tests where there was little difference in removal between the 1,000 and 10,000 mg/L Mg^{2+} concentrations, there is a noticeable difference in the $MgCl_2$ results suggesting that greater $Mg(OH)_2$ precipitation takes place in more heavily magnesium concentrated waters.
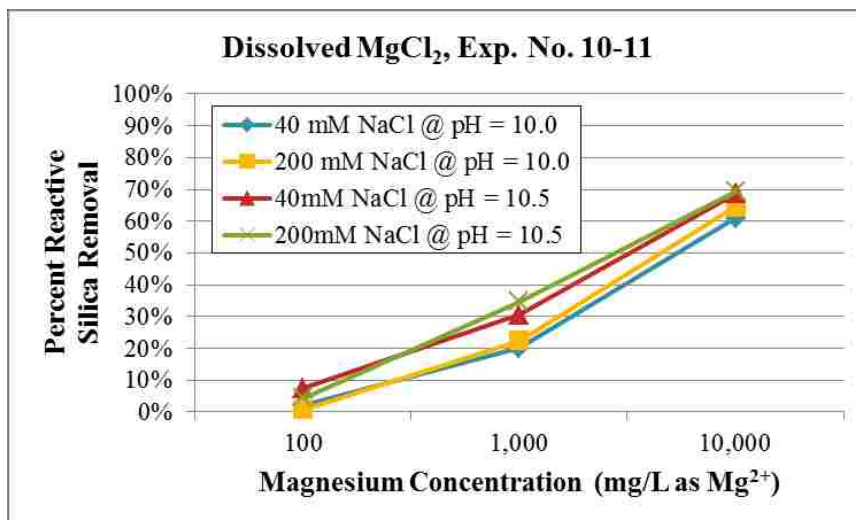
Figure 4-4: Silica Removal in Tests Using Dissolved MgCl₂ at Mg Doses from 100 to 10,000 mg/L, Initial pH from 10 to 10.5, and Average Initial Reactive Silica Concentration of 64.0 mg/L (Experiments No. 10-11)

Figure 4-5 captures the jar tests in experiments no. 7-8 and 10-11 that were conducted with an initial pH of 10. Very few solids can be seen in the 100 mg/L jar for the Mg(OH)₂ test and no solids precipitated for the MgCl₂ test, which explains the low removal by both compounds at that concentration. Overall, significantly more solids were present in the Mg(OH)₂ jars than in the MgCl₂ jars.
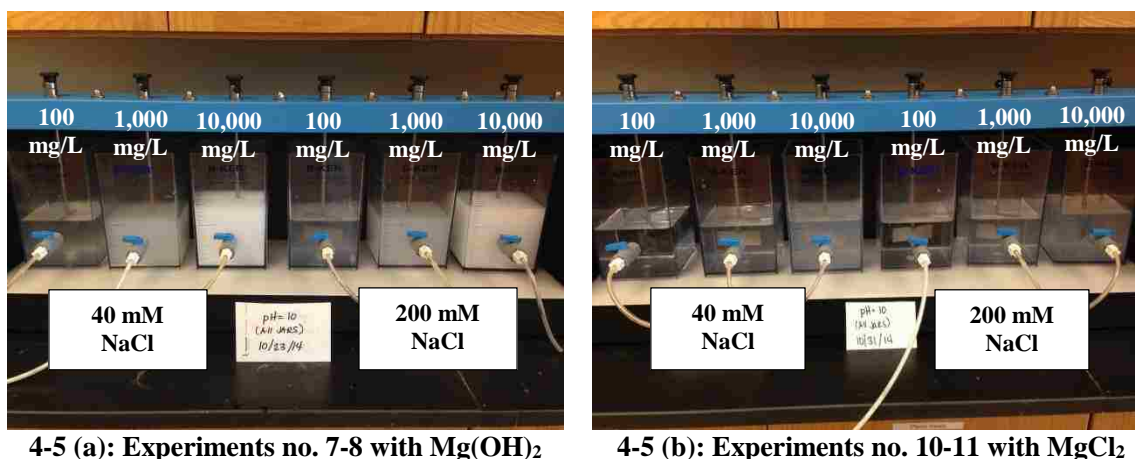
4-5 (a): Experiments no. 7-8 with Mg(OH)₂

4-5 (b): Experiments no. 10-11 with MgCl₂

Figure 4-5: Example of Jar Test Setup with Preformed Mg(OH)₂ and Dissolved MgCl₂ at an Initial pH of 10 Using Batch Waters C and D

Because the results of experiments no. 7-11 demonstrated that the influence of the NaCl concentration in Batch Waters C and D was minimal, the results for the two batch waters at the various pHs and magnesium concentrations were averaged to create Figure 4-6. Figure 4-6 offers a clearer picture of how silica removal was affected by pH, magnesium concentration, and magnesium compound. The preformed $Mg(OH)_2$ at concentrations of 1,000 and 10,000 mg/L as Mg^{2+} provided the best removal.
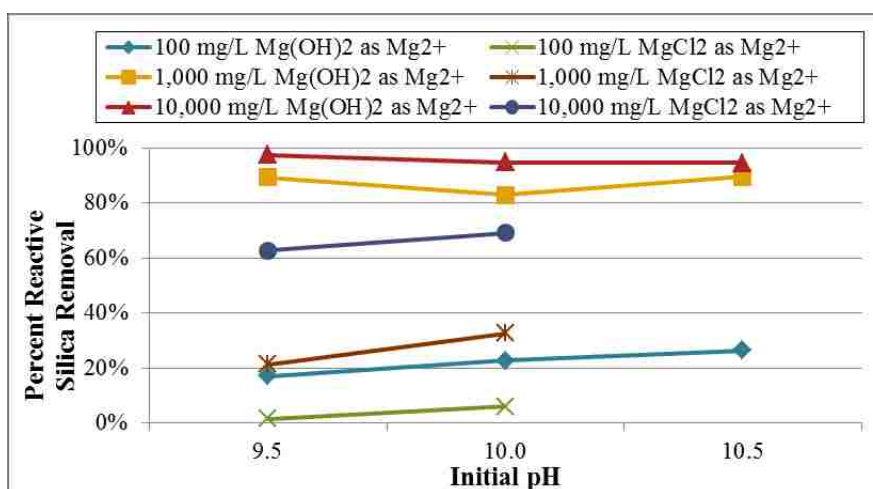

Figure 4-6: Average Silica Removal in Tests Using Dissolved MgCl₂ and Preformed Mg(OH)₂ at Mg Doses from 100 to 10,000 mg/L, Initial pH from 9.5 to 10, and Average Initial Reactive Silica Concentration of 63.9 mg/L (Experiments No. 7-11)

Removal by Brucite and Aged Mg(OH)₂

The magnesium hydroxide solids used in experiments no. 1-11 were freshly precipitated in the lab using a procedure outlined in Chapter 3. Brucite and aged $Mg(OH)_2$, both of which were in powder form, were tested to see if removal rates were the same, higher, or lower than those achieved with the freshly precipitated solids.

Experiments No. 12-14

Experiments no. 12-13 tested Brucite at concentrations of 100 and 1,000 mg/L over three initial pHs: 9.5, 10, and 10.5. The results of these jar tests are presented in

Figure 4-7. Experiment no. 14 tested aged $Mg(OH)_2$, which was prepared in the lab using a procedure outlined in Chapter 3, over a pH range of 9.5 to 10.5 for a concentration of 1,000 mg/L. These results of experiment no. 14 are displayed in Figure 4-8.

Virtually no removal was achieved by brucite or aged $Mg(OH)_2$. For that reason, no further tests were conducted with these two compounds. It was speculated that poor removal was related to the crystalline structure of brucite. It was theorized that perhaps the aged $Mg(OH)_2$ had a structure similar to that of brucite, since both served as such poor removal compounds. A detailed sample analysis, which is presented later in this chapter, was conducted to understand why freshly precipitated $Mg(OH)_2$ proved to be an excellent removal compound while brucite and $Mg(OH)_2$ did not.
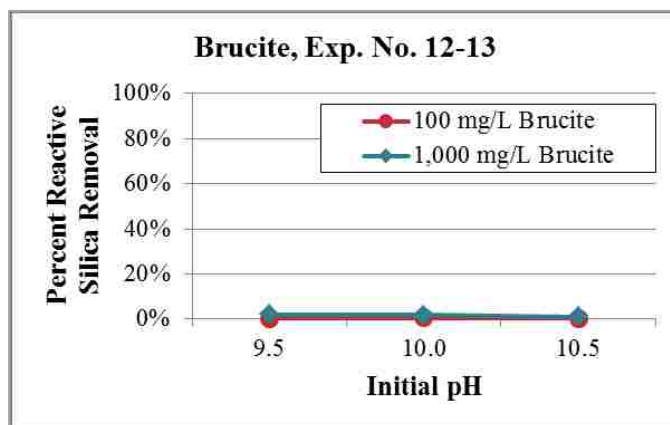

Figure 4-7: Silica Removal in Tests Using 100 mg and 1,000 mg Powdered Brucite at an Initial pH from 9.5 to 10.5 and an Initial Reactive Silica Concentration of 63.2 mg/L (Experiments No. 12-13)
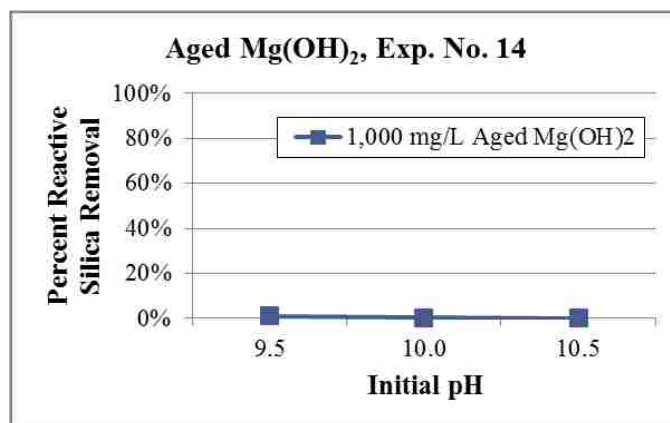
Figure 4-8: Silica Removal in Tests Using 1,000 mg Powdered Aged Mg(OH)$_2$ at an Initial pH from 9.5 to 10.5 and an Initial Reactive Silica Concentration of 65.3 mg/L (Experiment No. 14)

Initial pH vs. Final pH

Experiments no. 1-14 were performed using initial pH as a basis for comparison. Upon conclusion of these tests, it was suggested that initial pH was not offering an accurate comparison between removal by preformed Mg(OH)$_2$ and precipitated Mg(OH)$_2$ during tests with dissolved MgCl$_2$. Consider Table 4-1 below, which shows the initial and final pH values for experiments 7-11 (these are the averaged values from the tests with Batch Waters C and D). In preformed Mg(OH)$_2$ experiments 7-9, the final pH measurements were higher than the initial readings for all magnesium concentrations, with an increase between 0.3 and 1.6 pH units depending on dose and initial pH. For experiments 10-11 with dissolved MgCl$_2$, final pH was always lower than initial, with the decrease ranging from 0.06 to 1.3 pH units. A visual representation of the data is presented in Figures 4-9 and 4-10, which plot reactive silica removal against final pH and magnesium concentration.

Table 4-1: Summary of Results for Experiments No. 7-11

		Experiments No. 7 - 9 (Avg. Results)			Experiments No. 10 - 11 (Avg. Results)		
		Preformed Mg(OH)$_2$			Dissolved MgCl$_2$		
Mg^{2+} (mg/L)	Desired Initial pH	Initial pH (Measured)	Final pH (Measured)	% Reactive SiO$_2$ Removal	Initial pH (Measured)	Final pH (Measured)	% Reactive SiO$_2$ Removal
100	9.5	9.49	10.30	17.0%	-	-	-
1,000	9.5	9.49	10.78	89.3%	-	-	-
10,000	9.5	9.49	11.13	97.5%	-	-	-
100	10.0	10.01	10.76	22.6%	9.92	9.86	1.5%
1,000	10.0	10.01	11.40	83.0%	9.92	9.47	21.3%
10,000	10.0	10.01	11.27	94.7%	9.92	9.13	62.7%
100	10.5	10.51	10.87	26.4%	10.51	10.16	6.0%
1,000	10.5	10.51	11.39	89.4%	10.51	9.55	32.6%
10,000	10.5	10.51	11.92	94.5%	10.51	9.16	69.0%

In Figure 4-9 it is easy to see that, generally, as the magnesium concentration increases, the difference between initial and final pH grows larger. This occurs because Mg(OH)$_2$ is a strong base.
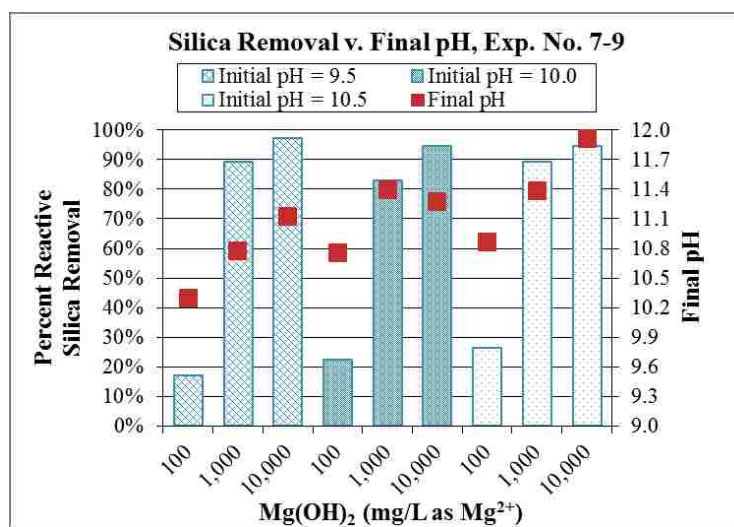

Figure 4-9: Reactive Silica Removal Plotted Against Final pH for Experiments No. 7-9 with Preformed Mg(OH)$_2$

A similar effect was found in the results of the dissolved MgCl$_2$ experiments no. 10-11 except that for these tests, final pH was lower than the initial pH. At high pH, Mg^{2+} acts as an acid according to the following reaction:

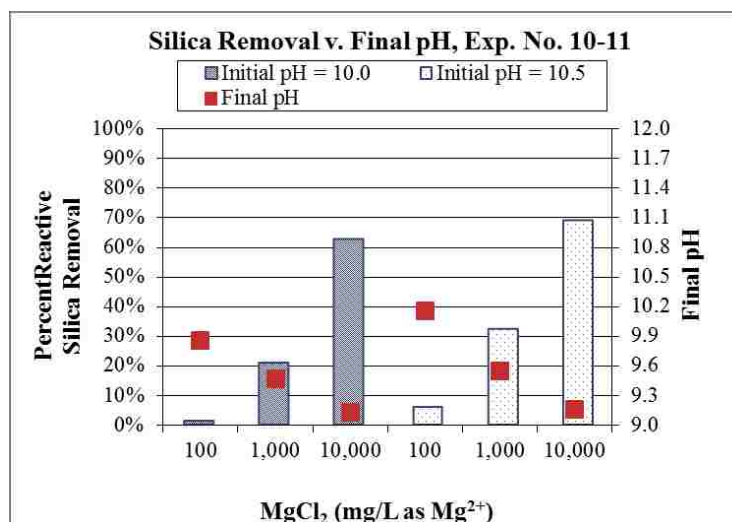$$Mg^{2+} + 2H_2O = Mg(OH)_2(s) + 2H^+.$$

Figure 4-10: Reactive Silica Removal Plotted Against Final pH for Experiments No. 10-11 with Dissolved MgCl$_2$

Figures 4-9 and 4-10 show that even though more removal was achieved by a 10,000 mg/L Mg(OH)$_2$ as Mg^{2+} than at the same concentration of MgCl$_2$, the tests likely were not operating at the same pH based on their final pH readings. This idea was explored further in Experiments no. 15-17, discussed in the next section.

Experiments No. 15-17

Experiments no. 15-17 were conducted to compare removal by preformed Mg(OH)$_2$ removal with precipitated Mg(OH)$_2$ (using dissolved MgCl$_2$) on the basis of final pH instead of initial pH. The goal of each test was to maintain a similar operational pH in the Mg(OH)$_2$ and MgCl$_2$ jars and to end at the same pH. A concentration of 1,000 mg/L Mg^{2+} was used in all tests and each test was 20 minutes long followed by a 10 minute settling period. The complete experimental procedure for experiments no. 15-17 was outlined in Chapter 3.

The results of Exp. No. 15 are shown in Figure 4-11. Batch Water C was used in both the MgCl$_2$ and Mg(OH)$_2$ tests. The average initial pH of the batch water was 10.92.

Prior to the start of the $MgCl_2$ test, the pH was reduced to 9.71 using 12N HCl. No pH adjustments were made to the $Mg(OH)_2$ solution. The pH of the $Mg(OH)_2$ jar was brought down over the course of the 20 minute jar test and ended at the same final pH as the $MgCl_2$ jar (see Figure 4-11 (a)). 30 minutes marked the end of a 10 minute settling period. Figure 4-11 (b) shows that much better removal was achieved with $Mg(OH)_2$; the result was not surprising considering previous experiments no. 5-11 that showed low removal by precipitated $Mg(OH)_2$ ($MgCl_2$ tests) at an initial pH of 10.

4-11 (a): pH over Time	4-11 (b): Reactive Silica Removed

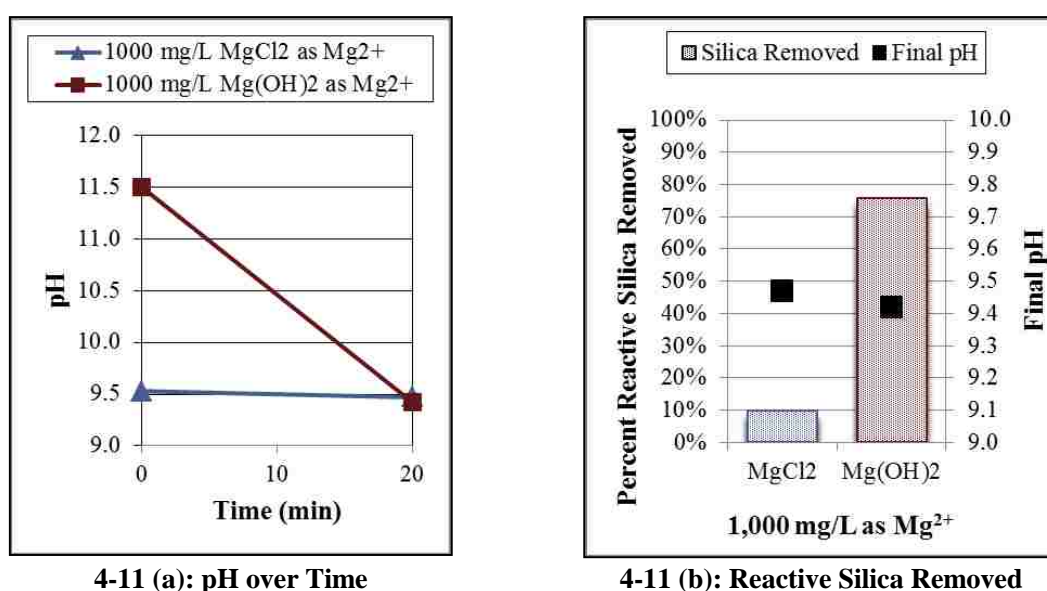**Figure 4-11: Comparison of Reactive Silica Removal vs. Final pH Using Dissolved $MgCl_2$ and Preformed $Mg(OH)_2$ with No Initial pH Adjustment to $Mg(OH)_2$ Jar (Experiment No. 15)**

Figure 4-12 shows the results of experiment no. 16. Batch Water C, with an average initial pH of 10.78, was used in both the $Mg(OH)_2$ and $MgCl_2$ tests. Prior to the start of the $MgCl_2$ test, the pH was reduced to 9.31 using 12N HCl. No pH adjustments were made to the $Mg(OH)_2$ jar. For this experiment, the $Mg(OH)_2$ and $MgCl_2$ jars were operating at the same pH at the 10 minutes mark and continued to do so for the remainder of the tests (see Figure 4-12 (a)). Figure 4-12 (b) shows that better removal was achieved

by $Mg(OH)_2$; however, the 60% silica removal achieved in this experiment was not as high as the roughly 75% observed in experiment no. 15. This is likely explained by the fact that the $Mg(OH)_2$ jar in experiment no. 15 operated at a higher pH for most of the test and did not reach a pH of 9.5 until the 20 minute mark (the end of the test). In experiment no. 16, the $Mg(OH)_2$ jar operated for a full 10 minutes more at pH 9.5; thus, experiment no. 16 is probably a more realistic representation of the amount of silica removed at a pH around 9.5.
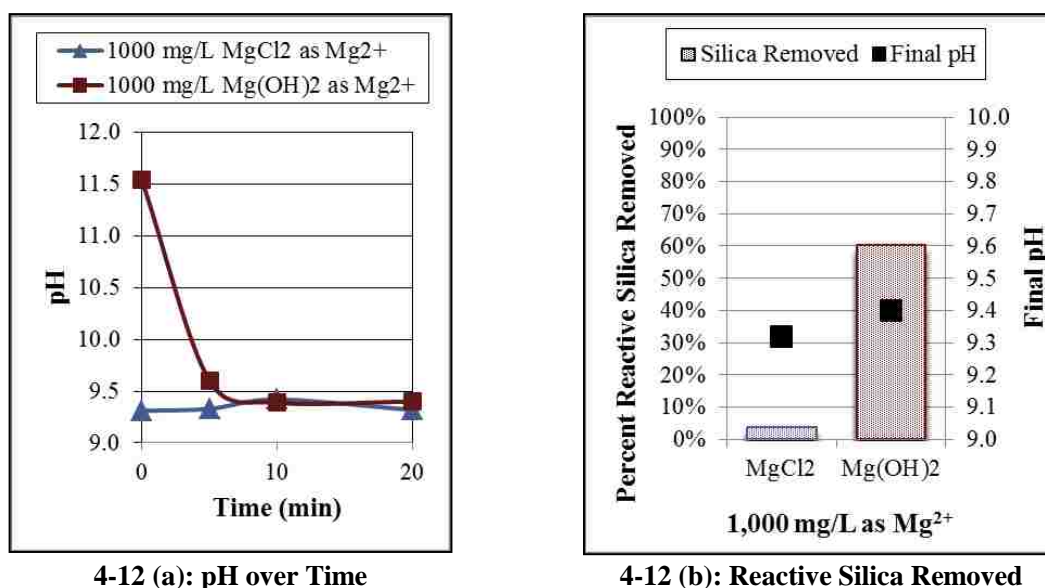

| 4-12 (a): pH over Time | 4-12 (b): Reactive Silica Removed |

Figure 4-12: Comparison of Reactive Silica Removal vs. Final pH Using Dissolved MgCl₂ and Preformed Mg(OH)₂ with No Initial pH Adjustment to Mg(OH)2 Jar (Experiment No. 16)

Results of experiment no. 17 are shown in Figure 4-13. Batch Water D was used in both the $MgCl_2$ and $Mg(OH)_2$ tests; the average pH of the batch water was 10.73. 12N HCl was used to reduce the pH of the $MgCl_2$ jar to 10.04 and to 1.66 in the $Mg(OH)_2$ jar test. Because of the significant pH reduction in the $Mg(OH)_2$ jar, both the $Mg(OH)_2$ and $MgCl_2$ jars were operating at roughly the same pH between 9.5 and 10 for the entirely of the test (see Figure 4-13 (a)). Removal by precipitated $Mg(OH)_2$ in the $MgCl_2$ tests was

higher than in experiments no. 15-16 but was still low at only 20%. Removal by

preformed $Mg(OH)_2$ was, again, significantly better than precipitated $Mg(OH)_2$.

4-13 (a): pH over Time   **4-13 (b): Reactive Silica Removed**

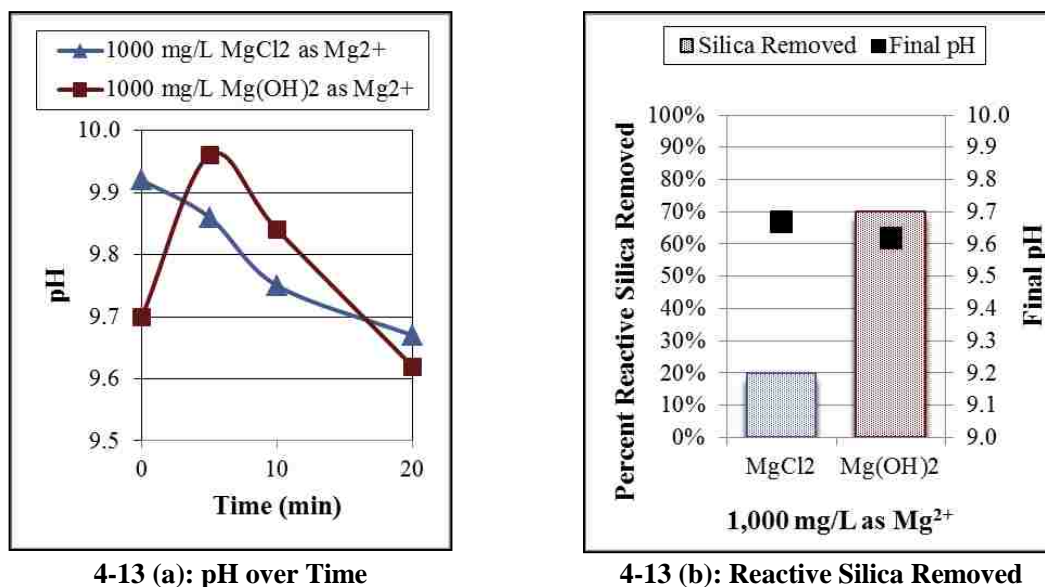**Figure 4-13: Comparison of Reactive Silica Removal vs. Final pH Using Dissolved $MgCl_2$ and Preformed $Mg(OH)_2$ with Pre-Test pH Adjustment to $Mg(OH)_2$ Jar (Experiment No. 17)**

The results of experiments no. 15-17 are significant because they demonstrated

that preformed $Mg(OH)_2$ achieved better removal in tests where operational pH was the

same in the $MgCl_2$ and $Mg(OH)_2$ jars. The results of the experiments no. 1-17 seem to

suggest that adsorption plays a larger role in removal of silica during a softening process.

Jar Tests to Determine Flow-Through HRT

Phase 2 of the project required the design of a flow-through system. The first step

in determining how large the system should be was establishing a hydraulic residence

time, or HRT. According to equation 3.3, volume, flow, and HRT are all related; thus,

selection of a flow rate and HRT would provide the desired volume of the system.

Experiments no. 18-20 were each conducted over a two hour period and the results were

used to estimate HRT for the flow-through system. A detailed explanation of the procedure for each test was provided in Chapter 3.

Figures 4-14 through 4-16 show the individual results of experiments 18-20 and Figure 4-17 graphs silica removal for the three experiments on a single chart. High silica removal was achieved quickly in all three experiments, but experiment no. 19, which operated at a pH between 9.95 and 10.15, realized the highest removal over the course of the entire test. Experiment no. 20 – operated at a pH between 9.35 and 9.70 – achieved the next highest level of removal over the course of the test. Experiment no. 18, which was operated at a pH of 11.40, demonstrated the least removal at the beginning of the test but continued to increase over time.

Based on the results of these experiments, an HRT of 20 minutes was selected. The percent silica removal in all three experiments at 20 minutes was 75% or above.
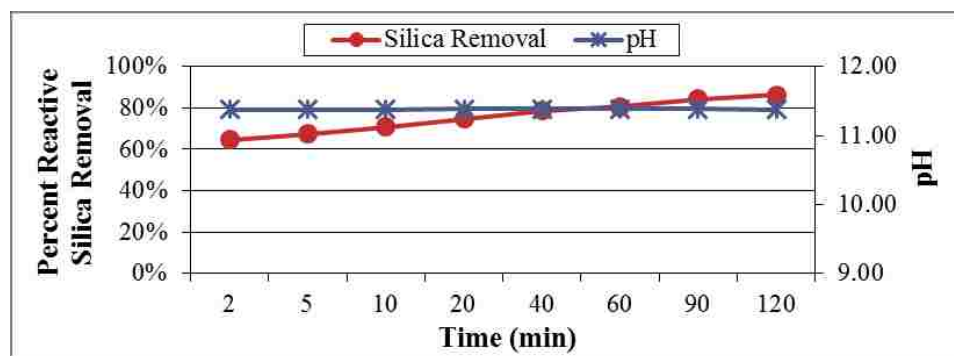

Figure 4-14: Reactive Silica Removal over Time Using Preformed Mg(OH)$_2$ in a Test Operated at pH 11.40 (Experiment No. 18)
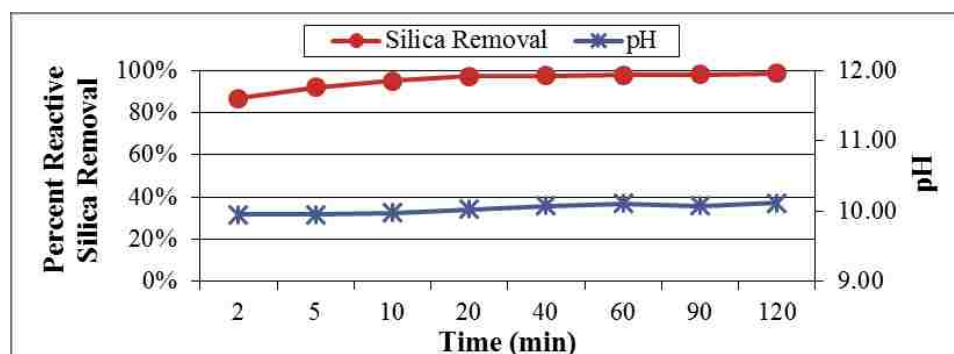
Figure 4-15: Reactive Silica Removal over Time Using Preformed Mg(OH)₂ in a Test Operated at pH 9.95-10.15 (Experiment No. 19)
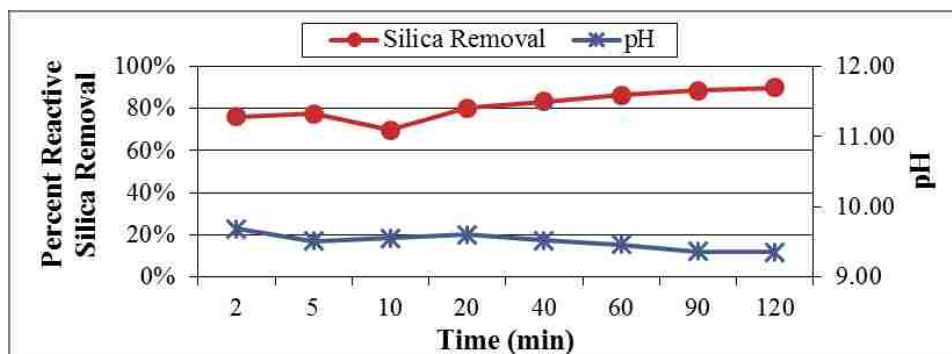

Figure 4-16: Reactive Silica Removal over Time Using Preformed Mg(OH)₂ in a Test Operated at pH 9.35-9.70 (Experiment No. 20)
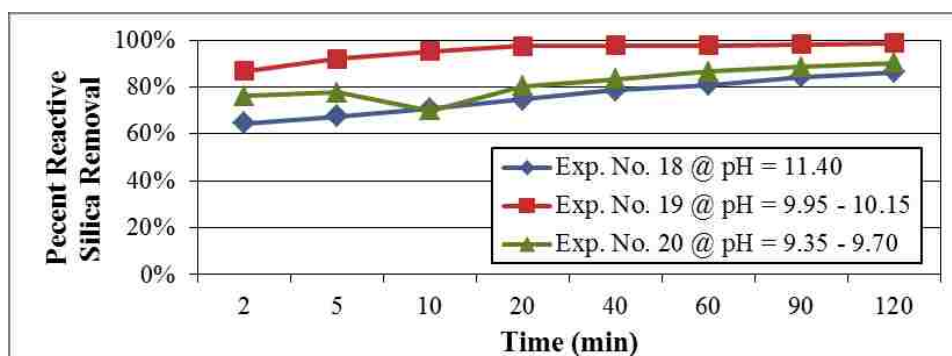

Figure 4-17: Summary of Results for Experiments No. 18-20 Showing Reactive Silica Removal over Time by Preformed Mg(OH)₂ at an Operational pH Range of 9.35 to 11.40

Jar Test with Iron Hydroxide

Analysis of results from experiments no. 1-20 led to the hypothesis that significant silica removal could be achieved at a pH of 10 or less, contrary to assertions in the literature that pH must be maintained at 10 or higher. The issue with operating a magnesium softening process for silica removal at a pH less than 10 is that magnesium hydroxide falls below the solubility limit at concentrations below 10,000 mg/L as Mg^{2+}; thus, over time, $Mg(OH)_2$ will dissolve and potentially reduce silica removal. Supplementing the softening process with another less soluble compound could abate the problem of magnesium hydroxide dissolution.

Aluminum and iron compounds have been reported in the literature to be good silica adsorbents (Al-Rehaili 2003; Cheng et al. 2009; Cob et al. 2014; Masarwa et al. 1997; Milne et al. 2014). Cheng et al. (2009) found the highest level of silica removal to be 65% with a 30 mg/L Al_2O_3 dose at a pH of 7.1. The authors concluded that silica was removed via co-precipitation with aluminum hydroxide, which they supported by comparing silica removal with remaining turbidity at different pH values. Sheikholeslami and Bright (2002) found that an alum dose of 0-15 mg/L achieved silica removal above 90% at a pH around 10.8. Removal decreased for doses of 20 and 25 mg/L to about 90% and 80%, respectively; it was argued that the decrease in removal corresponded to a lower pH range of 10.6-10.7. Removal by Fe largely followed the same trend. Roughly 90% removal was achieved for doses between 10 and 25 mg/L $FeCl_3$ at a pH of around 10.7. Cob et al. (2014) tested Fe^{3+} and Al^{3+} for silica removal in water containing 200 mg/L SiO_2. Al^{3+} was shown to both efficiently and rapidly remove silica. At a pH of 8.5 with a 400 mg/L (14.8 mM) Al dose, almost all silica was removed within ten minutes. 99.9% removal was achieved by 1 hour. For Al doses of 200 mg/L (7.4 mM) and 300 mg/L (11.1 mM), roughly 95% and 99% removal, respectively, was achieved by 1 hour. Fe doses of 100 mg/L (1.8 mM) and 200 mg/L (3.6 mM) were tested over a 6 hour period at a pH of 8.5. At 6 hours, both doses had achieved removal of around 35%, which was the maximum removal achieved during the test. Based on their numbers, a 100 mg/L Fe dose removed roughly 0.56 mol SiO_2 per mol Fe. For a 200 mg/L dose, 0.28 mol SiO_2 was removed per mol Fe; thus, removal was not enhanced with a higher test. Results of this thesis project (shown below) suggest there *is* an increase in remove with a higher dose.

Both Al and Fe were considered as options for inclusion in this project. Visual MINTEQ analysis (refer to Figure 3-8) was utilized to determine which compound is more insoluble. Iron was found to be less soluble; thus, iron hydroxide was selected for use in experiment no. 21, which evaluated silica removal by $Fe(OH)_3$ over a two hour period.

2,300 mg/L $Fe(OH)_3$ as Fe^{3+} – the molar equivalent of 1,000 mg/L $Mg(OH)_2$ as Mg^{2+} – was used in experiment no. 21. The results of experiment no. 21 are presented in Figure 4-18 and show that high silica removal was achieved within the first 5 minutes of the test. Milne et al. (2014) reported that iron compounds are generally very good silica adsorbents, but can form an unwanted hard, glass-like scale. Based on the result of this jar test, $Fe(OH)_3$ was selected for experimentation during Phase 2 to supplement $Mg(OH)_2$ solids, but it was acknowledged that iron hydroxide alone is probably not a feasible choice for a standalone, real world softening process.
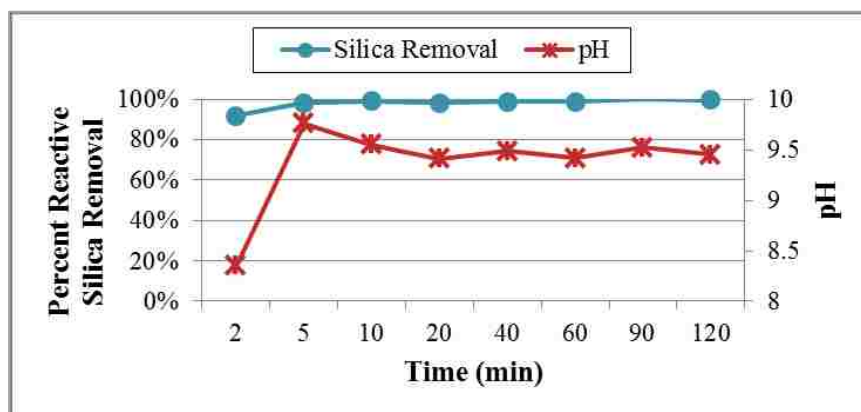

Figure 4-18: Reactive Silica Removal over Time Using Preformed $Fe(OH)_3$ in a Test Operated at pH 9.41-9.76 (Experiment No. 21)

Phase 2: Flow-Through Experiments

Phase 2 testing expanded on the experiments completed during Phase 1. The goal was to complete five tests – experiments no. 22-26 – over a longer time scale evaluated:

(1)   Whether or not the results of Phase 1 held up over a longer experimental

        period

(2)   Silica removal in a system with recirculating $Mg(OH)_2$ and $Fe(OH)_3$ solids

(3)   The adsorption capacity of magnesium and iron solids

(4)   Silica removal at a pH in the range of 9.5 to 10.5

(5)   Reactive and colloidal silica removal

The magnesium concentration, iron concentration, and desired pH range for each test are

summarized in Table 4-2 (this table was also included in Chapter 3 as Table 3-5).

Table 4-2: Solids Concentration and pH for Experiments No. 22-26

	$Mg(OH)_2$ Conc.	$Fe(OH)_3$ Conc.	Desired pH
Experiment No. 22	1 g/L	-	10
Experiment No. 23	3 g/L	-	10
Experiment No. 24	3 g/L	-	9.5
Experiment No. 25	0.5 g/L	1.15 g/L	10
Experiment No. 26	-	2.3 g/L	10

Experiment No. 22

        Experiment no. 22 was carried out near pH 10 with a $Mg(OH)_2$ concentration of 1

g/L as Mg^{2+}. Figure 4-19 shows the percent of reactive silica removed over the course of

the test. At 30 minutes, 76% reactive silica removal was achieved. Good removal was

demonstrated until about 90 minutes, but then declined throughout the course of the test.

The decline was fairly drastic from 30 minutes to 4 hours and then maintained a more

steady decline. The results suggest that the adsorption capacity of the solids had been

quickly reached and that there was not enough magnesium being fed into the system to

precipitate new $Mg(OH)_2$ to assist in silica removal. Based on the batch water magnesium

concentration of 15.2 mg/L (see Chapter 3), the rate of magnesium into the system was

0.13 g/hr. Another explanation was that ample magnesium was entering the system but that the operational pH was not high enough to precipitate $Mg(OH)_2$.
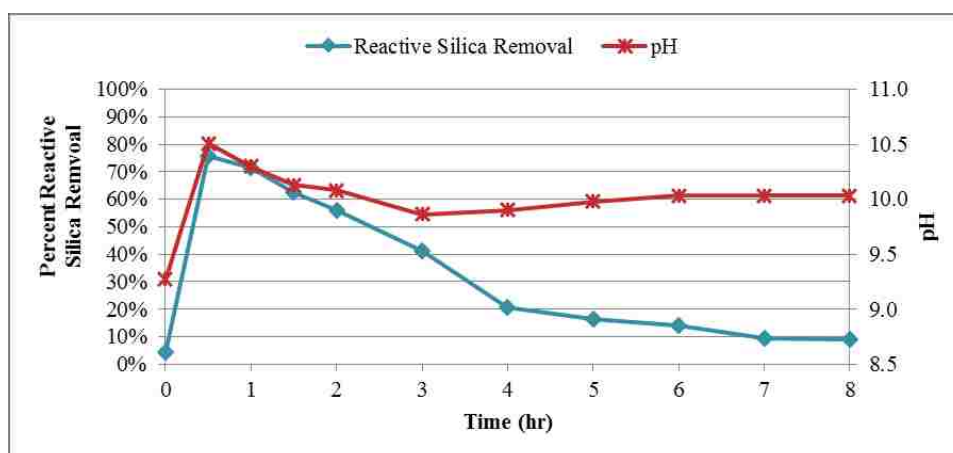

Figure 4-19: Reactive Silica Removal During Flow-Through Experimentation with a Preformed $Mg(OH)_2$ Dose of 1 g/L Mg, Operated Between pH 9.27 and 10.51 with a Feed Water Silica Concentration of 0.13 g/L (Experiment No. 22)

Experiment No. 23

To test the hypothesis that adsorption capacity in experiment no. 22 was exceeded, experiment no. 23 utilized a higher dosage of $Mg(OH)_2$. Figure 4-20 shows that removal was, in fact, much better than in experiment no. 22; however, the pH in experiment no. 23 remained around 10.5 for the first hour and a half of the test and did not drop down to 10 until the 4 hour mark. This may or may not influenced precipitation of additional $Mg(OH)_2$. Regardless of operational pH, results still seem to suggest that a higher solids concentration played a role in silica removal via adsorption.
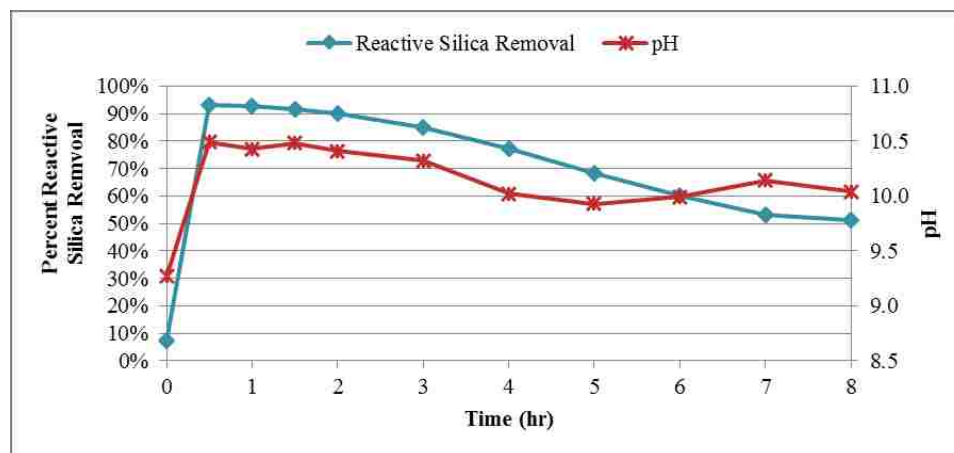
Figure 4-20: Reactive Silica Removal During Flow-Through Experimentation with a Preformed Mg(OH)$_2$ Dose of 3 g/L Mg, Operated Between pH 9.27 and 10.49 with a Feed Water Silica Concentration of 0.13 g/L (Experiment No. 23)

Experiment No. 24

Experiment no. 24 used an Mg(OH)$_2$ concentration of 3 g/L as Mg^{2+} and attempted to maintain an operational pH of 9.5 to explore the roles of adsorption capacity and precipitation of new Mg(OH)$_2$ solids in silica removal. The results presented in Figure 4-21 show good removal is maintained from 30 minutes until 3 hours, at which point it continues to steadily decline but still hovers around a sufficient removal rate of 60%. Up until the last hour, pH was maintained between 9 and 10. The fact that silica removal was relatively steady throughout the course of the test, even at a lower pH range, suggests that adsorption was playing the more dominant role.
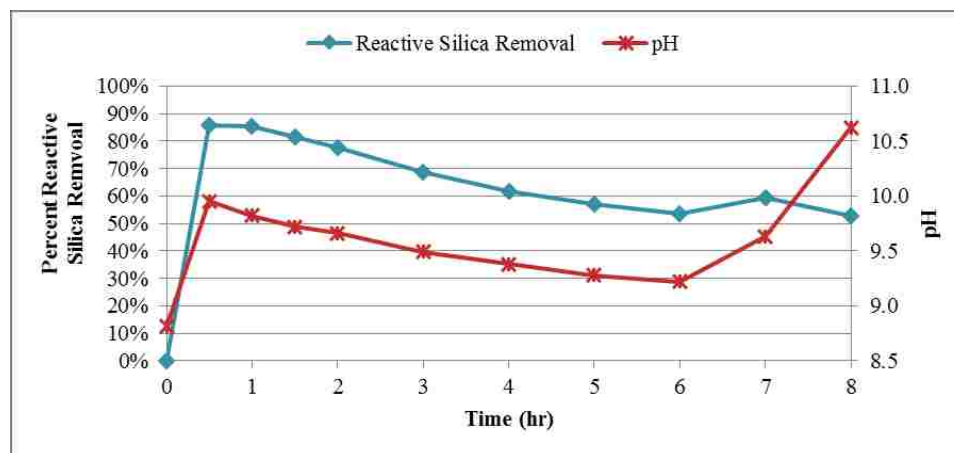
Figure 4-21: Reactive Silica Removal During Flow-Through Experimentation with a Preformed Mg(OH)₂ Dose of 3 g/L Mg, Operated Between pH 8.81 and 10.62 with a Feed Water Silica Concentration of 0.13 g/L (Experiment No. 24)

Experiment No. 25

Experiment no. 25 incorporated both magnesium and iron solids and aimed for an operational pH of 10. The sum of the $Mg(OH)_2$ and Fe(OH)3 concentrations used was the molar equivalent of 1 g/L $Mg(OH)_2$ as Mg^{2+}. The removal trend seen in Figure 4-22 is similar to that seen in experiment no. 22. More specifically, initial removal at 30 minutes was high – 84% – but it declined quickly until tapering off at the 4 hour mark. These results reinforce the hypothesis that 1 g/L solids do not provide ample surface area for adsorption.
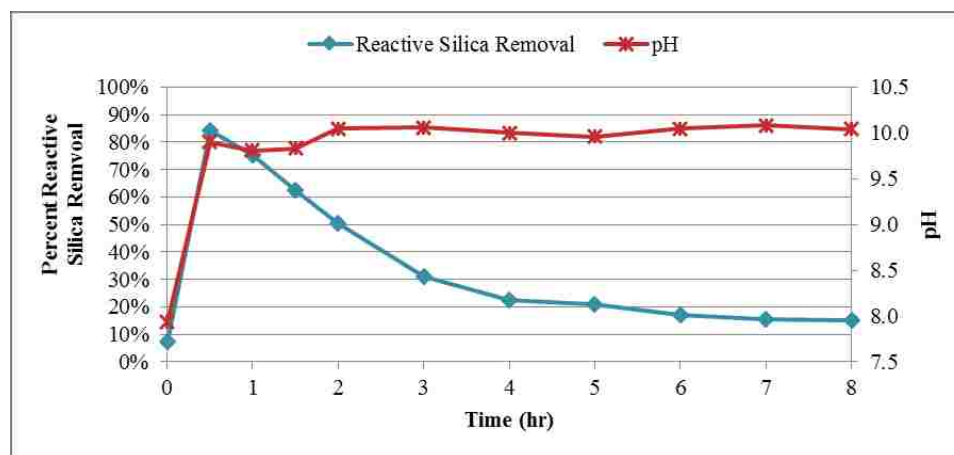
Figure 4-22: Reactive Silica Removal During Flow-Through Experimentation with a Preformed Mg(OH)$_2$ Dose of 0.5 g/L Mg and a Preformed Fe(OH)$_3$ Dose of 1.15 g/L Fe, Operated Between pH 7.94 and 10.08 with a Feed Water Silica Concentration of 0.13 g/L (Experiment No. 25)

Experiment No. 26

Experiment no. 26 was conducted with Fe(OH)$_3$ solids so that a comparison could be made with Mg(OH)$_2$ as a removal compound. 2.3 g/L as Fe^{3+}, the molar equivalent of 1 g/L Mg(OH)$_2$ as Mg^{2+}, was used in this experiment. pH was maintained around 10. Reactive silica removal, as shown in Figure 4-23, was good – around 80% – in the first hour but as with experiments no. 22 and 25, removal declined steadily and fell below 60% after 2 hours. These results further confirm the hypothesis that the adsorption capacity of the solids was being reached too quickly, thereby reducing silica removal.

The initial pH in experiment no. 26 was very low because some citric acid remained in the system following a cleaning after the previous experiment. pH was brought back up to an acceptable range within an hour of beginning the test.
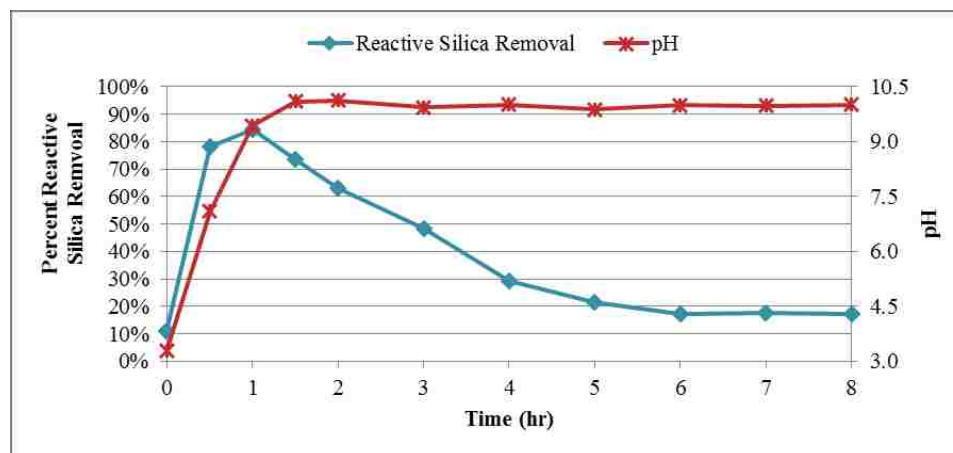

Figure 4-23: Reactive Silica Removal During Flow-Through Experimentation with a Preformed Fe(OH)$_3$ Dose of 2.3 g/L Fe, Operated Between pH 3.28 and 10.12 with a Feed Water Silica Concentration of 0.14 g/L (Experiment No. 26)

Summary of Results for Experiments No. 22-26

The results presented in Figures 4-19 through 4-23 are useful in observing how silica removal changed over time; however, the graphs do not account for flow in and out of various constituents during the course of each test. In addition to the $Mg(OH)_2$ and $Fe(OH)_3$ solids that were added at the beginning of a test, Mg, Ca, and SiO_2 were all present in the feed water and were continually flowing into the system. It should be noted that there was no Fe present in the feed water; thus, any Fe present in the system was added as $Fe(OH)_3$ for experiments no. 25-26. Dissolved forms of the aforementioned constituents were also flowing out of the system. Any Mg or Ca that remained in the system was assumed to be in solid form. Furthermore, the average concentrations of Mg, Ca, and SiO_2 flowing in to the system were 0.013 g/L (0.53 mM) Mg, 0.071 g/L (1.78 mM) Ca, and 0.133 g/L (2.21 mM) SiO_2. On a molar basis, roughly 4 times more SiO_2 than Mg was flowing into the system and about 1.25 times more SiO_2 than Ca was flowing in.

Figure 4-24 depicts the molar ratio of silica removed to magnesium in the system over the course of each 8 hour experiment. For experiment no. 26 with a dose of 2.3 g/L Fe, the ratio of SiO_2 removed to Mg is *much* higher than in the other four experiments because there was no magnesium added at the beginning of the test. The only magnesium present in the system was Mg that flowed in with the feed water. It is difficult to see how the results of experiments no. 22-25 compare, so these lines are also plotted in Figure 4-25.
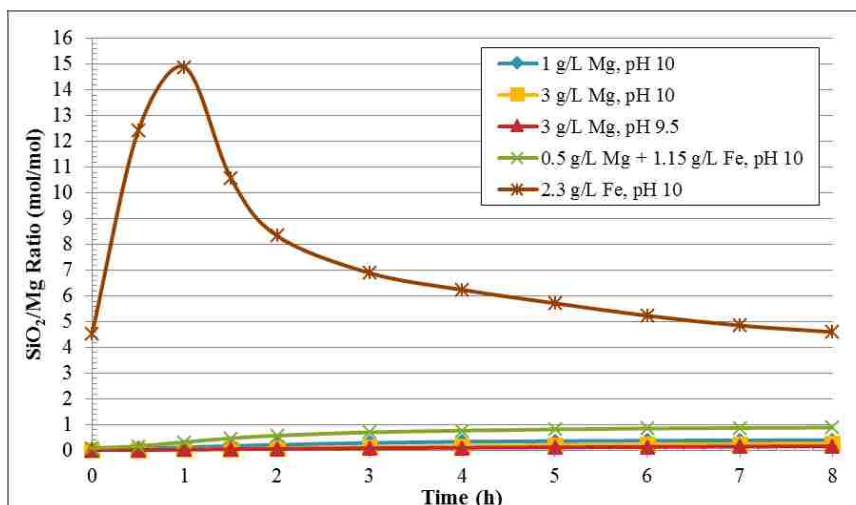
Figure 4-24: Molar Ratio of Silica Removed to Magnesium in the System over Time (Experiments No. 22-26)

Figure 4-25 shows how the SiO_2:Mg ratio increases as initial magnesium concentration decreases. This, again, is explained by the fact that SiO_2 is flowing into the system at a greater rate than Mg; thus, SiO_2 is accumulating while magnesium solids are actually shown to be dissolving. The dissolution of magnesium during each test is shown in Figures 4-26 through 4-30. Figure 4-31 shows the flow of Mg out of the system compared to the average flow in. In experiment no. 24 with a 3 g/L Mg dose with a pH maintained around 9.5, there was more dissolution of magnesium over time than there was in experiment no. 23 with the same Mg dose but an operational pH closer to 10. In experiments no. 25 and 26 where there was either a low dose of initial Mg solids or no initial dose, Mg tended to remain in the system. For experiment no. 25, this means that Mg solids were not dissolving much over time. For experiment no. 26 (which had no initial dose of Mg), Figure 4-30 suggests that Mg solids were precipitated during the test.
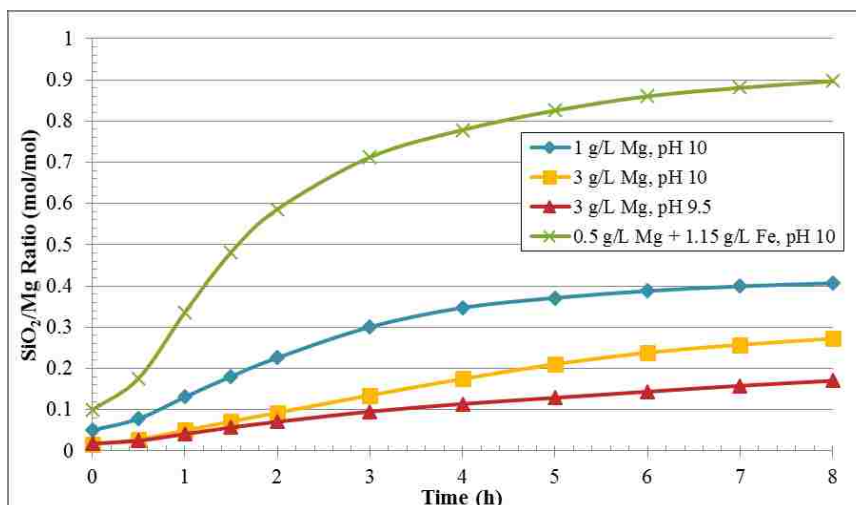
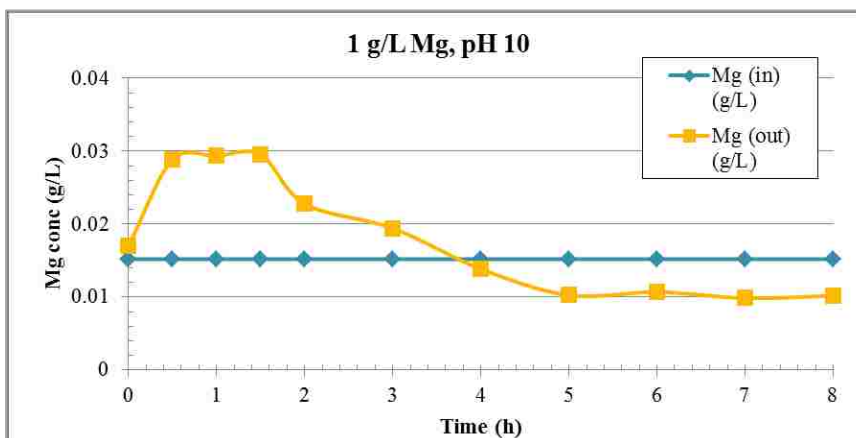**Figure 4-25: Molar Ratio of Silica Removed to Magnesium in the System over Time (Experiments No. 22-24)**

Figure 4-26: Concentrations of Mg Flowing In and Out of the System Indicating Dissolution of Magnesium over Time (Experiment No. 22)
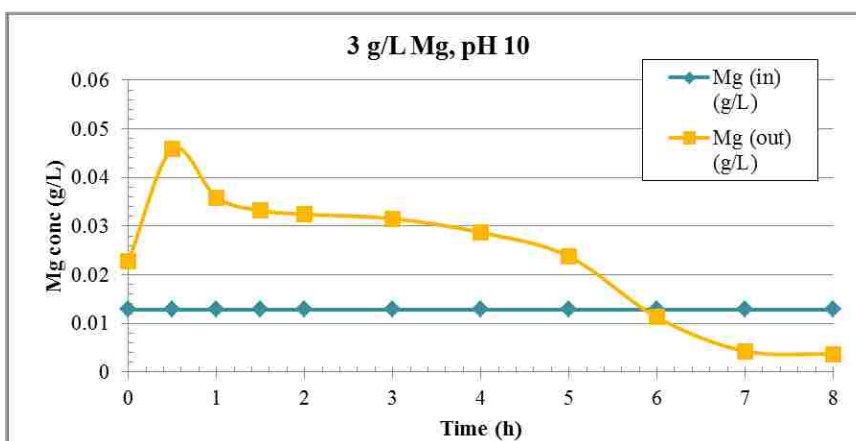
Figure 4-27: Concentrations of Mg Flowing In and Out of the System Indicating Dissolution of Magnesium over Time (Experiment No. 23)
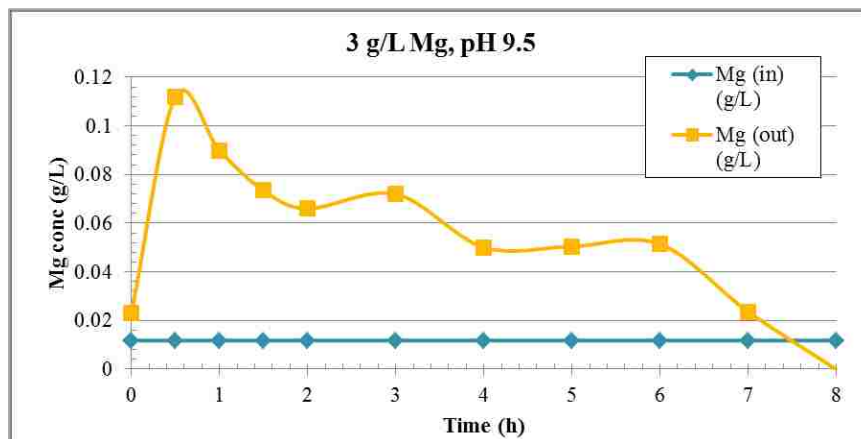

Figure 4-28: Concentrations of Mg Flowing In and Out of the System Indicating Dissolution of Magnesium over Time (Experiment No. 24)
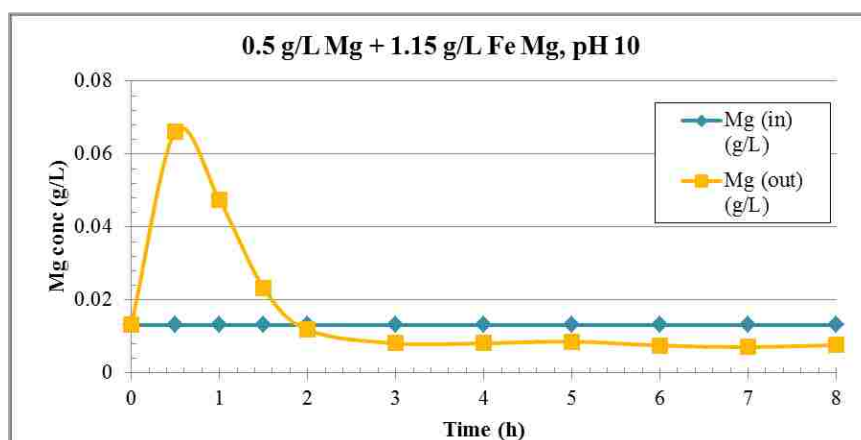

Figure 4-29: Concentrations of Mg Flowing In and Out of the System Indicating Dissolution of Magnesium over Time (Experiment No. 25)
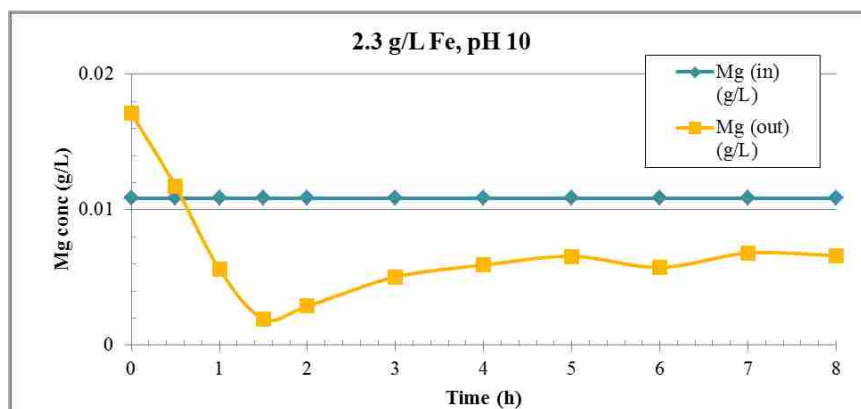
Figure 4-30: Concentrations of Mg Flowing In and Out of the System Indicating Dissolution of Magnesium over Time (Experiment No. 26)
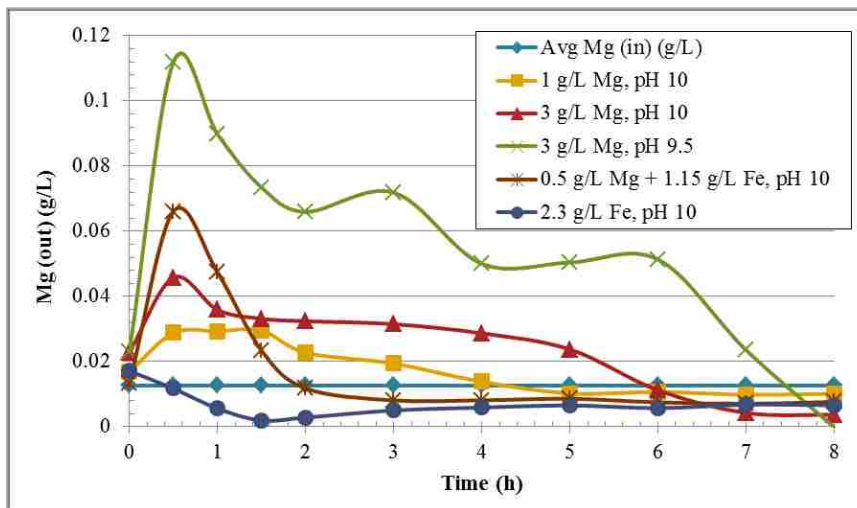

Figure 4-31: Average Mg Flow Into the System and Mg Flow Out of the System over Time (Experiments No. 22-26)

The ratio of moles SiO_2 removed per mole Fe is presented in Figure 4-32.

Because no iron was present in the feed water, the only iron in the system came from the

$Fe(OH)_3$ solids. Additionally, no iron was measured in the permeate indicating that no

iron dissolved over the course of the test. On a molar basis, Fe would appear to be a
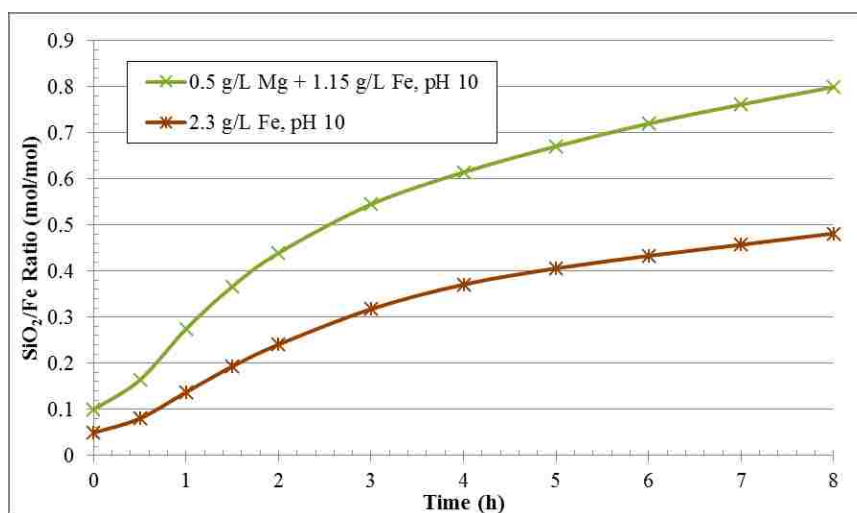
better silica adsorbent than Mg (see Figure 4-33).

Figure 4-32: Molar Ratio of Silica Removed to Iron in the System over Time (Experiments No. 25-26)
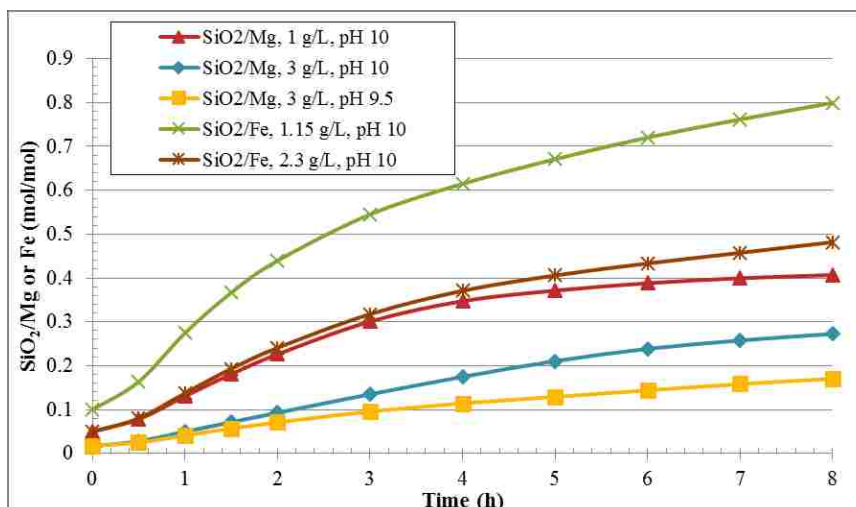
Figure 4-33: Molar Ratio of Silica Removed Per Mole of Magnesium or Iron in the System (Experiments No. 25-26)

The molar ratio of SiO_2 removed to calcium in the system is presented in Figure 4-34. Overall Ca accumulated in the system over time, meaning calcium solids were precipitating. This is why the SiO_2/Ca ratio decreases over time. To estimate how much silica was being removed by magnesium and calcium solids, it would have been necessary to carry out solids analysis at the end of each test; however, extensive solids analysis was not within the scope of this project.
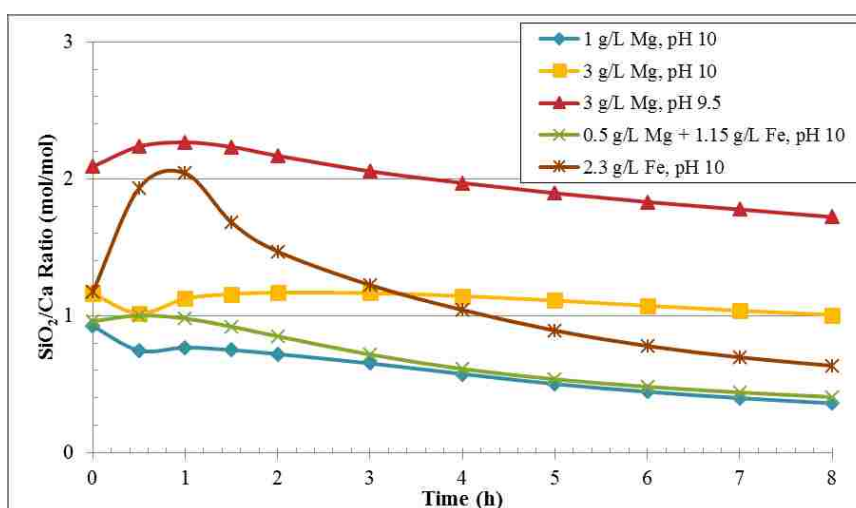

Figure 4-34: Molar Ratio of Silica Removed to Calcium in the System over Time (Experiments No. 22-26)

The ratio of moles SiO_2 removed per combined moles of Mg, Ca, and Fe is shown in Figure 4-35. This figure, like Figure 4-33, seems to suggest that iron enhances silica removal and is perhaps a better adsorbent than magnesium. It is also observed that the lines representing the three lower solids doses begin to decline after 5 or 6 hours, suggesting the adsorption capacity of the solids has been achieved. The solids in experiments with 3 g/L Mg doses do not reach adsorption capacity; however, removal at a pH of 10 with the 3 g/L dose was better than removal at a pH of 9.5.
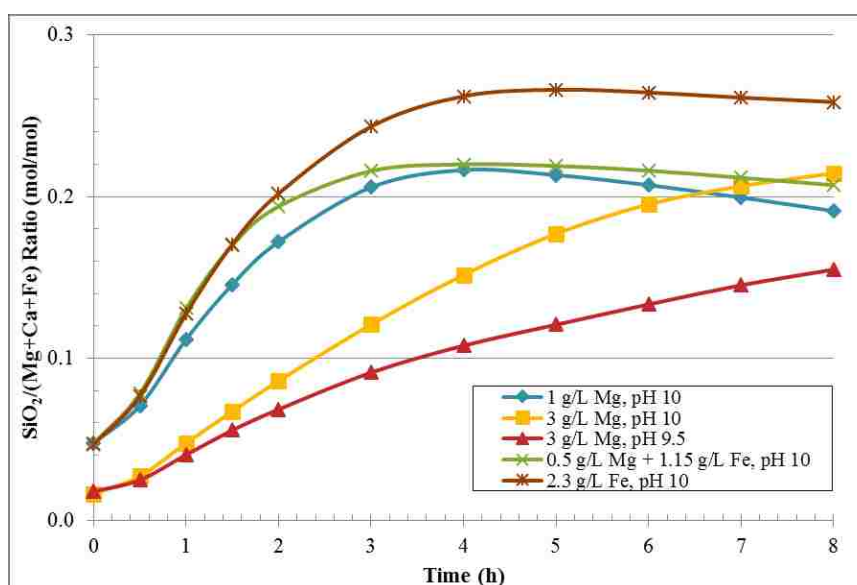

Figure 4-35: Molar Ratio of Silica Removed Per the Combined Molar Amount of Mg, Ca, and Fe in the System over Time (Experiments No. 22-26)

Figure 4-36 is useful because it shows the solids concentration necessary to achieve a certain removal efficiency. Furthermore, it shows that the two higher Mg doses achieved the highest silica removal efficiency. Removal efficiency decreased over time for all tests but remained at 50% or above for a 3 g/L Mg dose. For all lower initial solids concentrations, removal efficiency declined to around 10 or 20%. In the graph, the points

for all lower initial solids doses begin to curve around near the 30% removal mark; this corresponds to adsorption capacity of the solids being met (see Figure 4-35). Another important consideration, which was touched on previously, is that it is not known exactly how much removal can be attributed to the different solid compounds. This would require additional post-test solids analysis.
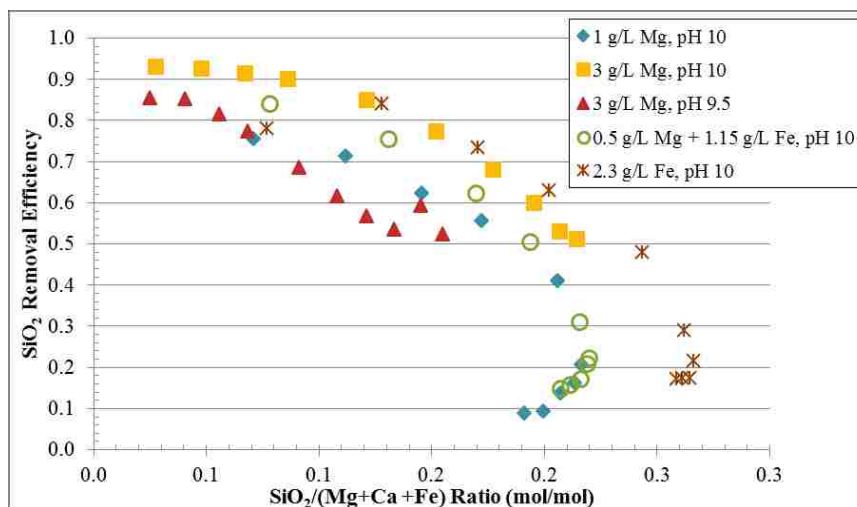

Figure 4-36: Silica Removal Efficiency Plotted as a Function of the Ratio of SiO₂ Removal Per Total System Solids (Mg, Ca, and Fe) (Experiments No. 22-26)

Membrane Fouling

Permeate flow (Q_p) in experiment no. 22 was roughly 116 mL/min. During experiment no. 23, there was a gradual decrease in Q_p. By the end of the test, flow was measured as 73 mL/min. Permeate flow continued to decrease in experiment no. 24 and at the beginning of the test was measured as 80 mL/min; by the end of the test it had dropped to 43 mL/min. It was speculated that the reduction of flow was due to membrane fouling by the solids used in experiments no. 22-24. Figure 4-37 shows magnesium and iron solids flowing through the system during experiments no. 22 and 24.

Figure 4-37 (a): Magnesium Solids
(Experiment No. 22)

Figure 4-37 (b): Iron Solids
(Experiment No. 24)

Figure 4-37: Magnesium and Iron Solids Observed in the Flow-Through System

Membrane fouling affects system flux (J), which is equal to permeate flow over the surface area of the membrane (A_m):

$$J = \frac{Q_p}{A_m}$$

(4.1)

A 1% citric acid solution was used to clean the system and restored permeate flow to a range of 109-118 mL/min. The silica removal and flux for experiments no. 22-26 were both plotted in Figures 4-38 and 4-39, respectively, to observe the trend in removal as membrane flux changed. The graphs demonstrate that a decline in flux did not result in a decrease in silica removal.
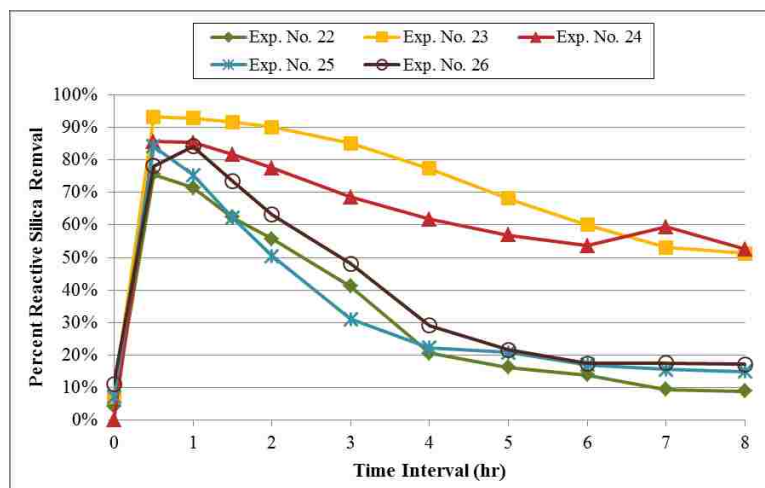
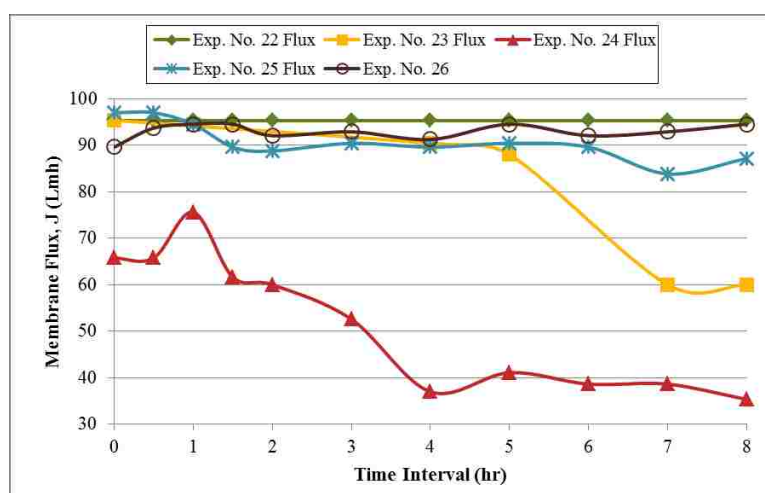**Figure 4-38: Reactive Silica Removal over Time for Experiments No. 22-26**

Figure 4-39: Membrane Flux over Time for Experiments No. 22-26

Sample Analysis

SEM

The SEM images for preformed $Mg(OH)_2$, aged $Mg(OH)_2$, and brucite are presented in Figure 4-40. As was expected, preformed $Mg(OH)_2$ had an amorphous structure, while brucite was more crystalline. It was theorized that the aged $Mg(OH)_2$ would have a structure similar to that of brucite, since both compounds were poor silica adsorbents. The aged $Mg(OH)_2$ was actually more amorphous in appearance, so its poor

removal could instead be attributed to minimal surface area. The aged $Mg(OH)_2$ in Figure 4-40 (h) looks less porous in contrast with the preformed $Mg(OH)_2$ surface in Figure 4-40 (d). BET surface area analysis (see discussion below) confirmed that aged $Mg(OH)_2$ had the least amount of surface area of all three samples.
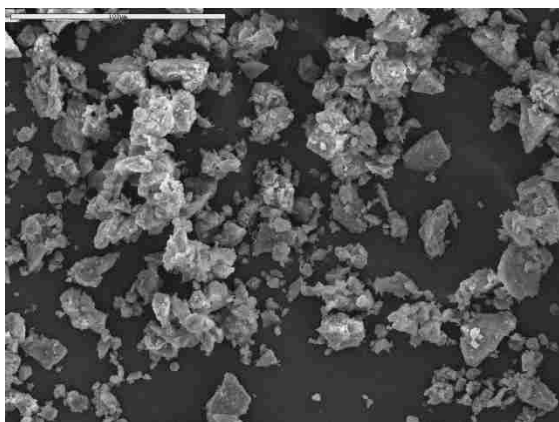
4-40 (a): Preformed Mg(OH)₂, 450x
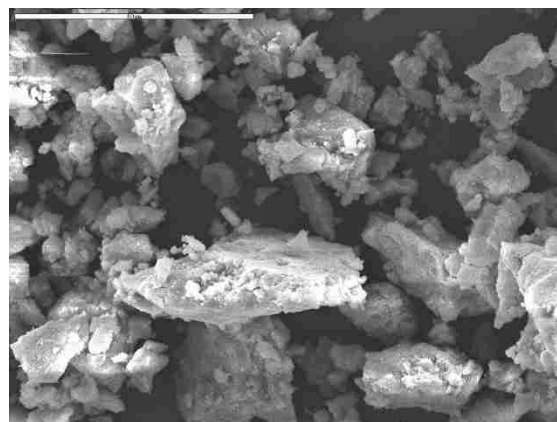
4-40 (b): Preformed Mg(OH)₂, 1000x
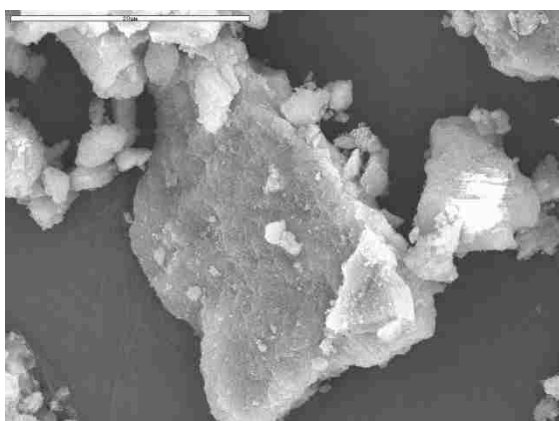
4-40 (c): Preformed Mg(OH)₂, 2500x
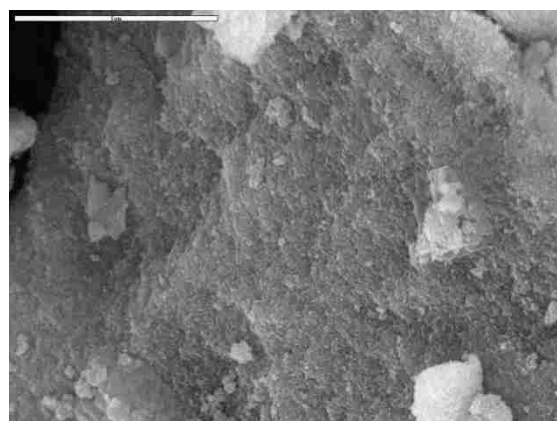
4-40 (d): Preformed Mg(OH)₂, 8500x
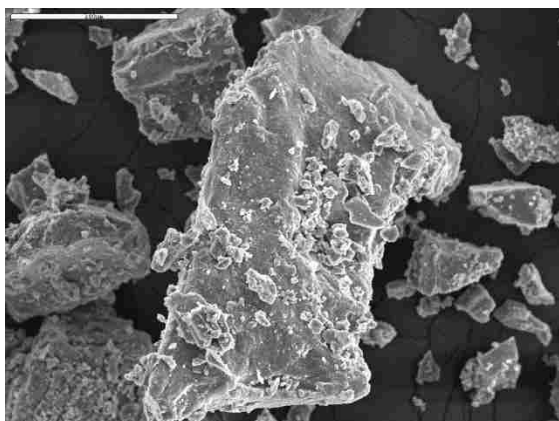
4-40 (e): Aged Mg(OH)₂, 350x
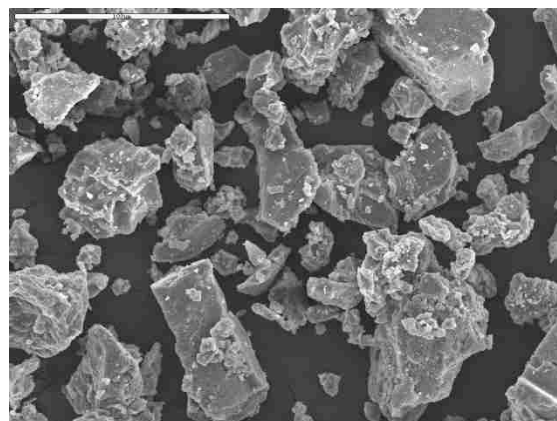
4-40 (f): Aged Mg(OH)₂, 450x
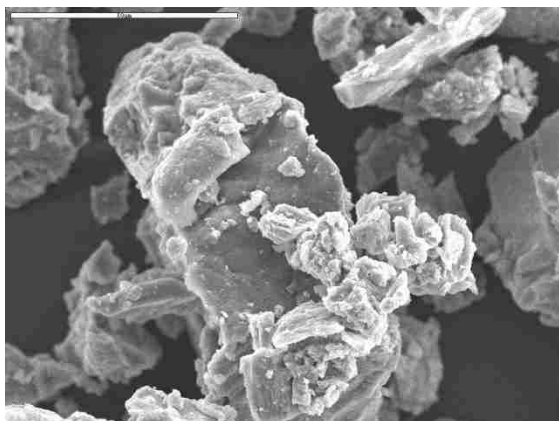
4-40 (g): Aged Mg(OH)₂, 950x
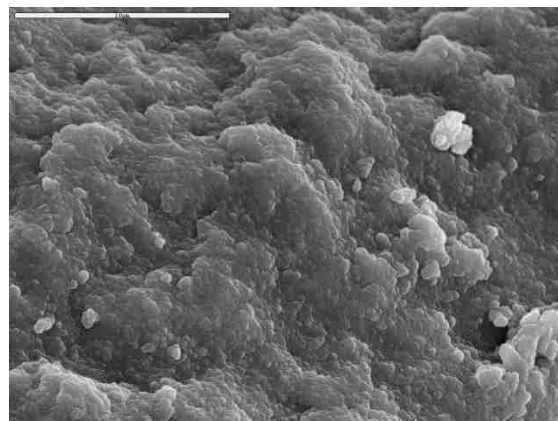
4-40 (h): Aged Mg(OH)₂, 4500x
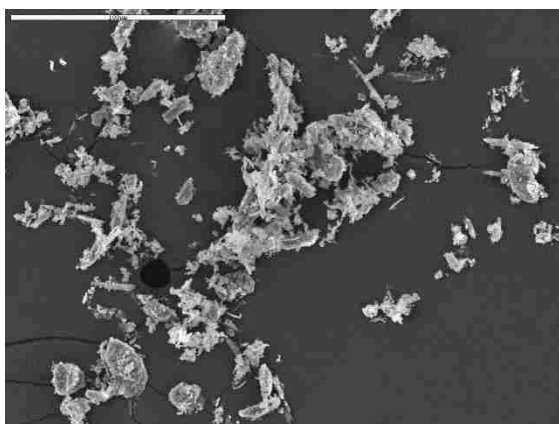
4-40 (i): Brucite, 450x
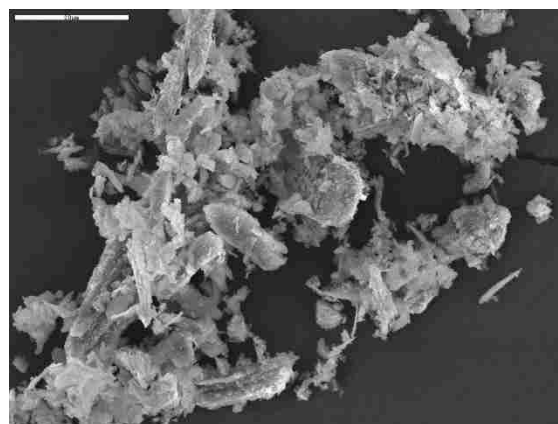
4-40 (j): Brucite, 1200x
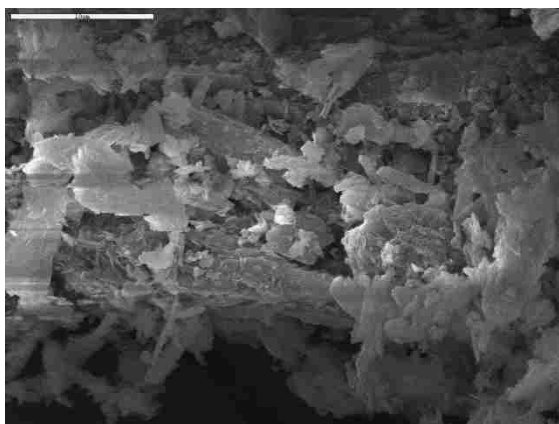
4-40 (k): Brucite, 3000x
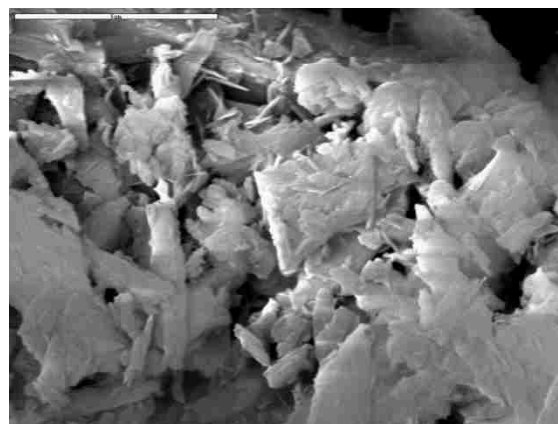
4-40 (l): Brucite, 8500x

Figure 4-40: SEM Images of Preformed Mg(OH)₂, Aged Mg(OH)₂, and Brucite

BET Surface Area Analysis

The Gemini 2360 Surface Area Analyzer measured the following surface areas for each sample:

Preformed Mg(OH)$_2$: 23.28 m^2/g

Aged Mg(OH)$_2$: 0.53 m^2/g

Brucite: 4.46 m^2/g

The surface area available on the preformed Mg(OH)$_2$ was much higher than the surface area of the other two samples, which explains in part why it achieved significantly better silica removal. The results of the BET analysis also correspond with SEM images that appear to show aged Mg(OH)$_2$ and brucite are less porous than preformed Mg(OH)$_2$.

XRD

The results of the XRD analysis for the samples of Preformed Mg(OH)$_2$, Aged Mg(OH)$_2$, and brucite are presented in Figures 4-41 through 4-43. It was expected that the preformed and aged Mg(OH)$_2$ samples would have a similar composition because they were both made by mixing MgCl$_2$ and NaOH solutions; the only difference was that aged Mg(OH)$_2$ was dried in an oven at a high temperature and the preformed Mg(OH)$_2$ sample was dried at room temperature. According to the analysis, brucite was the only Mg mineral present in the aged and preformed Mg(OH)$_2$ samples. Somehow, carbon was introduced to the aged Mg(OH)$_2$ sample, resulting in the presence of natrite. The carbon likely came from CO$_2$ in the atmosphere. The NaCl (halite) present in the preformed and aged Mg(OH)$_2$ samples was a product of the reaction between MgCl$_2$ and NaOH to make Mg(OH)$_2$. Brucite was not expected to be a completely pure sample, based on the sample data sheet provided by Garrison Minerals.
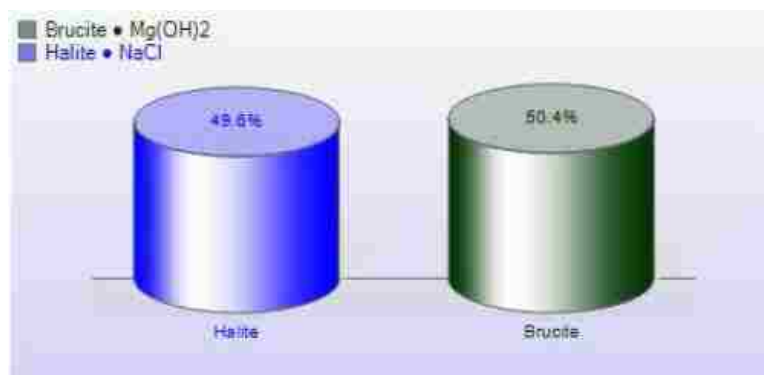
Figure 4-41: Results of XRD Analysis for Preformed Mg(OH)₂

Figure 4-42: Results of XRD Analysis for Aged Mg(OH)₂

Figure 4-43: Results of XRD Analysis for Brucite

Colloidal Silica Analysis

The project attempted to draw some conclusions about the presence and removal of colloidal silica during both Phase 1 and Phase 2 testing. To do so, both total silica and reactive silica were measured in some of the jar tests and flow-through experiments.

Recall that colloidal silica is defined as the difference between total silica as measured by ICP and reactive silica measured by the molybdosilicate colorimetric method; however, this definition does not allow for a distinction between polymeric silica and nano-sized amorphous or crystalline silica particles that would pass through membrane filters. The charts presented in Figure 4-44 show colloidal silica concentration plotted against reactive silica removal during experiments no. 7, 8, 12, and 13. The graphs show that there is no consistent pattern in colloidal silica removal during jar testing. Furthermore, colloidal silica does not correspond with reactive silica removal. For instance, in experiment no. 7 for magnesium concentrations of 1,000 and 10,000 mg/L where reactive silica removal was high, colloidal silica removal was fairly low, between 0-40%. In experiment no. 8 for the same magnesium concentrations where reactive silica removal was high, colloidal silica concentrations were higher than in experiment no. 7 in the range of 3-to 16 mg/L (corresponding to colloidal removal rates of 0-0.5%). In experiments no. 12 and 13 where reactive silica removal was extremely low, colloidal silica concentrations were in the range of 7 to 11 mg/L in experiment no. 12 but only 0 to 4 mg/L in experiment no. 13.
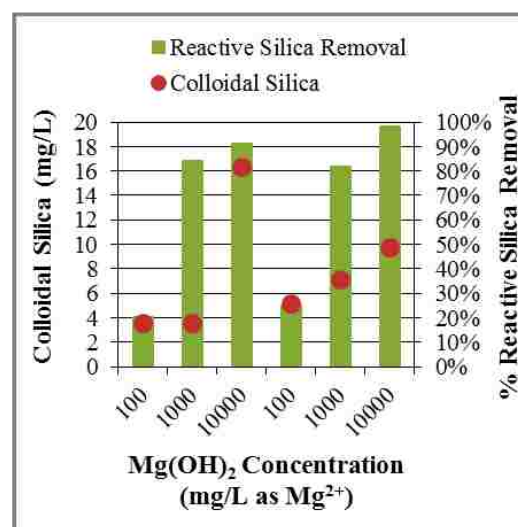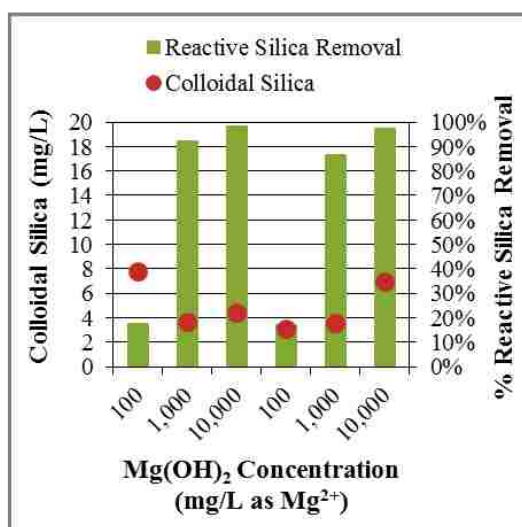
4-44 (a): Experiment No. 7   **4-44 (b): Experiment No. 8**
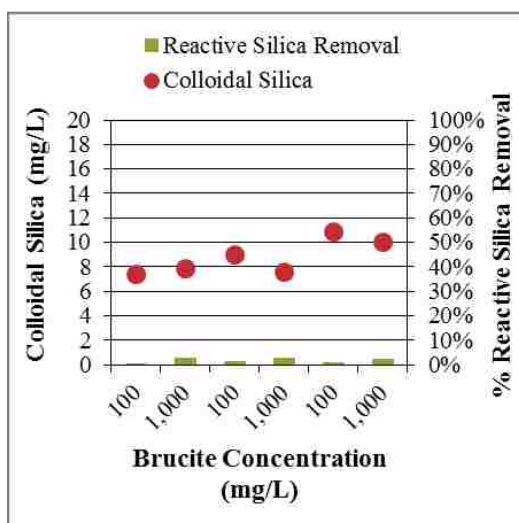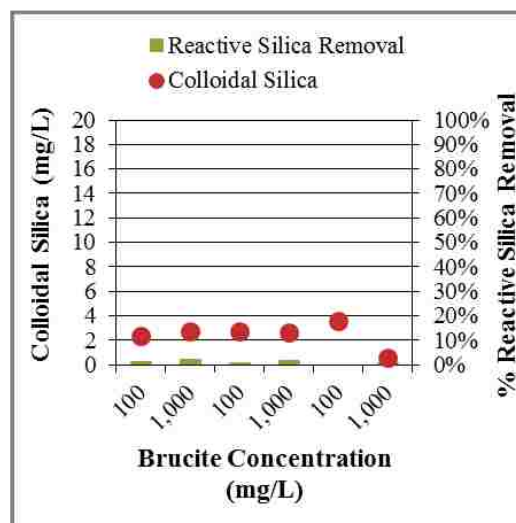
4-44 (c): Experiment No. 12   **4-44 (d): Experiment No. 13**

Figure 4-44: Colloidal Silica v. Reactive Silica Removal Observed in Phase 1

A similar observation was made for colloidal silica in the results of experiments no. 22-26. Colloidal silica removal did not correspond to reactive silica removal. For experiments no. 22 and 23, low concentrations of colloidal silica were measured in the permeate and corresponded to higher rates of reactive silica removal; yet, in experiments no. 24, colloidal silica concentrations in the permeate where in a higher range while reactive silica removal rates were high. Figure 4-45 presents colloidal silica concentration plotted against reactive silica removal for experiments no. 22-26.
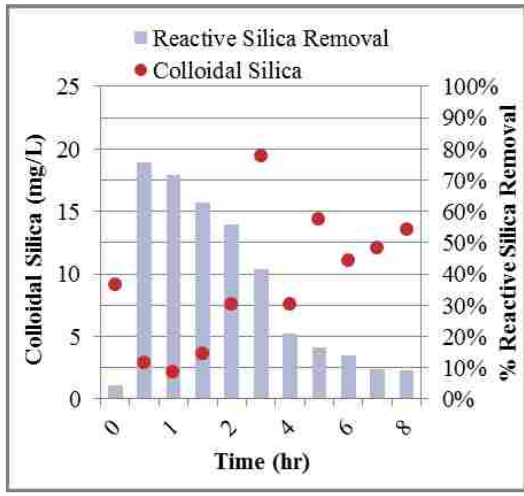
4-45 (a): Experiment No. 22
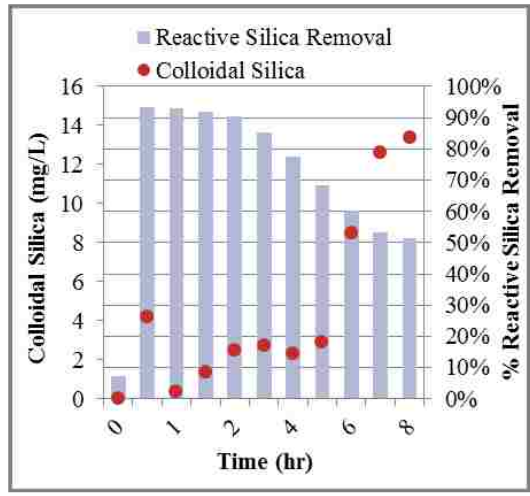
4-45 (b): Experiment No. 23
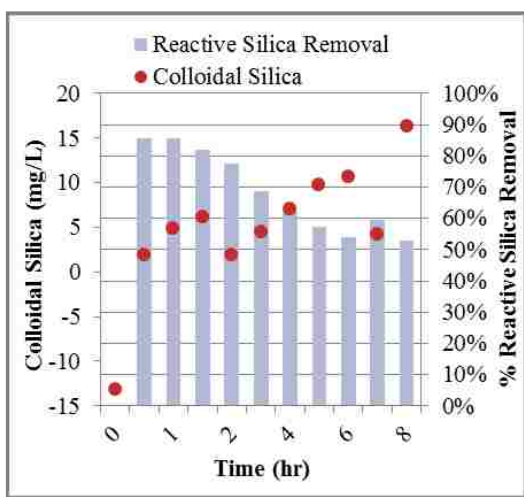
4-45 (c): Experiment No. 24
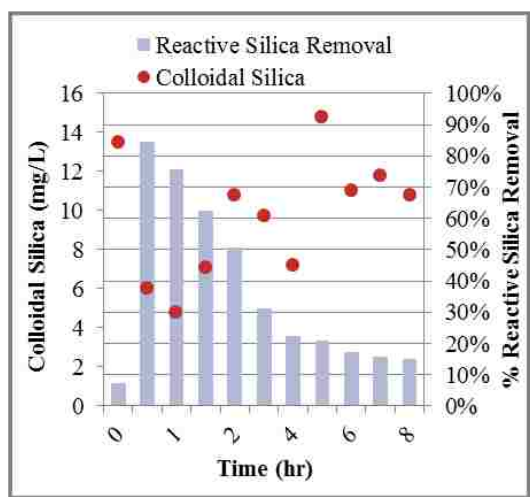
4-45 (d): Experiment No. 25
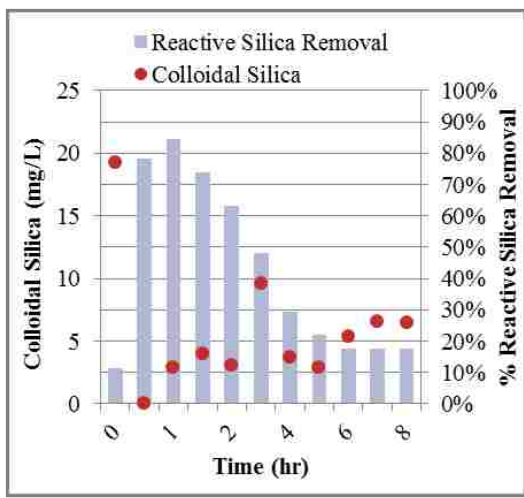
4-52 (e): Experiment No. 26

Figure 4-45: Colloidal Silica v. Reactive Silica Removal Observed in Phase 2

CHAPTER 5: CONCLUSIONS

Silica is understood to be a problematic constituent because it forms insoluble precipitates (i.e., scale) on the surfaces of industrial equipment and reverse osmosis membranes. Unlike other constituents, which can generally be removed by various treatment methods, silica is complex and not readily removed from water. It exists in water in different species and forms different solid phases when precipitated. Speciation is dependent on variables like pH, temperature, concentration, and ionic composition. Silica speciation is one of the main reasons that it can be such a tricky constituent to remove from water. At a neutral pH – i.e., in a pH range typical of most natural waters – silica exists largely as monomeric silica, an uncharged species. Furthermore, as monomeric silica polymerizes it can begin to form colloidal silica, which is argued to be one of the most undesirable scalants in RO treatment (Neofotistou and Demadis 2004).

Silica is most often removed during a lime softening process; thus, silica removal via lime treatment has been the focus of the majority of research on the subject of silica removal. Other research has focused on removal methods including adsorption to metal hydroxides, coagulation with filtration, and electrocoagulation with ultrafiltration. Even though silica is commonly removed during lime softening, research has shown that its removal is tied largely to the presence of magnesium or magnesium hydroxide solids (Al-Mutaz and Al-Anezi 2004; Chao and Westerhoff 2002; Chen et al. 2006; Cob et al. 2014; GE Water & Process Technologies n.d.; Sheikholeslami et al. 2001; Sheikholeslami and Bright 2002). $Mg(OH)_2$ solids may either be precipitated during treatment or added to the system during softening. There is some ambiguity with regards to exactly how magnesium hydroxide removes silica. Some report that it is removed during co-

precipitation with $Mg(OH)_2$, while others report that it is removed via adsorption to $Mg(OH)_2$ solids; however, removal by adsorption really has two components: (1) $Mg(OH)_2$ solids are already present in the system and available as adsorbents, and (2) $Mg(OH)_2$ precipitates during the softening process, which means that the newly formed solids are available for adsorption but also that removal by co-precipitation could be occurring simultaneously.

It is clear that the subject of silica removal is complex and warrants further research. As such, this project sought to: explore the removal of silica by a chemical softening process with $Mg(OH)_2$ or $Fe(OH)_3$ that utilized solids recycle; understand the relationship between silica removal, pH, and magnesium concentration; establish ideal operating parameters for the softening process; and gain further insight into adsorption and co-precipitation as the mechanisms for silica removal. To achieve these goals, the project was divided into two phases. Phase 1 included 21 jar tests – experiments no. 1-21 – conducted on a small scale over a short time period. Phase 2 included 5 flow-through tests – experiments no. 22-26 – that were larger scale and had a longer run time.

Experiments no. 1-4 showed that at an initial pH of 7, removal by both precipitated and preformed $Mg(OH)_2$ was minimal. Results at the higher initial pH of 11 and concentration of 200 mg/L as Mg^{2+} showed that precipitated $Mg(OH)_2$ in the $MgCl_2$ tests removed an average of 64% reactive while preformed $Mg(OH)_2$ only removed an average of 33.2% reactive silica; thus, precipitated $Mg(OH)_2$ removed twice as much reactive silica. The discrepancy was not quite as large at a concentration of 600 mg/L Mg^{2+} with average removal by precipitated $Mg(OH)_2$ ($MgCl_2$ tests) and preformed $Mg(OH)_2$ at 80.9% and 66.5%, respectively. At a concentration of 1,000 mg/L Mg^{2+},

removal by the two magnesium compounds was virtually the same with removal rates of 82.8% in the $MgCl_2$ test and 80.5% for the $Mg(OH)_2$ test. The results suggest that co-precipitation was playing a larger role in silica removal and that pH and magnesium concentration were adequate enough in the $MgCl_2$ tests to precipitate $Mg(OH)_2$. In the preformed $Mg(OH)_2$ tests, removal steadily increased as magnesium concentration increased, indicating that the amount of surface area available in the system for adsorption affected removal. The initial conclusions drawn from this test are complicated by the fact that the batch water used in experiments no. 1-4 contained bicarbonate and calcium chloride and it was determined that at a pH above 8, calcium carbonate would precipitate out of solution; thus, silica removal at an initial pH of 11 in these tests cannot be entirely attributed to magnesium. In fact, later tests where the calcium chloride was omitted from the batch water demonstrated that preformed $Mg(OH)_2$ almost always performed better than those with dissolved $MgCl_2$.

In experiments no. 5-6, removal via co-precipitation with $Mg(OH)_2$ (in the $MgCl_2$ tests) at an initial pH of 10 was extremely low and remained below 10% at all three concentrations of 600, 1,000, and 1,400 mg/L as Mg^{2+}. Based on the results of experiments no. 1-4, removal would have been expected to be higher but the low numbers are most likely indicative of the role that $CaCO_3$ played in the first four experiments (batch water used in experiments no. 5-6 did not include $CaCl_2 \cdot 2H_2O$). Removal by preformed $Mg(OH)_2$ at an initial pH of 10 was not exceptional, but it steadily increased as magnesium concentration increased demonstrating the importance of providing ample solids to the system for adsorption. As with $MgCl_2$, it would have been reasonable to expect higher removal based on the results of the first four

experiments; but, again, this can be attributed to the absence of $CaCO_3$. The increasing trend in removal as solids concentration increased was a meaningful result and suggested that Phase 2 tests could expect to achieve high levels of removal if operated with high magnesium concentrations, even at a pH on the lower end of the spectrum.

For experiments no. 5-6, at an initial pH of 12, removal by preformed $Mg(OH)_2$ and precipitated $Mg(OH)_2$ was high with an average of 80.8% and 70.9%, respectively. These results confirm assertions in the literature that chemical softening for silica removal is most effective when operated at a higher pH. Overall, experiments no. 5-6 suggested that adsorption was the more dominant removal mechanism at a lower pH. At the higher pH, both adsorption and co-precipitation facilitated removal because there were ample solids present in the system in the case of the $Mg(OH)_2$ tests or because the pH was high enough in the $MgCl_2$ experiments to precipitate $Mg(OH)_2$.

Experiments no. 7-11 further explored the role of adsorption and co-precipitation in silica removal during a softening process with magnesium. These tests used batch water made up only of NaCl so that removal could be solely attributed to magnesium.

Experiments no. 7-9 that studied removal with preformed $Mg(OH)_2$ found that a 100 mg/L magnesium dose at all three pHs – 9.5, 10, and 10.5 – achieved little silica removal in the range of 17% to 26%. Precipitated $Mg(OH)_2$ in the $MgCl_2$ tests, similarly, only achieved 1.5% and 6% removal at the low Mg^{2+} dose for initial pHs of 10 and 10.5. At the two higher magnesium doses, removal by $Mg(OH)_2$ was exceptional with about 89% removal observed for of 1,000 mg/L as Mg^{2+} and 96% for 10,000 mg/L as Mg^{2+}. The results show that there was not a huge increase in removal by a 10,000 mg/L dose meaning the 1,000 mg/L offered an acceptable amount of surface area. Another key

finding from these results was that good removal was achieved at all three pHs tested; so, even though it is largely reported that pH must be maintained above a pH of 10, good removal was found to occur in these tests at an initial pH of only 9.5. The implication of using such a low pH, though, is that $Mg(OH)_2$ could begin to dissolve over a longer period of time – i.e., in a longer time scale test. This issue was explored during Phase 2.

Removal by precipitated $Mg(OH)_2$ in experiments no. 10-11 using $MgCl_2$ was observed to be only slightly higher at a pH of 10.5. For a magnesium concentration of 1,000 mg/L, roughly 21% removal was achieved at an initial pH of 10 and about 33% at an initial pH of 10.5. For the highest magnesium concentration of 10,000 mg/L, better removal was observed at about 63% and 69% for initial pH values of 10 and 10.5, respectively. Although it was promising to see removal during $MgCl_2$ tests increase as magnesium dose increased, a magnesium concentration greater than 10,000 mg/L would be necessary to achieve the same level of removal observed with 1,000 mg/L $Mg(OH)_2$ as Mg^{2+}.

Experiments no. 1-11 seem to suggest that adsorption is the critical mechanism in silica removal. $Mg(OH)_2$ solids may be precipitated in solution to facilitate removal by adsorption and co-precipitation, but the results discussed above demonstrated that freshly precipitated, amorphous $Mg(OH)_2$ is a highly effective adsorption medium.

Experiments no. 12-14 showed that brucite and aged $Mg(OH)_2$ are extremely poor silica adsorbents. SEM imaging and BET surface area analysis showed that both compounds were not highly porous nor did they have very high surface area – 4.46 m^2/g for aged $Mg(OH)_2$ and 0.53 m^2/g for brucite. The freshly precipitated $Mg(OH)_2$ sample,

by contrast, had much higher surface area of 23.28 m^2/g. It also appeared to be much more porous in SEM images.

All jar tests discussed thus far were conducted using initial pH as a basis for comparison; however, it was determined that operational and final pH would offer a more accurate comparison between precipitated Mg(OH)$_2$ and preformed Mg(OH)$_2$ because both MgCl$_2$ and Mg(OH)$_2$ compounds were observed to change the pH of the water after addition. Experiments no. 15-17 were conducted so that the operational and final pH values of tests with both MgCl$_2$ and Mg(OH)$_2$ were as similar as possible. Results showed that preformed Mg(OH)$_2$ was, by a significant margin, more effective than precipitated Mg(OH)$_2$; this not only confirmed the results of previous experiments but was further testament to the importance of adsorption in silica removal.

Experiments no. 7-9 and 16-17 demonstrated that good silica removal could be achieved at a low pH of 9.5. The implication of this finding, which was discussed above, is that Mg(OH)$_2$ can begin to dissolve over time; this is shown in the Visual MINTEQ analysis presented in Figure 3-5. In preparation for Phase 2, during which longer experiments would be conducted, iron and aluminum compounds were considered as potential candidates to supplement magnesium solids during tests where pH would be low and could potentially result in dissolution of Mg^{2+} solids over time. Visual MINTEQ analysis (see Figure 3-8) that compared the solubility of an iron compound with that of an aluminum compound showed the iron option to be the more insoluble of the two; thus, it was selected for testing in experiment no. 21. Iron hydroxide solids were shown in experiment no. 21 to be extremely effective at removing silica removal. 92% reactive silica removal was achieved in the first two minutes and by 5 minutes, 98% had been

removed. With such a high removal achieved so quickly, it was wondered why $Fe(OH)_3$ is not used more often as a sole silica adsorbent. Milne et al. (2014) provide an answer, indicating that although adsorption to iron compounds can be quick and effective, they can form an unwanted glass-like scale.

Experiments no. 22-26 were part of Phase 2 flow-through experimentation. Each experiment lasted 8 hours and explored silica removal over time. Magnesium testing during Phase 1 showed $Mg(OH)_2$ to be the more effective removal compound during; thus, it was the focus of Phase 2. $Fe(OH)_3$ was also tested during Phase 2 to understand its effect on silica removal over an extended period of time. The exploration of adsorption capacity of $Mg(OH)_2$ was a main focus of flow-through experimentation. The impact of pH and concentration were also key considerations.

One of the key findings during flow-through experimentation was that solids recycle and solids concentration influences silica removal. A higher dose of solids (0.12 M) was found to be more effective in removing silica than a dose of 0.04 M. For the three flow-through tests that used lower initial solids doses (1 g/L Mg, 0.5 g/L Mg with 1.15 g/L Fe, and 2.3 g/L Fe), adsorption capacity of the solids was reached at 4 or 5 hours into the test. Adsorption capacity was not achieved in the two tests with a 3 g/L Mg dose.

Results also suggested that $Fe(OH)_3$ served as a better silica adsorbent than $Mg(OH)_2$. It would have been interesting to carry out a test with $Fe(OH)_3$ at a higher dose to observe how removal compared with the higher $Mg(OH)_2$ dose. One of the reasons iron hydroxide may have served as a better adsorbent was because it did not dissolve over the course of the 8 hour test (indicated by the fact that no iron was measured in the permeate stream). $Mg(OH)_2$, on the other hand, was found to dissolved over time,

especially during the test where pH was maintained around 9.5; so, even though good removal was achieved at this pH range with the 3 g/L Mg dose, 8 hours is likely too long a run time for operation at this pH.

It can be concluded from this project that magnesium hydroxide is responsible for silica removal largely via an adsorption mechanism at a pH less than 11. Furthermore, freshly precipitated $Mg(OH)_2$ was shown to be an extremely effective silica adsorbent. Based on SEM and BET analysis, it was theorized that the preformed $Mg(OH)_2$ was a good removal compound owing to its amorphous structure, high surface area, and porous surface. It is also possible that surface charge plays a role. $Mg(OH)_2$ is said to have a positive surface charge (Lawler and Kweon 2004; Russell et al. 2009), which could attract the negatively charged silicate ions present in solution at a pH above 9.5. Consider also the point of zero charge (PZC) values for some Mg, Fe, and Ca compounds. MgO has a high PZC, meaning many of its surface sites are positively charged which, again, would attract negatively charged silica ions. Recall the solubility of silica modeled in Figure 2-1. At a pH of 9, there is about 10-15% charged silica species present in solution; so, even at a lower pH range silica removal could be achieved owing to an attraction between positively charged Mg and negatively charged silica. Calcite has a lower ZPC, which could be one of the reasons that it is not shown to be as effective a silica remover as Mg. The Fe species shown in Table 5-1 also have low ZPCs; however; this project showed $Fe(OH)_3$ to be a good silica remover. So for $Fe(OH)_3$, there is some other factor at play. For example, it may have a much higher surface area than $Mg(OH)_2$.

Table 5-1: PZCs for Mg, Ca, Fe, and SiO_2 Compounds (Benjamin 2010)

Material	pH_{PZC}
Fe_3O_4	6.5
α-FeOOH	7.8

Fe(OH)$_3$ ferrihydrite	8.5
Calcite	8.5
MgO	12.4
SiO$_2$	2.0

Though it is largely reported in the literature that pH needs to be greater than 10 to facilitate good silica removal, Phases 1 and 2 of this project demonstrated high removal can actually be achieved at a low pH of 9.5. This is an important finding, because operating a softening process at a lower pH means less base is required for operation.

There were many important findings gleaned from this study, and there are also a number of possible opportunities for future research associated with this project. For example, additional solids analysis could offer insight into how much silica is being removed by different solids in the system. Additionally, a wider range of solids and pH values could be tested to determine an ideal dose for use during softening. Lastly, a more detailed study of the mineralogy of the Mg(OH)$_2$ solids could elucidate how SiO$_2$ is incorporated into the solids or adsorbed to a surface.

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