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JOHN AND WILLIE LEONE FAMILY DEPARTMENT OF ENERGY AND
MINERAL ENGINEERING

MAGNESITE DISSOLUTION RATES AFFECTED BY INLET FLOW VELOCITY
AND MINERAL SPATIAL DISTRIBUTION

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ABSTRACT

The information presented in this thesis was modeled after an experiment performed by graduate assistant Fatemeh Salehikoo in the Fall of 2012, which examined the role of mineral spatial distribution and flow velocity in determining magnesite dissolution rates at different spatial scales. The experiment conducted for this thesis still examined these same effects on magnesite dissolution, but utilized smaller magnesite grains in order to differentiate and form conclusions on how grain size affect experiment results. The conclusions in this thesis will be compared to Fatemeh's work to determine future courses of action in further exploring subsurface carbonate mineral reactions.

The role of magnesite dissolution is important to investigate in petroleum engineering because it is a commonly-found mineral in numerous carbonate reservoirs throughout the world (Chou 1989). Additionally, it is a vital concept in acidification processes during secondary and tertiary recovery methods in the field. In order to investigate the dissolution and reaction of magnesite at different experimental conditions, three different columns were used with varying spatial compositions. The columns were labeled according to the individual distribution of magnesite grains and were constructed to model typical reservoir types in the field. In the mixed column, magnesite grains were evenly distributed within a quartz matrix across the entire column. In the one-zone column, magnesite grains were distributed in one isolated zone in the quartz matrix and in the two-zone column the magnesite grains were distributed in two isolated zones of the column. Identical quantities of quartz were used in each column. Additionally, varying flow velocities were used to understand the role of magnesite dissolution in regard to rate

of fluid injection. Flow velocities of 1.23 mL/min, 2.35 mL/min, and 6.30 mL/min were used in this experiment to examine slow, medium, and fast rates respectively.

After completing each of the experiments, chemical compositions of the samples were analyzed in regard to elemental concentrations as well as pH and magnesium. Afterward, it was observed that the mixed-zone column experienced the most dramatic increase in magnesium concentration due to the fact that there is more mass transport between the grains and the inlet solution. Additionally, the slower flow velocity experiments yielded higher rates of dissolution. Similar conclusions were drawn when compared to Fatemeh's experiment, indicating that flow velocity and mineral spatial distribution can lead to orders of magnitude difference in column-scale dissolution and can affect physical properties such as porosity and permeability (Li et al., 2009).

In field studies, weathering rates are typically inferred from profiles of mineral concentrations of effluent concentrations at different depth or position along flow paths (Saleikhoo et al., 2012). Detailed concentrations at different positions or different times are largely unknown and it is challenging to quantify the contribution of different reservoir factors. This thesis will serve as a stepping stone toward determining how field-scale rates are affected by different distributions of magnesite and how acidification processes tie in to dissolution and mass transportation of carbonate minerals.

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Chapter 1: Introduction to Magnesite

Mineral dissolution plays a key role in various subsurface processes that are important in the earth sciences and petroleum engineering, particularly in chemical weathering processes and biogeochemical processes in watersheds (Chou 1989). In the subsurface environment, minerals are typically distributed unevenly but this heterogeneity is rarely incorporated explicitly in models. This experiment worked to further explore the role of magnesite dissolution within quartz-packed columns in order to try and model heterogeneity in reservoirs in order to better understand how subsurface reactions may affect oil and gas production, particularly during acidizing processes.

Magnesite, commonly referred to as magnesium carbonate (MgCO_3), is commonly found in sedimentary environments and sediment in hydrocarbon reservoirs. It is a colorless mineral with medium hardness, and it dissolves rapidly when it reacts with water (Moller 1989). Magnesite can form under a variety of conditions: as a result of weathering and hydrothermal alteration of ultramafic rocks, by diagenesis of carbonate sediments, and during metamorphic reactions where carbon dioxide is present (Moller 1989). It is mainly used as a basic refractory lining of furnaces in iron and steel metallurgy, in addition to being consumed by the building and chemical industries. The present world production of magnesite is approximately 12 million tons per year (Sayed et al., 2012). On a global scale, the formation of magnesite following chemical weathering of calcium silicate minerals also plays a vital role in reducing levels of

atmospheric carbon dioxide over long periods of time (Higgins and Boram 2002). In nature, there are two major types of magnesite that are commonly found. Kraubath-type magnesite deposits are crypto-crystalline magnesites associated with ultramafic rocks, which are commonly found near volcanic eruptions (Moller 1989). Veitsch-type magnesite deposits are sparry magnesites that form localized lenses or stocks within marine platform carbonates (Moller 1989). In this experiment, Veitsch-type magnesite grains will be used since they are more commonly found near hydrocarbon reservoirs.

Veitsch-Type Magnesite Deposits

Veitsch-type magnesite deposits are large yet short lens grains that are typically found in marine clastic/carbonate shelf sediments consisting of dolomite, limestone, black and grey shales, and sandstones (Moller 1989). The rock itself can be white, grey, black, or yellow in color depending on the depositional environment, and the crystals can be sugary to coarsely crystalline in texture with a xenotopic fabric. Its hardness is usually 3.5-4.5, with a porosity of less than five percent and pore size decrease downwards (Moller 1989). Veitsch-type deposits are also characterized by an elevated iron content of several percent and can contain a variety of compounds such as FeCo_3 , FeO , and Al_2O_3 . As stated previously, these deposits are most commonly found within marine carbonate and clastic shelf suites offshore, and have been commonly documented in the Gulf of Mexico. Many sedimentary structures have been observed in magnesite rock of Veitsch-type magnesite deposits, including bedding and lamination, cross and oblique bedding, ripple marks, intraformational erosion, and micro faulting (Chou 1989). While magnesite grains typically range on the order of 300-500 microns, grain sizes between

100-150 microns were used in this experiment and were separated using sieves in the laboratory.

Minor and Trace Elements in Magnesite

In analyzing dissolution reactions, it is vital to fully analyze the chemical composition of the substance that is being dissolved in order to fully understand the chemical reactions that are subsequently occurring during dissolution. Many studies have been published on the trace elements in magnesite in order to determine the source rocks from which the magnesium ions were derived. In order to understand the multiple elements that precipitate out of the magnesite into the core environment, they will be discussed in detail below. Elemental abundance diagrams of individual elements will be given to show the concentration of the elements below in the different environments that magnesite is commonly found (ultramafic, lacustrine, etc.). The x-axis of all of these diagrams will be log concentration, and the length and thickness of the black line will demonstrate the distribution of the given element. It is important to keep in mind that lacustrine marine/evaporate magnesites were utilized in this experiment.

Chromium (Cr)

Chromium is most present in chrome-spinels, which are chromite grains found within meta-carbonate rocks (Mogessie 1992). The concentration of chromium is most prolific in ultramafic environments, but can be found in marine environments at very low concentrations.

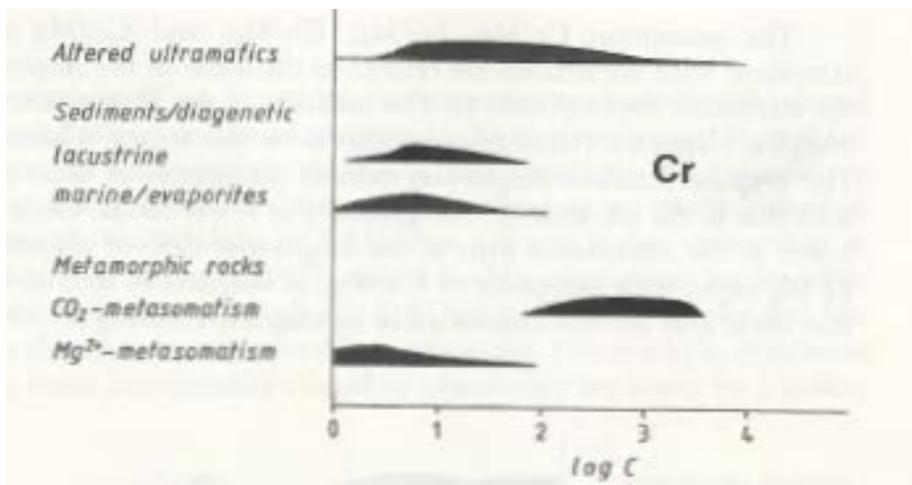


Figure 4-1. Distribution of Chromium in Different Environments

Nickel (Ni)

Nickel (Ni^{2+}) mainly substitutes for magnesium (Mg^{2+}) in serpentine minerals enclosed by magnesite, or it forms sulfide minerals together with iron, copper, and cobalt as precipitates in marine environments (Moller 1989). The concentration of Ni is fairly constant in ultramafic environments, and once again is found in marine environments at very low concentrations.

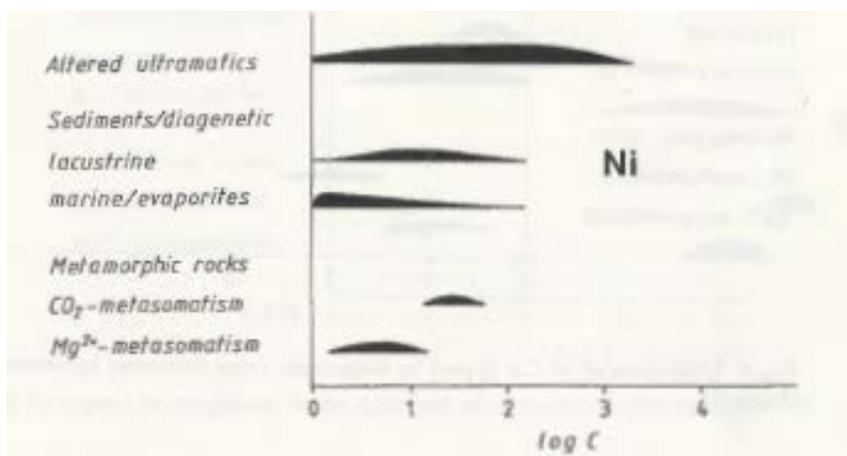


Figure 4-2. Distribution of Nickel in Different Environments

Copper (Cu)

Magnesite vein fillings in ultramafic rocks have a lower concentration of copper than magnesite in weathering crusts, which explains the two humps in the Cu distribution graph. Magnesite found in lacustrine environments is very low in copper because copper ions (Cu^{2+}) form sulfides during fluid migration (Moller 1989). Copper also scatters considerably in marine environments because copper becomes enriched in the brine.

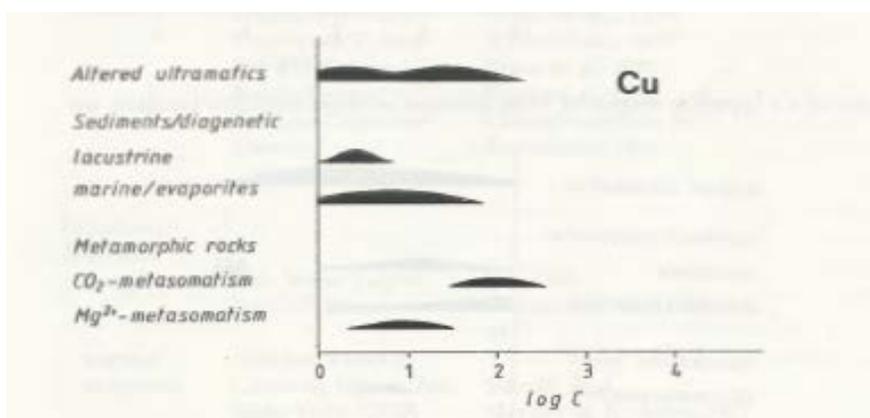
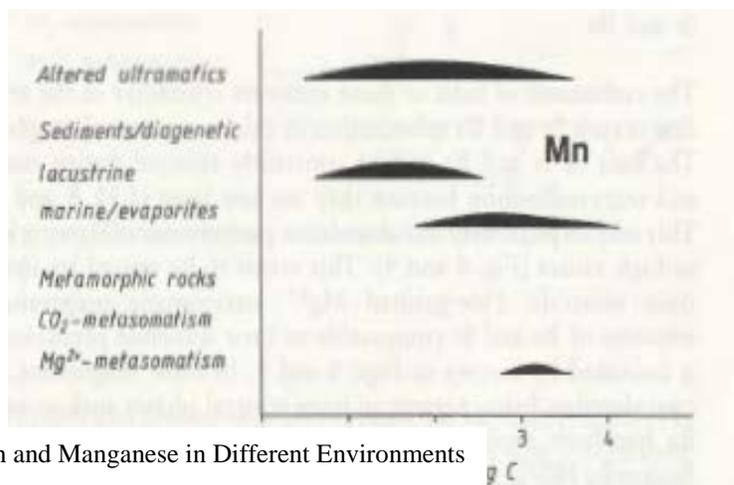
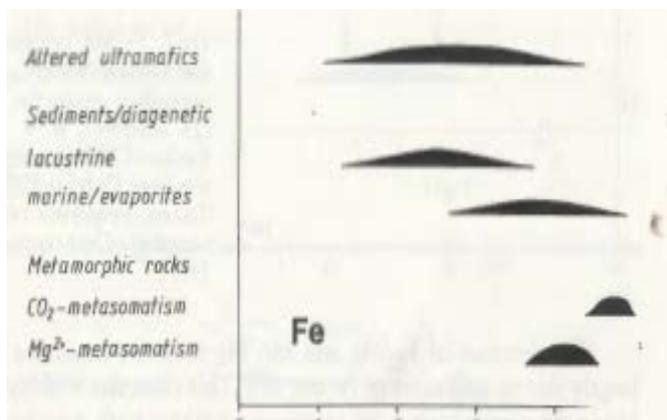


Figure 4-3. Distribution of Copper in Different Environments

Iron (Fe) and Manganese (Mn)

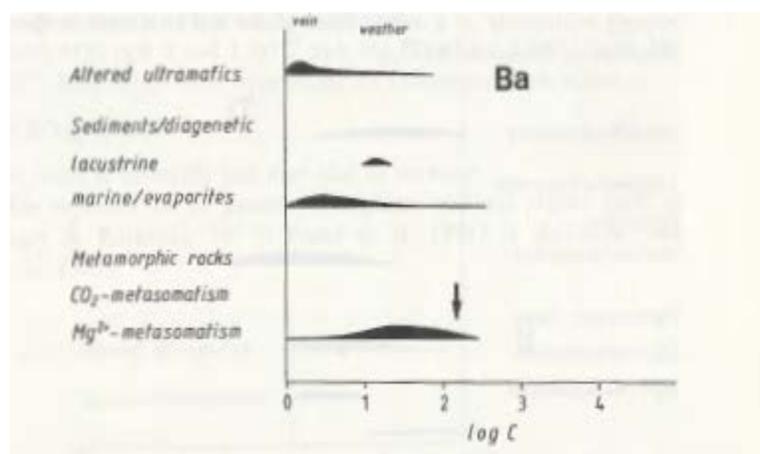
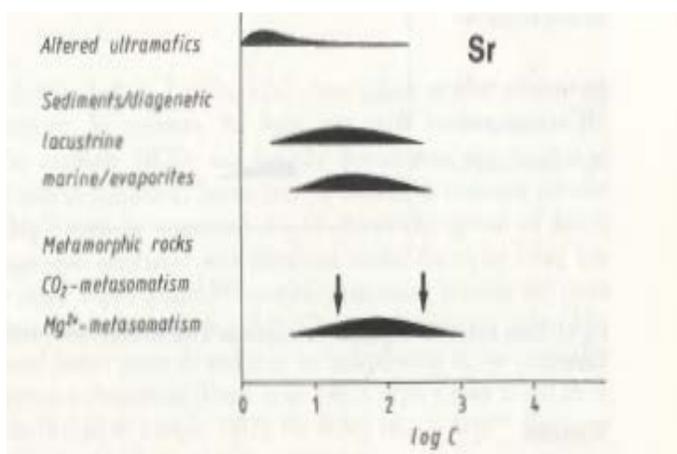
Iron and manganese are both partly hosted in magnesite, and cover similar concentration ranges for ultramafic and lacustrine environments. However, Fe/Mg and Mn/Mg ratios in lacustrine environments decrease due to the oxidation of Fe and Mn.



Figures 4-4 and 4-5. Distribution of Iron and Manganese in Different Environments

Strontium (Sr) and Barite (Ba)

Strontium and barite are only negligibly hosted in the magnesite lattice due to the fact that the Sr and Ba ions will be constantly rejected during magnesite crystallization because they are too large (Moller 1989). Therefore, the presence of these elements in magnesites in all environments can be largely ignored.



Figures 4-6 and 4-7. Distribution of Strontium and Barium in Different Environments

Mercury (Hg)

Mercury concentration is low in ultrabasic rocks and is high in high temperature lacustrine magnesite environments (Moller 1989). The distribution of mercury in marine environments is very scattered at low concentrations.

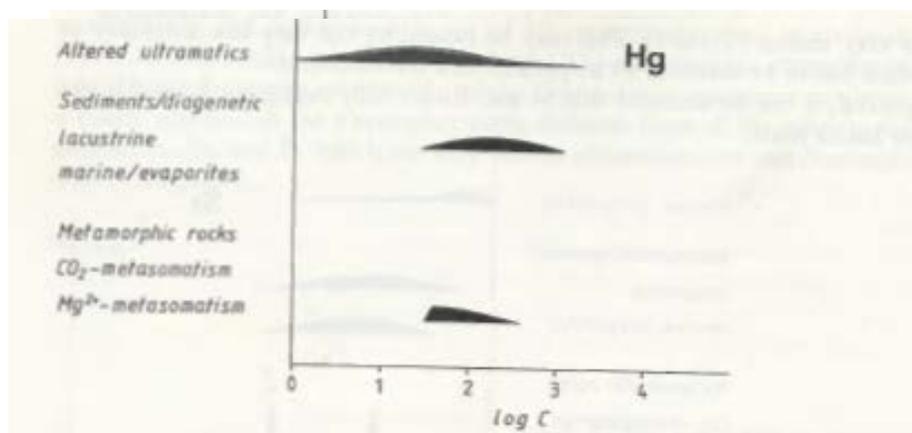


Figure 4-8. Distribution of Mercury in Different Environments

Titanium (Ti)

The concentration of titanium is low in magnesites that reside in ultrabasic rocks and slightly higher in marine environments (Moller 1989). It is only present as a minor trace element and is always an insoluble residue.

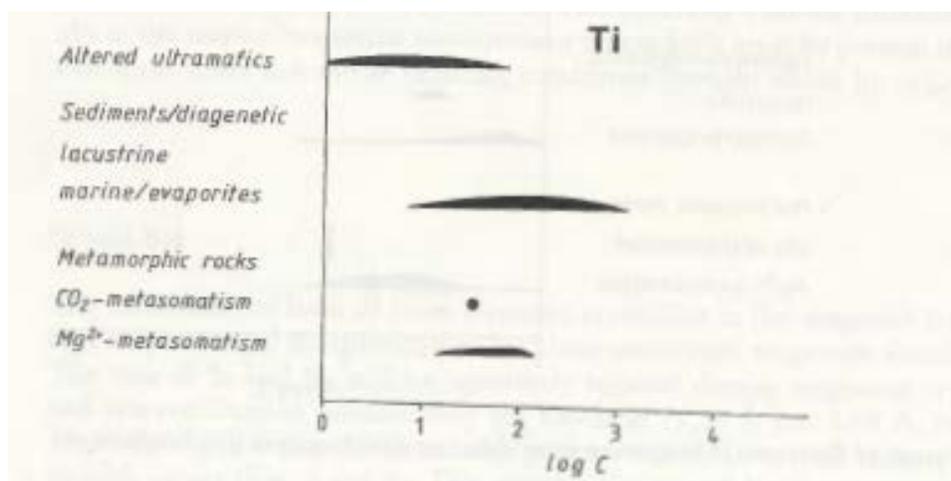


Figure 4-9. Distribution of Titanium in Different Environments

Boron (B)

Marine magnesites tend to contain the most boron, and it is quantitatively retained by the magnesite itself. Boron is often reported to be present in separate mineral phases in magnesite, such as tourmaline or danburite (Moller 1989).

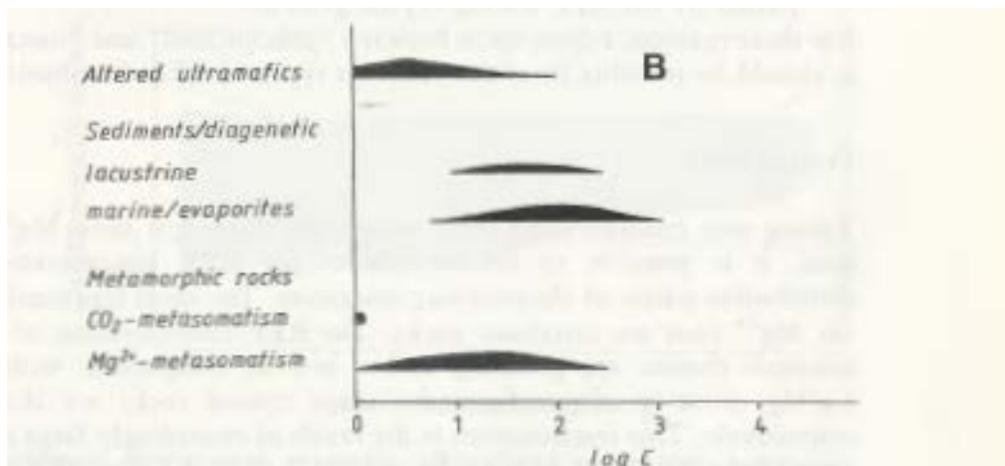


Figure 4-10. Distribution of Boron in Different Environments

Chapter 2: Magnesite Dissolution and Acidification Applications

While the science behind magnesite dissolution is closely related to environmental fields, the one main application of magnesite dissolution to the field of petroleum engineering is during acidification processes. Matrix acidizing is a technique designed to improve the productivity of oil and gas wells through the injection of acid and the subsequent dissolution of some of the formation rock (Chang 2008). During matrix acidizing, acid penetrates into and flows through the natural pore space of the rock, and these pores are enlarged while materials that plug the pore space and inhibit flow are removed through dissolution (Chang 2008). The chemical nature of sandstone rocks makes acidizing an effective matrix stimulation technique due to the fact that the acid creates wormholes (referred to as flow channels) in the rock to extend the effective drainage radius of the wellbore (Chang 2008). It is important to rationalize the properties of the reservoir (such as porosity, permeability, and chemical composition) in order to formulate a wormhole pattern that will be effective in achieving the well deliverability. Therefore, it is important to study the dissolution of magnesite in carbonate reservoirs because it can potentially inhibit or assist in the matrix acidizing process according to the chemical properties of the reservoir.

Matrix acidizing is especially effective in carbonate formations because the dissolution rates of minerals are relatively slow (Chang 2012). The key to increasing production in a reservoir is to ensure that the flow channels are not being interrupted by other rock materials (such as magnesite), and the key to ensuring that magnesite does not inhibit production is to analyze the kinetics and mechanisms behind the dissolution process. As previously stated, the kinetics involved with dissolution will depend on the flow velocity, length scale, and mineral distribution of the reservoir (Saleikho 2012). Additionally, kinetic parameters such as type and strength of fluid, reaction temperature and time, and formation reactivity will affect the amount of magnesite dissolved during the acid treatment process (Chang 2012). The main reaction equation can be seen below:



The rate that this reaction occurs is given by a relatively simple equation, given by $R = C \cdot Q$ where C is the concentration of magnesium (given in moles/volume) and Q is the velocity of the inlet solution (given in volume/time). Therefore, the rate that the reaction occurs (R) is given in units of moles/time. The concentration of magnesium will be plotted for each flow velocity to determine different rates within different spatial distributions of magnesite.

Magnesium carbonate dissolves into magnesium and CO_3 ions when reacted in water, raising the PH of the sample. The rate of dissolution is important in this experiment because dissolution can change many properties of the source rock, including porosity and permeability. The reaction rate of the magnesite has been proven to follow a Transition State Theory based rate law from Fatemeh's experiment, which states that

magnesite reaction rates depend on mineral reactivity, surface area, and aqueous geochemistry, including pH and deviation from equilibrium (Salehikhoo 2012).

Much work has been done in terms of calcite and dolomite dissolution in reservoirs, but much is still unknown about the effects of magnesite on critical rock properties. In the case of magnesite (as with other acid dissolving minerals) the solid-liquid interaction involves three distinct steps . The first step is the diffusion of liquid phase to the rock, the second phase is the reaction of the liquid at the rock surface, and the third step is the diffusion of reaction products into bulk solution (Chang 2012). When all three of these processes occur, chemical changes can be detected in order to sense changing rock and fluid properties, such as measuring pH and the concentration of certain minerals such as magnesium. The rate of mass transfer and the surface reaction will dictate how these properties may change over a period of time, and the results can be used to determine the changes in the composition of the magnesite as well as the physical properties of the reservoir. The surface reaction controls the reaction between acid and rock and the rock surface, while the mass transfer rate controls the diffusion of acid toward the rock surface (Li 2008). The goal is to physically eliminate the magnesite through the matrix acidizing process until the wormhole networks can transport hydrocarbons with ease.

As opposed to the sandstone acidizing process, the fluid injection rate plays a key role in magnesite dissolution rate. In this experiment, three different flow rates will be used to determine the differences in the kinetics of the dissolution process. The concentration of magnesium, in addition to the concentration of trace elements, will be

analyzed along with pH values to analyze chemical changes in the reservoir before, during, and after dissolution. The rate of mass transport from each column will also be analyzed to determine how the isolation of magnesite affects its dissolution in different areas. In general, the limiting behavior of dissolution reactions that involve magnesite is governed by sluggish heterogeneous chemical reactions in a purely kinetically controlled reaction and by mass transport in the case of infinitely fast heterogeneous kinetics (Higgins, Boram et al. 2002).

While much work has been done in regard to wormhole and flow channel networks, one of the major obstacles of this experiment is a basic lack of understanding of the fundamental processes controlling flow, reaction, and dissolution in natural porous media such as carbonate rock (Chang 2012). Deeper penetration and more effective acid treatments can be achieved if these fundamental processes are understood, which is why multiple studies on the role of mineral spatial distribution on flow velocity have recently been published. Additionally, there is really not even a basic understanding of the effects of various treatment parameters such as the mineral dissolution rate on the effectiveness of the acid treatments. This thesis will attempt to analyze this exact situation, and attempt to solve some of the uncertainties regarding matrix treatments in carbonate reservoirs and the role of magnesite dissolution in flow channel networks.

Other Factors Affecting Dissolution

While not studied in this particular experiment, there are a variety of other factors that affect the dissolution of carbonates. In the petroleum field, additives are commonly

used in combination with matrix acidizing in order to reduce impurities in the wormholes and increase permeability. One study was published on the effect of additives on acid dissolution rates of calcium and magnesium carbonates. The additives used included, but were not limited to: corrosion inhibitor, polymer, surfactant, mutual solvent, citric acid, and dissolved iron (Sayed 2012). The study found that with no additives present, the dissolution-rate measurements were in direct agreement with literature values and research studies. However, adding polymers to the acidizing process decreased the calcite and dolomite dissolution rates significantly, and changed the acid/rock reaction from mass transfer limited to surface reaction limited (Taylor 2004). Additionally, adding solvent to the process increased the acid dissolution rate significantly, while corrosion inhibitor decreased the magnesium dissolution rate but not the calcite rate. Furthermore, impurities in magnesite and calcite can also dramatically affect dissolution rates. The same study found that clay impurities in calcite rock reduced the dissolution rate by nearly an order of magnitude (Taylor 2004). For example, some rocks with clay contact as low as 1% by weight showed acid reactivity similar to that of 100% weight dolomite.

Chapter 3: Methodology

Material Preparation

The first step in conducting this experiment was to sort the magnesite grains into different sizes using sieves in the laboratory. Most of the magnesite was already granulated and ready to be sieved, but the remaining magnesite was crushed in a glass bowl before being placed into the sieves. The three sieve sizes used were 300, 150, and 50 microns respectively. The medium-sized grains (150-300 microns) were used for this experiment to compare to Fatemeh's work with magnesite grains on the order of 300-500 microns, and the other two sieves were used to separate the grains that were too large and too small. Once all of the grains had been sieved and the total mass of magnesite was close to 50 grams on the balance, the magnesite was cleaned with 1% HCL for several seconds before being placed into an ultrasonic cleaning apparatus with acetone to remove any fine particles on the magnesite grains. The grains were then dried overnight in an oven set to 70 C, and were then stored in a desiccator for packing. This process was repeated several times until enough magnesite was obtained for the experiment, and was also repeated for the quartz (sand) grains to be used for the packing of the columns. The total mass of quartz used was approximately 140 grams.

Mineral Spatial Distribution

Three different columns, all with different magnesite spatial distributions were used in this experiment. The ratio of magnesite per quartz in each column was approximately 1:7 (10 g of magnesite for every 70 g of quartz). The mixed column consisted of a random yet uniform mixture of magnesite and quartz, the one-zone column

consisted of a linear vertical distribution of magnesite isolated from the quartz system, and the two-zone column consisted of two linear vertical distributions of magnesite once again isolated from the quartz system. The magnesite was the reactive substance with the injection solution while the quartz was the neutral unreactive substance, creating different reactive zones within the three columns. In the mixed case, the reactive zone was randomly spaced throughout the quartz interface. The reactive zone of the one-zone column was isolated from the surrounding sand matrix, and the reactive zone of the two-zone column was twice as large as the one-zone column. Chemical analyses of the reactions that take place within these columns will dictate how dissolution plays a role in magnesite decomposition.

Column Packing

Chromatography columns were used for the packing procedure consisting of two fixed end caps and a 20 micron polytetrafluoroethylene frit to hold the porous media in place (Saleikhoo 2012). In the mixed column, the initial solution was poured slowly into the column to fill the space in an upward manner to establish the column height. After a certain height was reached (approximately 1cm), the mix of quartz and magnesite was added incrementally until the entire column was filled to the top. In the one-zone column, the frit was placed at the center of the column and was filled with about 1 cm of magnesite. The quartz was then added incrementally to the top of the magnesite height, and the solution was injected from a syringe to just above the height of the quartz. This process was repeated (ensuring that the solution level was always above the level of the quartz and magnesite) until the entire column was filled. This same process was repeated

for the two-zone column while using two frits to hold the magnesite in place. During the packing process, the columns were tapped on all four sides to remove air bubble and ensure that the layers of magnesite and quartz were uniform. After packing, the columns were secured with the end-cap and connected to a syringe pump to keep the columns saturated with fluid.

Flow Through Experiments

The experiments were all operated at room temperature with the influent solution flowing upward. The inlet solution contained 10^{-3} NaCl in deionized water with pH adjusted to 4.0. The inlet reservoir solution was in equilibrium with the partial pressure of carbon dioxide in the atmosphere (Saleikhoo 2012). Samples of fluid were collected depending on the residence times of each experiment and the PH of each was tested before sending to the lab for analysis. All columns were first injected with an inlet solution of NaCl with a PH of 9 two to three times for flushing purposes before starting each experiment. Flow rates of 1.23 mL/min, 2.35 mL/min, and 6.30 mL/min were used in this experiment to determine low, medium, and high velocity effects on dissolution rates.

Chapter 4: Experiment Results

Three 150 mL syringes were filled with inlet solution and were assembled to the three packed cores to begin the experiment. The automatic flow apparatus was set to the desired flow rate and time sheets were constructed to record PH values based on the residence times for each flow rate. Small plastic test tubes were placed at the outlet of each core to collect the dissolved magnesite solution to be tested in the laboratory.

Ph readings for each fluid sample were taken directly in the laboratory, and the concentration of Mg (along with other trace minerals discussed earlier) was taken to determine the dissolution effects at different spatial scales. The fluid samples were diluted with approximately 2 mL of diluted HCl before being sent to the laboratory for chemical analysis. The effects of flow velocity will first be discussed, followed by a discussion on the effects of mineral spatial distribution, and finally both factors will be discussed in detail together.

Effects of Flow Velocity on pH

Figures 4-11 through 4-13 can be seen below which depict the effects of different flow velocities on PH values. The values on the x-axis each denote a different residence time.

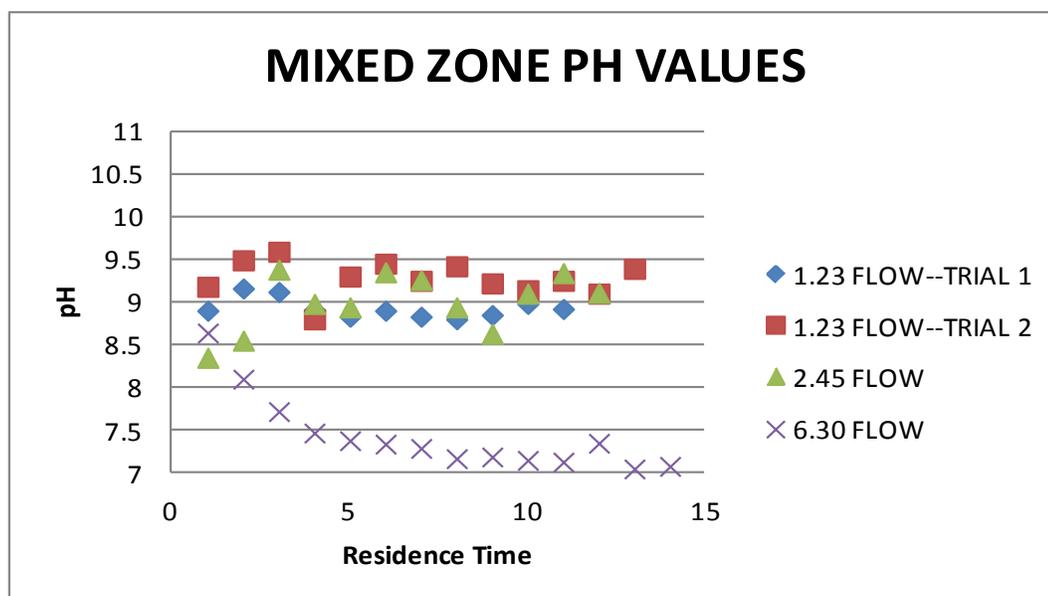


Figure 4-11. Mixed Zone PH Values

Overall the pH values of the fluid samples decrease with increasing residence time, which makes sense considering the ongoing reaction of magnesite with the inlet solution within the columns. However, there are variations to this pattern. In the 1.23 mL/min flow case for the first trial, the pH values actually increase between residence times 1 and 3 from 8.90 to 9.16 before decreasing into the 8.70-8.90 range for the subsequent times. The pH values did not change much between residence times 3 and 12 indicating that the reaction is not affecting the properties of the magnesite. The results of the second 1.23 mL/min trial were similar to the first trial, but the pH values were slightly higher on average. The pH values in this trial fluctuated between values of 9.30 and 9.50 but leveled out at the later residence times. For the 2.45 mL/min trial there was once again

an inconclusive increasing/decreasing pattern, with pH values rising between residence times 4 and 7 and pH values falling between residence times 8 and 10 (in a sinusoidal fashion). However, the 6.30 mL/min trial tells a different story. There is a very clear correlation of decreasing pH values with increasing time, with pH values starting around 8.64 and decreasing to 7.08 by the end of the experiment. The shape of the curve is an almost perfect logarithmic fit, and after the tenth residence time pH values stay fairly constant.

The heterogeneity of the quartz and magnesite grains in the mixed column likely made it difficult to get an accurate pH reading at the lower flow rate because the reaction was not able to completely occur in the presence of quartz grains. The reaction was not isolated from the quartz system and therefore the pH meter likely also picked up on the presence of sand during the dissolution process.

Effects of Flow Velocity on pH—1-Zone Column

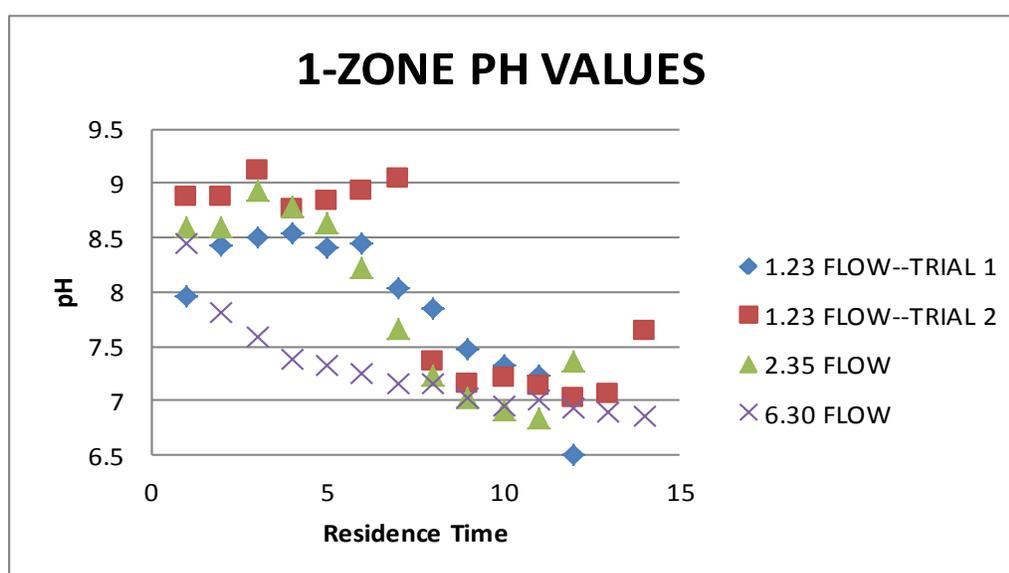


Figure 4-11. 1-Zone pH Values

Overall, the one-zone column had a much better correlation between pH and time than the mixed column case, especially when looking at the medium and fast velocities. In the 1.23 mL/min case (first trial), the pH values increased from 7.96 to 8.54 during the first four residence times before decreasing at a relatively constant rate down to 7.24 at the final residence time. The slope of the line between residence times 6 and 10 is almost exactly one (negative slope). The second trial for the 1.23 mL/min case was quite different, with higher constant pH values between residence times 1 and 6 and a significant drop in pH between residence times 6 and 7. The decrease in pH during this time is unrealistic, with a value of 9.14 at residence time 6 and a value of 7.33 at residence time 7. Therefore, only trial one was considered in analysis. The 2.35 mL/min trial once again resulted in increasing pH values for the first three time steps and generally decreasing pH values in an exponential fashion during the remaining time periods. As with the 1.23 mL/min velocity case, the most dramatic decrease in pH values occurred during residence times 6 and 9. Once again, the 6.30 mL/min trial was different in the fact that the pH values for each residence time decreased in an almost perfect linear fashion. The highest pH value was experienced at time step one and all values thereafter decreased by an average of 0.10 per time step. Because the magnesite was isolated from the surround quartz matrix, the dissolution reaction that took place did not experience sand effects during the PH measurement process and a “cleaner” reading was able to be obtained. The faster flow rate also resulted in a faster reaction rate since $R = C \cdot Q$ and Q was highest in this case, assuming constant concentration.

Effects of Flow Velocity on pH—2-Zone Column

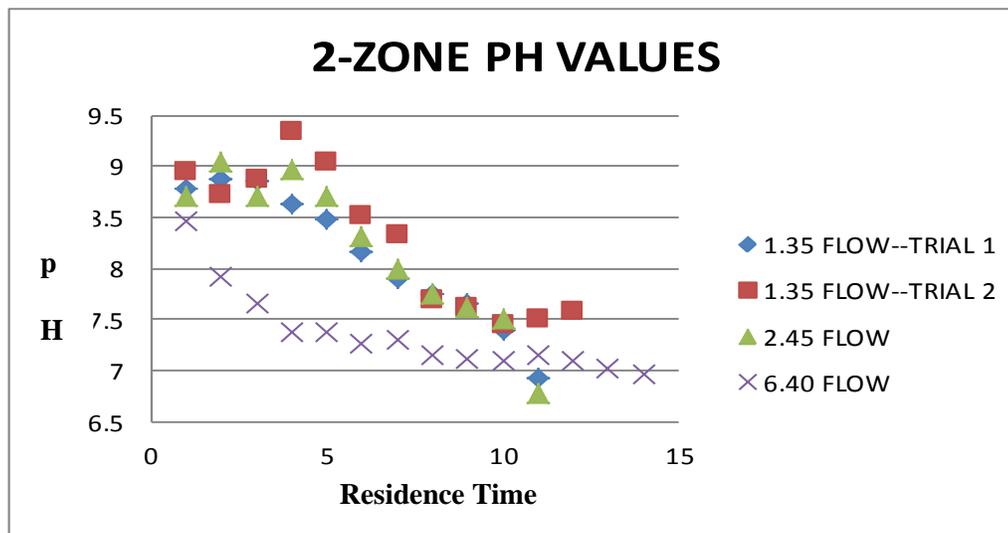


Figure 4-12. 1-Zone PH Values

It is quite clear from looking at the figure above that the two-zone column has the best relationship between decreasing pH values with increasing residence time. All three flow regimes represented above show clear linear or exponential relationships between pH and time. Additionally, in all three cases the maximum pH value was reached around residence time 5, demonstrating that flow velocity has a similar impact at all rates in the 2-zone region. Once again, the best relationship came within the 6.30 mL/min flow regime as the inlet solution more rapidly reacted with the magnesite. It is also interesting to note that both trials at 1.23 mL/min and the trial at 2.35 mL/min experienced almost identical pH values at all residence times. This is due to the fact that the 2-zone column has more contact area with the inlet solution than the 1-zone column, resulting in more mass transport of magnesite out of the isolated zones.

Effects of Flow Velocity on Mg (2+) Concentration

In the following figures, the concentration of magnesium (in ug/mL) will be plotted for each residence to determine the effect of flow velocity on magnesite concentration.

Figures 4-14 through 4-16 will graph Mg concentration versus residence time for each column.

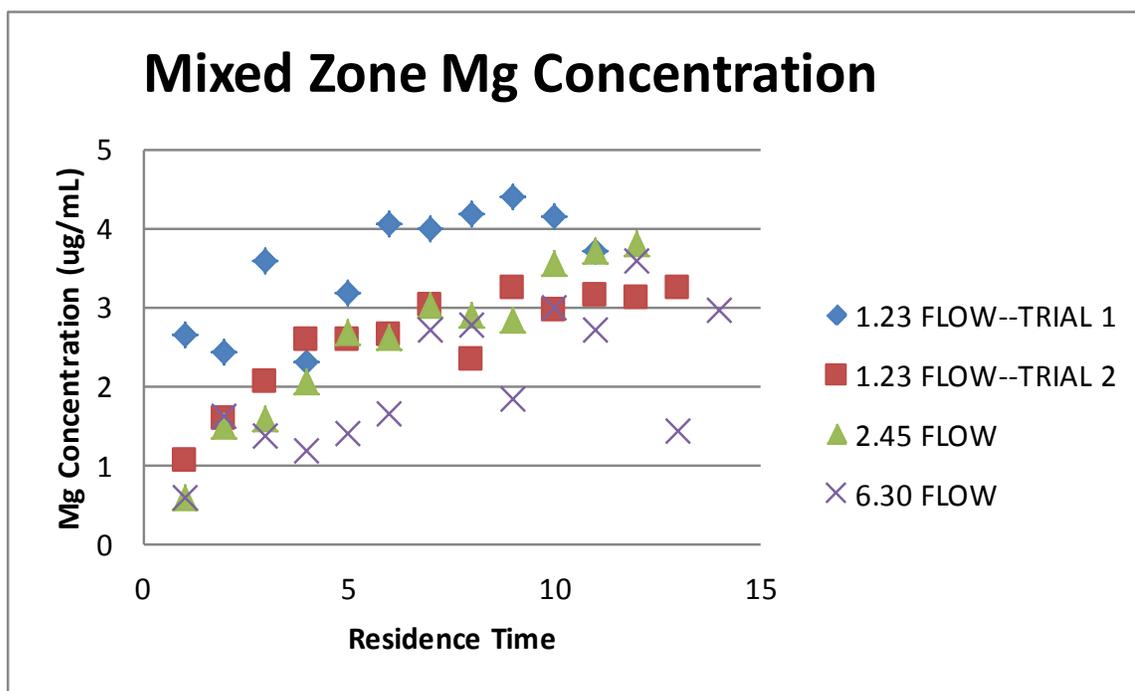


Figure 4-14. Mixed Zone Mg Values

When looking at the concentration of magnesium over time, it is clear that the concentration should generally increase with increasing residence since magnesium ions drop out of the magnesium carbonate compounds during the reaction with the inlet solution. During the first 1.23 mL/min trial, values of Mg do not increase significantly until after the fifth residence time, where values soar to over 4 ug/mL. These values stay relatively constant from this point until the end of the experiment. However, during the second trial for the same flow a much more linear trend is observed starting from the first residence time, which is more in line with the other flow velocity graphs. Mg values increase steadily from 1.15 ug/mL at the beginning to just above 3 ug/mL before leveling off as in the first trial. The 2.35 mL/min trial followed a very similar linear increasing trend as in the second 1.23 mL/min trial, with magnesium values increasing to a maximum of 3.8 g/cc at the ninth residence time. Finally, the 6.35 mL/min case again showed a general increase in the concentration of magnesium from 0.58 g/cc to 3.58 g/cc, but there was a wide spread of values toward the end of the experiment ranging from 1.33 ug/mL to 3 ug/mL at late times. This may be due to the fact that the mixed heterogeneous distribution of quartz and magnesite prevented the dissolution reaction from completely dissolving all of the Mg ions out of the zone.

Effects of Flow Velocity on Mg Concentration —1-Zone Column

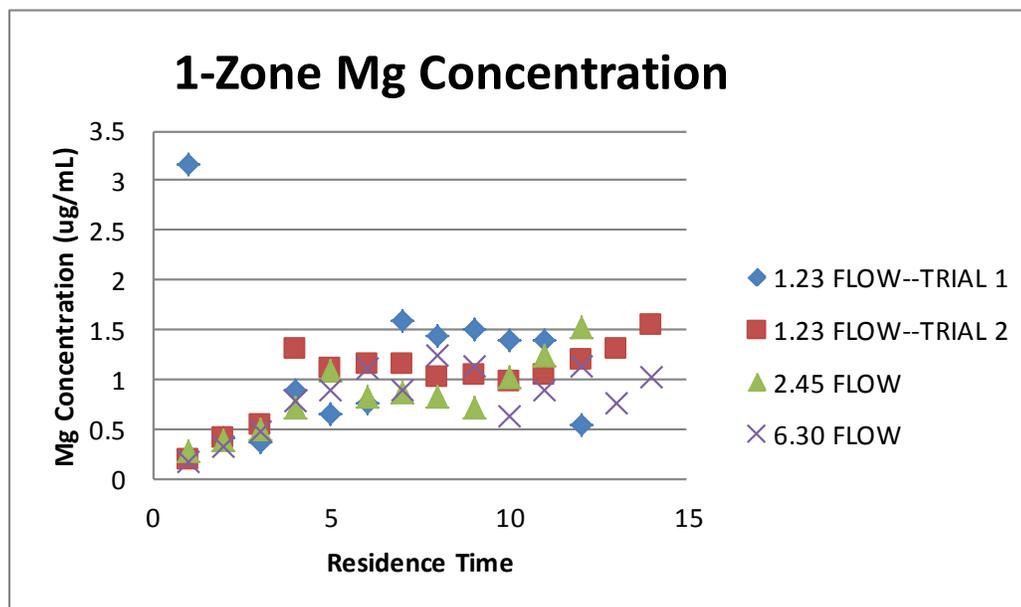
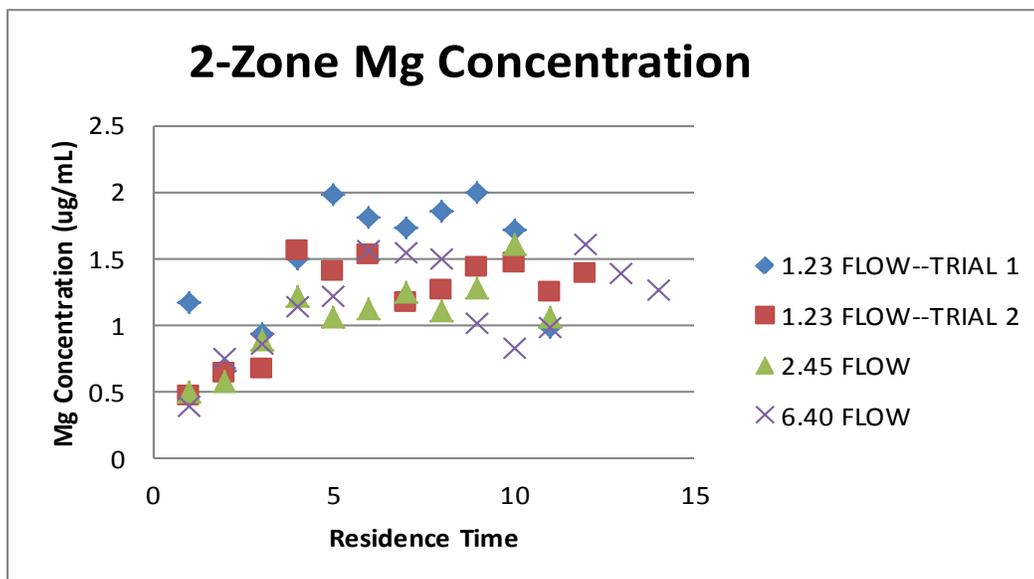


Figure 4-14. 1-Zone Mg Values

In contrast to the mixed-zone case, all four curves for the 1-zone column are very similar, demonstrating a sharp increase in the concentration of magnesium ions at the beginning of the experiment which flattens out toward the end of the experiment. The slope of the increasing Mg values for all flow rates is very close to one between residence times 1 and 5. The initial Mg value of 3.15 ug/mL for the first trial was ignored because it was not consistent with the rest of the data. The concentration of magnesium for the medium and fast flow rates increased from about 0.2 g/cc to 1.3 g/cc in about five time steps before leveling out to a level at approximately 1.5 g/cc. Mg values also seem to increase slightly at high residence times for the second trial of the 1.23 mL/min case.

Effects of Flow Velocity on Mg Concentration—2-Zone Column



The 2-zone magnesium concentrations curves for each flow rate were once again similar, but values were not as closely grouped together as with the 1-zone case. Both 1.23 mL/min flow rate trials had fairly constant concentrations of magnesium during the first five residence times (around 1 g/cc) before sharply increasing to values of 1.98 g/cc for trial 1 around the 8th time step and 1.52 g/cc for trial 2 at the same time. The medium and fast flow rates tell a different story, however. In both of these trials, the concentration of magnesium significantly increased during the early residence times and increased at a slower rate during the remainder of the experiment. The 2.35 mL/min trial saw the concentration of magnesium jump from 0.50 g/cc to 1.22 g/cc in four residence times, while the 6.30 mL/min trial saw the concentration of magnesium jump from 0.39 g/cc to 1.14 g/cc in four time steps. The increasing flow rates resulted in a lower concentration of Mg, as well as a delayed start of the dissolution reaction in this region.

Effects of Mineral Distribution on pH

Listed below are figures showing the concentration of pH for the mixed, one-zone, and two-zone columns in regard to mineral distribution. All three data sets are plotted on the same graph for comparison purposes.

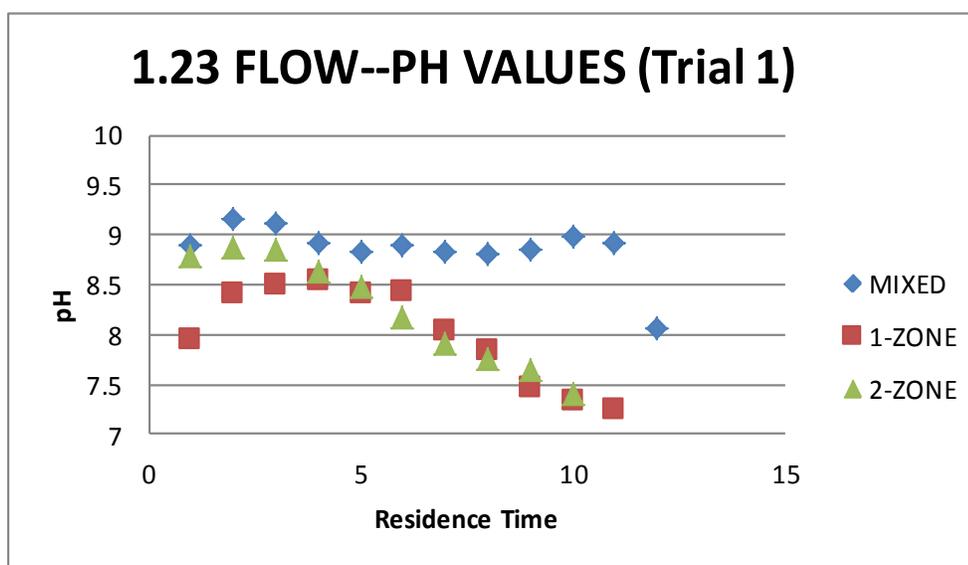


Figure 4-17. 1.23 mL/min Flow PH Values (1st trial)

A first glance at the lowest flow rate shows a close correlation for the one-zone and two-zone columns with the outlier being the mixed zone case. The pH values for the mixed zone case are also much higher than the other two cases indicating that the magnesite dissolution does not readily occur in the mixed zone region. The pH values for the one and two-zone columns almost exactly align at residence times 4 and 5 indicating that the reaction of magnesite with the inlet solution is occurring at almost the exact same time. It is also clear that the dissolution reaction does not occur in the mixed zone region, until the very last time step where the pH value drops from 8.88 to 8.03 in one residence time.

The pH values in both the one-zone and the two-zone regions level out toward the end of the experiment indicating that the reaction has reached a state of equilibrium.

Effects of Mineral Distribution on pH—1.23 mL/min (Trial 2)

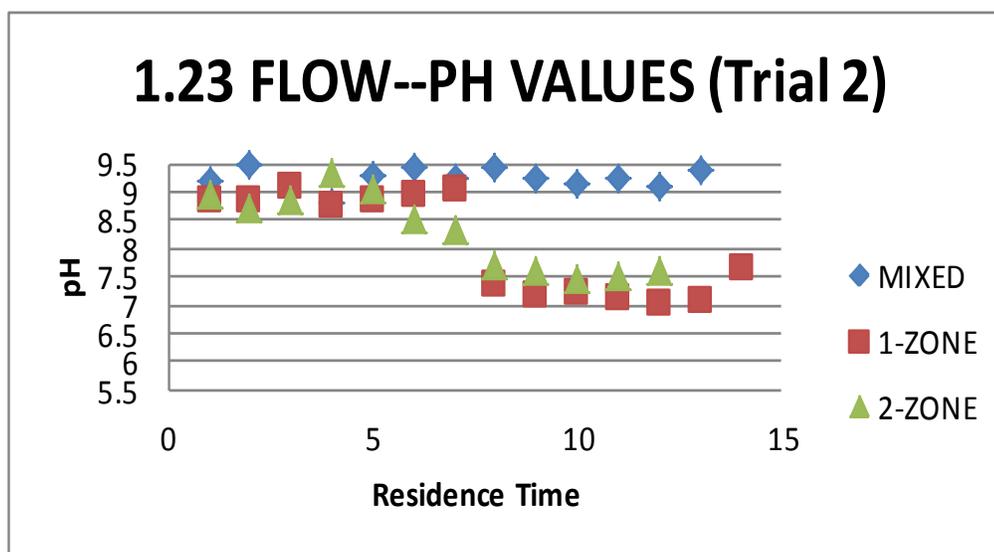


Figure 4-18. 1.23 mL/min PH Values (2nd trial)

During the second trial run for the 1.23 mL/min flow rate, similar results were obtained when compared to the first trial run, which is encouraging. The mixed-zone column still had higher pH values overall than the other two columns, while the one-zone and two-zone column values closely resembled each other. However, in this trial run the mixed-zone PH values did not decrease toward the end of the experiment. The 1-zone and 2-zone PH values did drop after the fifth time step, which was still consistent with the first trial run. After this drop in pH, the values remained constant until the last residence time.

Effects of Mineral Distribution on pH—2.35 mL/min

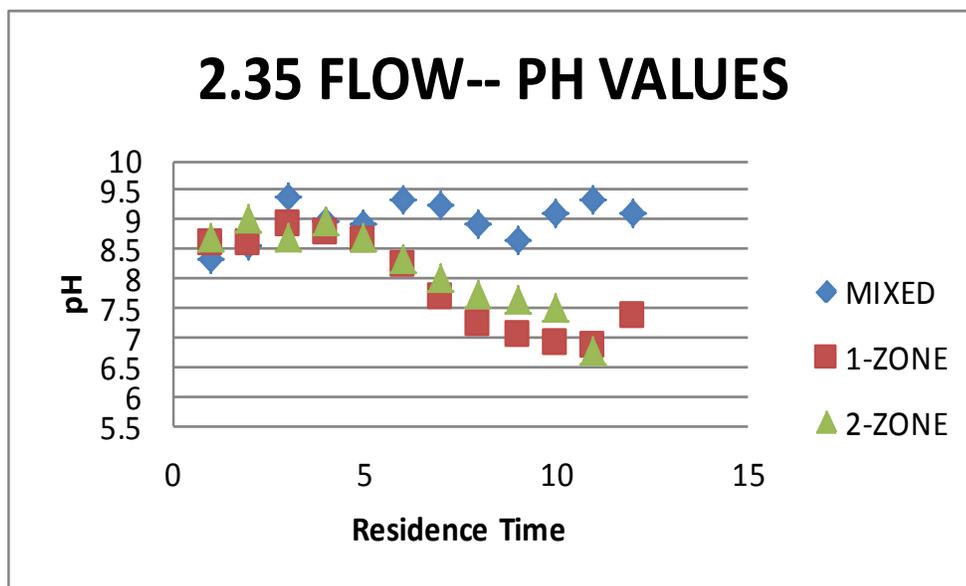


Figure 4-19. 2.45 mL/min Flow PH Values

The medium flow rate case as depicted above is quite similar to the slow flow rate case in that the mixed column still experiences pH values well above the other two columns. In fact, when comparing the graph above to the 1.23 mL/min case it is clear that they are almost identical, with a sharp decrease in pH for the one and two-zone columns around the fifth time step and a gradual leveling out of PH values at the tenth residence time. Average PH values for the mixed column remained above 9.0, while pH values toward the end of the experiment for the other two columns approach 7.0.

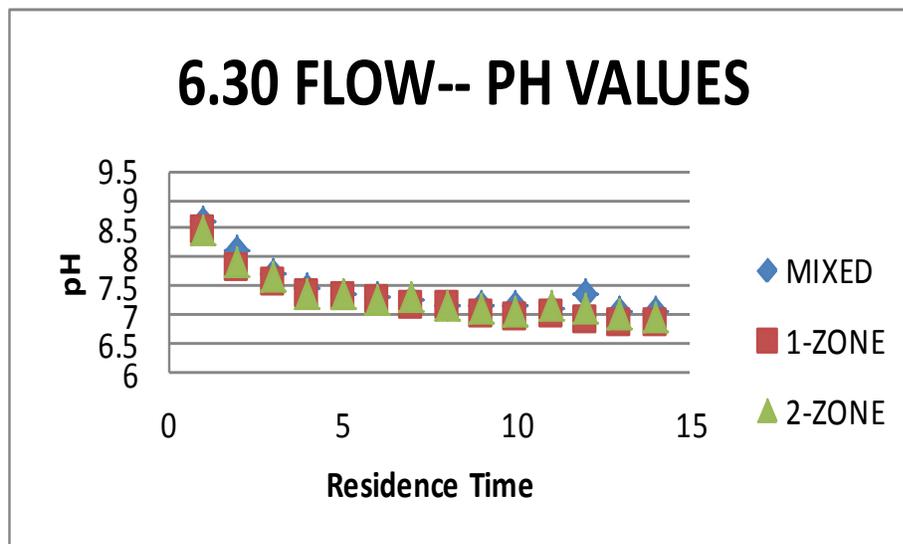
Effects of Mineral Distribution on pH—6.30 mL/min

Figure 4-20. 6.35 mL/min Flow PH Values

It is very interesting to note that at the fast flow rate (6.30 mL/min) all three PH curves are nearly identical. One would expect that the mixed-zone pH values would stay higher than the one and two-zone values as in the previous experiments, but this was certainly not the case for the fastest velocity. In fact, all three graphs have identical curvatures as pH values sharply declined during the first 4-5 residence times before leveling off toward the end of the experiment in a perfect logarithmic fit. From this, we can conclude that the rate of magnesite dissolution is independent of the column distribution at high flow rates since all pH values for all columns align at this velocity.

Effects of Mineral Distribution on Mg Concentration

Now that mineral spatial distribution has been discussed in terms of how it affects pH readings, it is now time to take a look at how the concentration of magnesium is affected with different column mineral distributions. The figures below will depict the concentration of magnesium based on different flow rates for each mineral distribution.

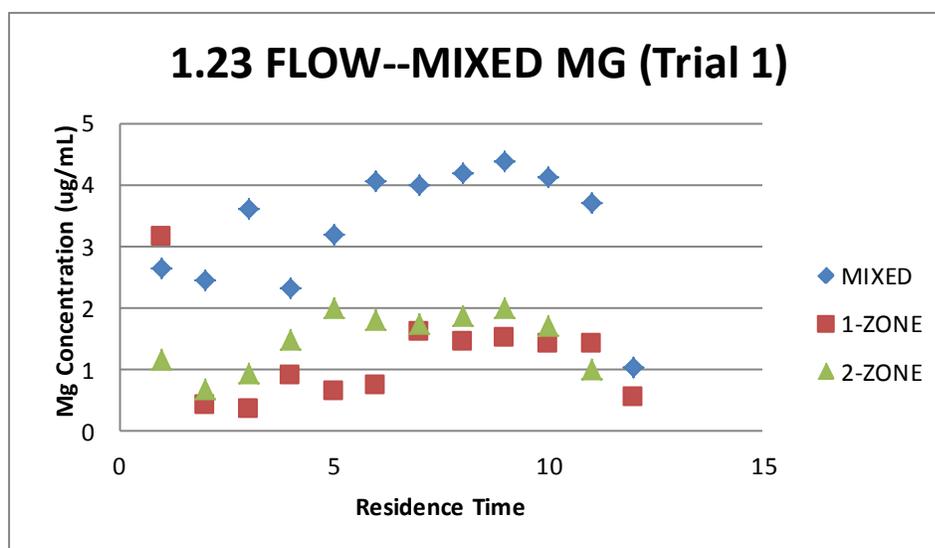


Figure 4-21. 1.23 Flow Mg Values (1st trial)

At a first glance, it does not appear as if there are any glaring trends present in the data. However, we can clearly see that the concentration of magnesite in the mixed column increases significantly after the fifth time step indicating that the Mg ions have started to precipitate from the solution. The significant drop in Mg values toward the end of the experiment may indicate that the ions have completely been flushed from the system, resulting in almost no magnesite remaining within the mixed region. The drop is so significant that in 12 minutes the concentration of magnesite drops from 3.7 g/cc to 1.04 g/cc. The average concentration of 4.13 g/cc in the mixed column is significantly higher

than the 1 and 2-zone columns, however there is a large difference in the starting concentrations of Mg at the beginning of the experiment (3.16 g/cc for the 1-zone and 1.16 g/cc for the 2-zone) before following similar concentration levels for the duration of the experiment, especially at high residence times.

Effects of Mineral Distribution on Mg Concentration—1.23 mL/min (2nd trial)

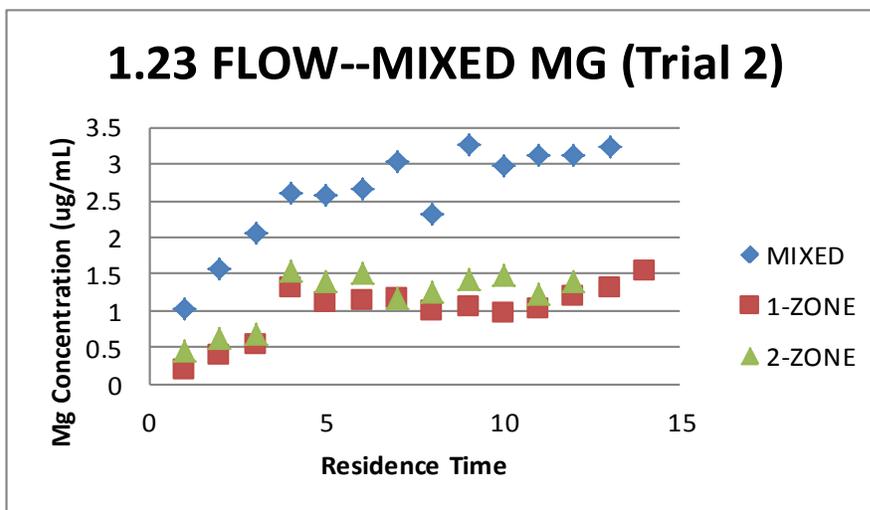


Figure 4-22. 1.23 Flow Mg Values (2nd trial)

During the second trial for the 1.23 mL/min flow rate, it is interesting to note that there is hardly ever a decrease in the concentration of magnesium in all three columns, indicating a stronger indication of the dissolution reaction occurring. This is what is expected during the experiment, so the first trial results may not be very accurate. The concentration of magnesium is once again highest in the mixed column as it increases from values around 1 g/cc to values above 3 g/cc, due to the high amount of contact area with the inlet solution. The concentration of magnesium ions actually stays fairly constant in the 1-zone and 2-zone cases, fluctuating between 1.0 g/cc and 1.2 g/cc before increasing to approximately 1.5 g/cc at the end of the experiment.

Effects of Mineral Distribution on Mg Concentration—2.35 mL/min

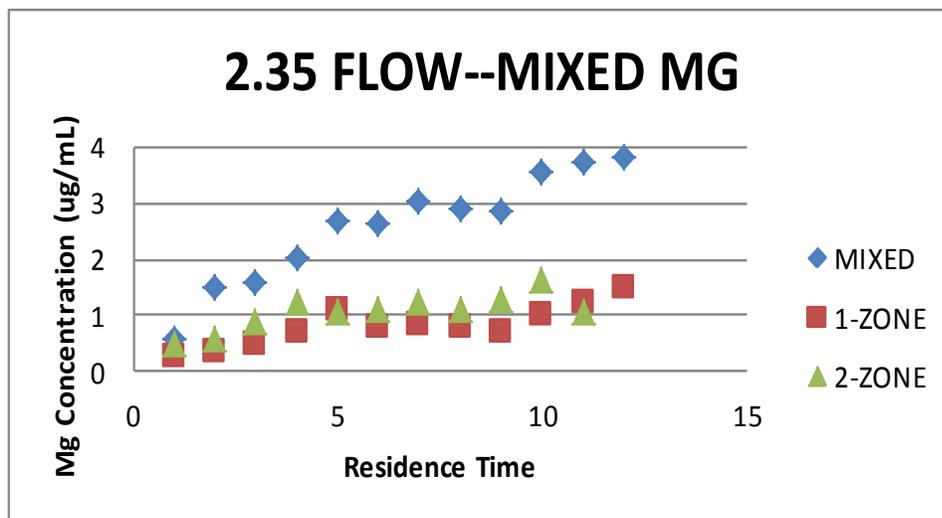


Figure 4-23. 2.35 Flow Mg Values

A direct relationship between increasing time and higher magnesium concentrations becomes even more apparent at the medium flow rate. The mixed column still contains the highest overall concentration of magnesium due to the fact that the magnesite is in direct contact with the inlet solution (in the quartz matrix). The 1-zone and 2-zone columns once again follow similar concentrations which increase to maximum values of 1.24 g/cc and 1.04 g/cc at the end of the experiment. The 2-zone column in general contains higher Mg concentration values than the 1-zone column. The mixed zone still had the overall largest increase in magnesium concentration, from 0.57 g/cc at the beginning to almost 4 g/cc at the conclusion of the experiment.

Effects of Mineral Distribution on Mg Concentration—6.35 mL/min

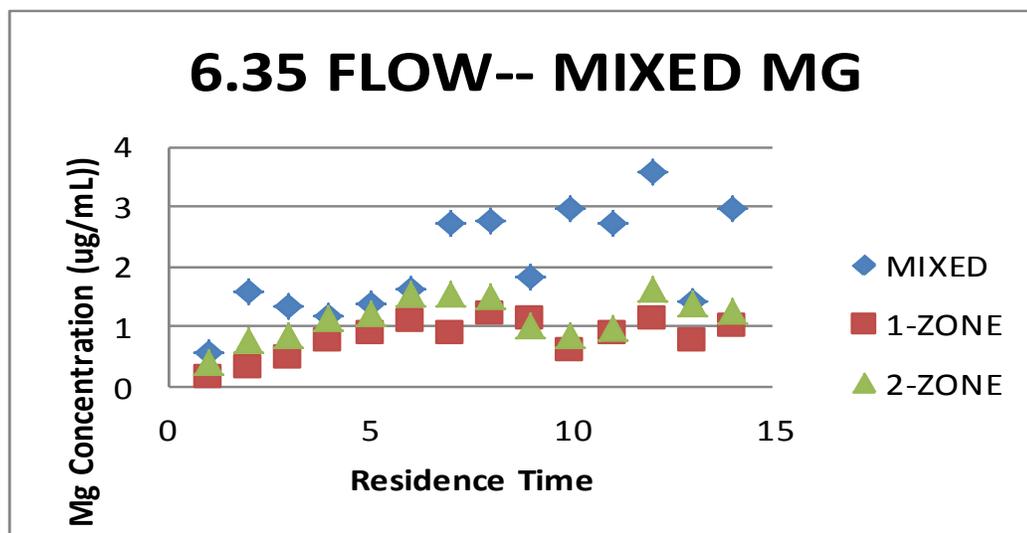


Figure 4-24. 6.30 Flow Mg Values

There are not too many different observations to make for the fastest flow rate other than the fact that the mixed column concentration follows Mg values much closer to the 1-zone and 2-zone columns before increasing significantly around residence time 5. However, there is a very wide spread in data points for the mixed column at high residence times, with concentrations ranging from 3.58 g/cc in the second-to-last time step to 2.85 g/cc in the final time step. 1-zone and 2-zone readings are much more consistent, staying within a range of 0.8-1.3 g/cc throughout the entire experiment, with 2-zone Mg values once again greater than the 1-zone values.

pH Ratios based on Mineral Distribution (1.23 mL/min—Trial 1)

The tables shown below will compare the 1-zone and 2-zone pH values versus the mixed column pH values and will calculate the ratios of each compared to the mixed column.

Table 4-4. 1.23 mL/min pH Ratios (Trial 1)

Residence Time	Mixed pH	1-Zone pH	2-Zone pH	Ratio (1-zone/Mixed)	Ratio (2-zone/Mixed)
0	8.9	7.96	8.78	0.89438202	0.98651685
0.5	9.16	8.42	8.88	0.91921397	0.96943231
1	9.12	8.5	8.86	0.93201754	0.97149123
2	8.91	8.54	8.63	0.95847363	0.96857464
3	8.83	8.41	8.48	0.95243488	0.9603624
4	8.9	8.44	8.17	0.94831461	0.91797753
5	8.83	8.04	7.9	0.91053228	0.89467724
6	8.8	7.84	7.75	0.89090909	0.88068182
7	8.85	7.48	7.65	0.84519774	0.86440678
8	8.98	7.33	7.4	0.81625835	0.82405345
9	8.92	7.24	6.93	0.81165919	0.77690583

pH Ratios based on Mineral Distribution (1.23 mL/min—Trial 2)

Table 4-5. 1.23 mL/min pH Ratios (Trial 2)

Residence Time	Mixed pH	1-Zone pH	2-Zone pH	Ratio (1-zone/Mixed)	Ratio (2-zone/Mixed)
0.5	9.18	8.88	8.95	0.96732026	0.97494553
1	9.49	8.87	8.72	0.93466807	0.91886196
2	9.59	9.11	8.87	0.94994786	0.92492179
3	8.8	8.77	9.35	0.99659091	1.0625
4	9.3	8.84	9.04	0.95053763	0.97204301
5	9.45	8.94	8.51	0.94603175	0.9005291
6	9.25	9.05	8.33	0.97837838	0.90054054
7	9.42	7.36	7.7	0.78131635	0.81740977
8	9.22	7.15	7.62	0.77548807	0.82646421
9	9.14	7.21	7.45	0.78884026	0.81509847
10	9.25	7.13	7.51	0.77081081	0.81189189

pH Ratios based on Mineral Distribution (2.35 mL/min)

Table 4-6. 2.35 mL/min pH Ratios

Residence Time	Mixed pH	1-Zone pH	2-Zone pH	Ratio (1-zone/Mixed)	Ratio (2-zone/Mixed)
1	8.55	8.59	8.7	1.00467836	1.01754386
2	9.38	8.59	9.04	0.91577825	0.96375267
3	8.98	8.94	8.7	0.99554566	0.9688196
4	8.94	8.78	8.97	0.98210291	1.0033557
5	9.35	8.63	8.71	0.92299465	0.9315508
6	9.26	8.23	8.32	0.8887689	0.89848812
7	8.94	7.67	8	0.85794183	0.89485459
8	8.63	7.23	7.75	0.8377752	0.89803013
9	9.1	7.03	7.62	0.77252747	0.83736264
10	9.34	6.91	7.51	0.73982869	0.80406852
11	9.11	6.84	6.77	0.75082327	0.74313941

pH Ratios based on Mineral Distribution (6.30 mL/min)

Table 4-7. 6.30 mL/min pH Ratios

Residence Time	Mixed pH	1-Zone pH	2-Zone pH	Ratio (1-zone/Mixed)	Ratio (2-zone/Mixed)
1	8.64	8.45	8.46	0.97800926	0.97916667
2	8.1	7.81	7.92	0.96419753	0.97777778
3	7.72	7.58	7.65	0.98186528	0.99093264
4	7.47	7.39	7.37	0.9892905	0.98661312
5	7.38	7.32	7.37	0.99186992	0.99864499
6	7.34	7.25	7.27	0.98773842	0.99046322
7	7.29	7.15	7.3	0.98079561	1.00137174
8	7.17	7.16	7.15	0.9986053	0.9972106
9	7.19	7.03	7.12	0.97774687	0.99026426
10	7.15	6.95	7.09	0.97202797	0.99160839
11	7.13	7	7.15	0.98176718	1.00280505
12	7.35	6.93	7.1	0.94285714	0.96598639

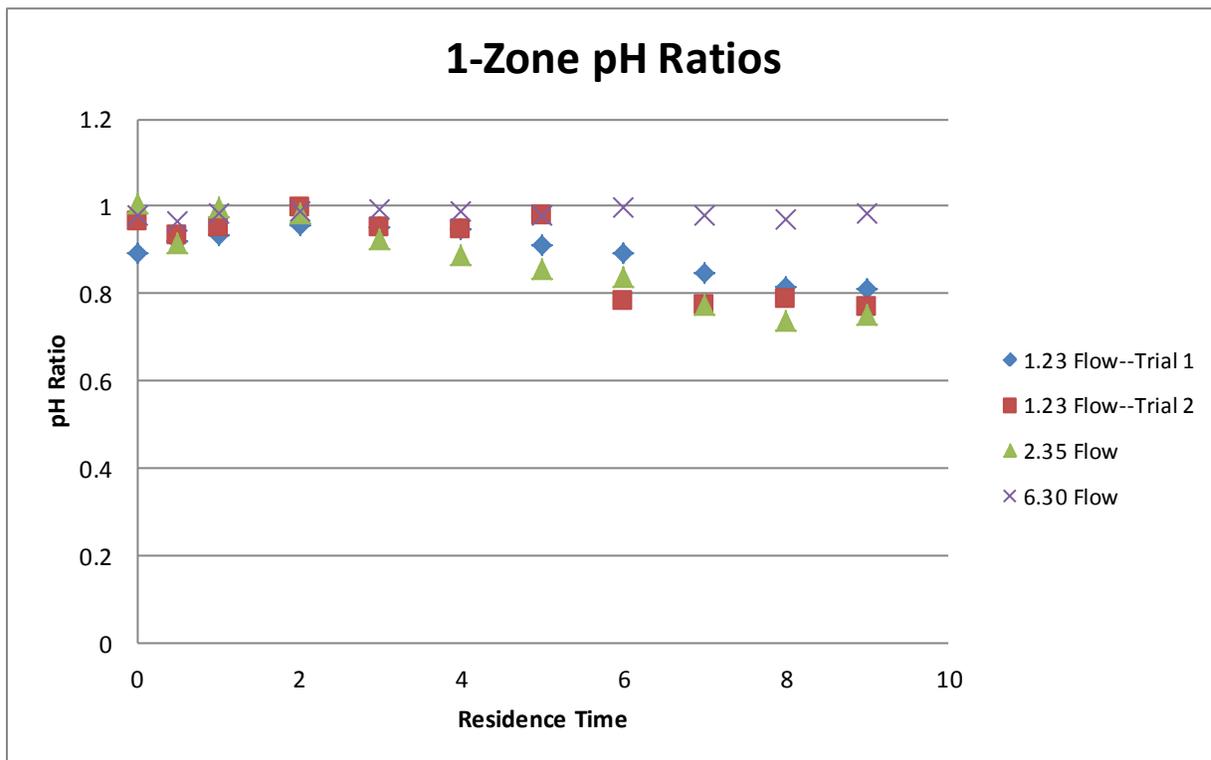


Figure 4-25. 1-Zone pH Ratios

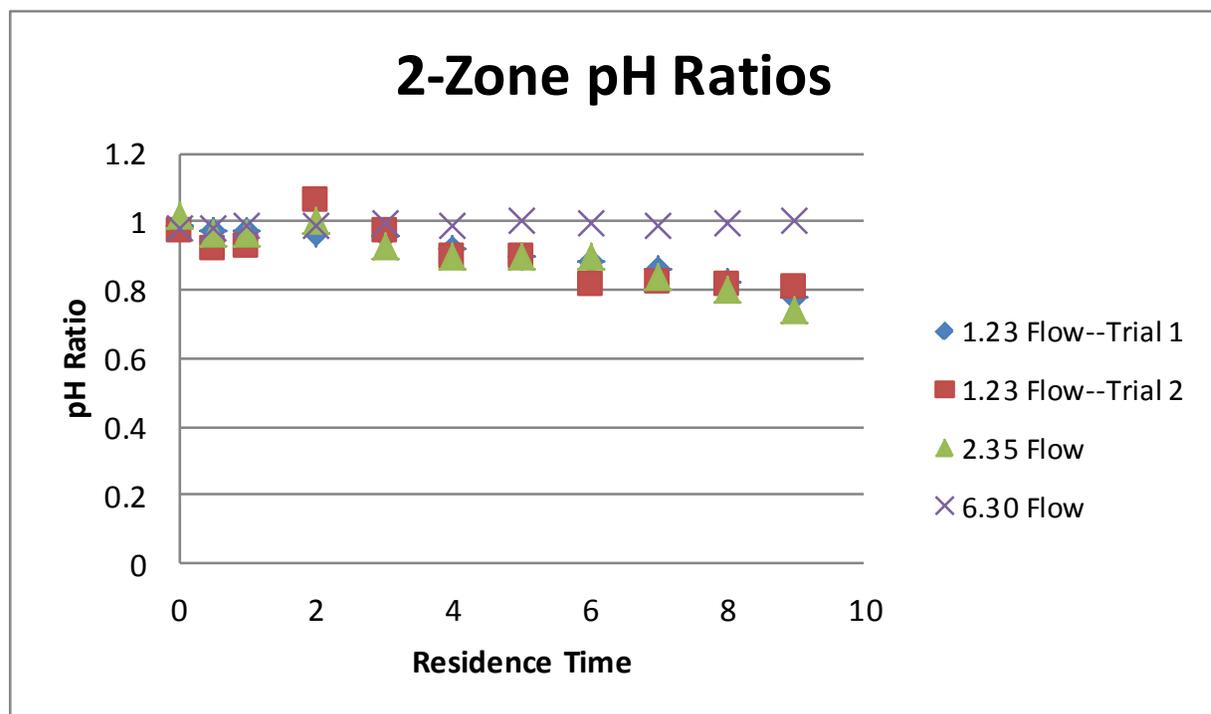


Figure 4-26. 2-Zone pH Ratios

When looking at the data for all three columns, it first becomes apparent that almost all of the ratios for all residence times are less than one, meaning that the one and two-zone column pH values are almost always less than the mixed zone pH values. This tells us that the majority of magnesite dissolution is occurring in the one and two-zone regions. The deviation of the one and two-zone columns from the mixed column also becomes much more apparent at high residence times for the low and medium flow rates, especially after about six residence times. However, when looking at the 6.30 mL/min case we see that a decrease in pH does not occur, even at high residence times. This may occur due to the fact that the flow rate is too fast for any significant dissolution to occur, as the time for any reaction to take place would not occur during the shorter residence times.

For the slow flow rate (1.23 mL/min) it is apparent that the two-zone column has higher pH ratios than the one-zone column for all residence times, meaning that the one-zone pH values are less than the two-zone pH values. Even though the two-zone region has more surface area in contact with the quartz, at slow flow rates the magnesite seems to be reacting faster in the one-zone region. This same trend also applies to the 2.35 mL/min case, although it is not as apparent as before. Additionally, the one-zone and two-zone pH ratios start to converge toward the end of the experiment (at high residence times). At the highest flow velocity, both pH ratios are almost identical, showing that at the higher flow rates the dissolution of magnesite occurs at the same rate for both columns. There is no clear trend for which ratio is usually larger (sometimes it is the one-zone, other times it is the two-zone).

Mg Ratios based on Mineral Distribution (1.23 mL/min—Trial 1)

Similar we will look at the ratio of Mg in the one-zone and two-zone columns to the ratio of magnesium in the mixed column. See the tables below.

Table 4-8. 1.23 mL/min Mg Ratios (Trial 1)

Residence Time	Mixed Mg (ug/mL)	1-Zone Mg (ug/mL)	2-Zone Mg (ug/mL)	Ratio (1-zone/Mixed)	Ratio (2-zone/Mixed)
0.5	2.63	3.16	1.16	1.20152091	0.44106464
1	2.43	0.4	0.66	0.16460905	0.27160494
2	3.59	0.36	0.94	0.10027855	0.26183844
3	2.31	0.88	1.49	0.38095238	0.64502165
4	3.19	0.64	1.98	0.20062696	0.62068966
5	4.05	0.75	1.8	0.18518519	0.44444444
6	3.98	1.6	1.73	0.40201005	0.43467337
7	4.19	1.43	1.85	0.34128878	0.44152745
8	4.38	1.5	1.99	0.34246575	0.4543379
9	4.13	1.4	1.71	0.33898305	0.41404358
10	3.7	1.4	0.98	0.37837838	0.26486486

Mg Ratios based on Mineral Distribution (1.23 mL/min—Trial 2)

Table 4-9. 1.23 mL/min Mg Ratios (Trial 2)

Residence Time	Mixed Mg	1-Zone Mg	2-Zone Mg	Ratio (1-zone/Mixed)	Ratio (2-zone/Mixed)
1	9.18	8.88	8.95	0.96732026	0.97494553
2	9.49	8.87	8.72	0.93466807	0.91886196
3	9.59	9.11	8.87	0.94994786	0.92492179
4	8.8	8.77	9.35	0.99659091	1.0625
5	9.3	8.84	9.04	0.95053763	0.97204301
6	9.45	8.94	8.51	0.94603175	0.9005291
7	9.25	9.05	8.33	0.97837838	0.90054054
8	9.42	7.36	7.7	0.78131635	0.81740977
9	9.22	7.15	7.62	0.77548807	0.82646421
10	9.14	7.21	7.45	0.78884026	0.81509847
11	9.25	7.13	7.51	0.77081081	0.81189189
12	9.1	7.02	7.59	0.77142857	0.83406593

Mg Ratios based on Mineral Distribution (2.35 mL/min)

Table 4-10. 2.35 mL/min Mg Ratios

Residence Time	Mixed Mg	1-Zone Mg	2-Zone Mg	Ratio (1-zone/Mixed)	Ratio (2-zone/Mixed)
1	0.57	0.28	0.5	0.49122807	0.87719298
2	1.48	0.38	0.57	0.25675676	0.38513514
3	1.58	0.49	0.89	0.31012658	0.56329114
4	2.04	0.71	1.22	0.34803922	0.59803922
5	2.66	1.09	1.06	0.40977444	0.39849624
6	2.62	0.82	1.12	0.3129771	0.42748092
7	3.01	0.86	1.24	0.28571429	0.41196013
8	2.88	0.82	1.1	0.28472222	0.38194444
9	2.83	0.71	1.28	0.25088339	0.45229682
10	3.56	1.03	1.61	0.28932584	0.45224719
11	3.7	1.24	1.06	0.33513514	0.28648649
12	3.8	1.52	1.09	0.4	0.28684211

Mg Ratios based on Mineral Distribution (6.30 mL/min)

Table 4-11. 6.30 mL/min Mg Ratios

Residence Time	Mixed Mg	1-Zone Mg	2-Zone Mg	Ratio (1-zone/Mixed)	Ratio (2-zone/Mixed)
1	0.58	0.16	0.39	0.27586207	0.67241379
2	1.6	0.33	0.75	0.20625	0.46875
3	1.35	0.48	0.85	0.35555556	0.62962963
4	1.18	0.77	1.14	0.65254237	0.96610169
5	1.39	0.89	1.21	0.64028777	0.8705036
6	1.63	1.1	1.55	0.67484663	0.95092025
7	2.72	0.89	1.54	0.32720588	0.56617647
8	2.76	1.23	1.49	0.44565217	0.53985507
9	1.82	1.13	1.01	0.62087912	0.55494505
10	2.98	0.62	0.83	0.20805369	0.27852349
11	2.72	0.88	0.98	0.32352941	0.36029412
12	3.58	1.12	1.61	0.31284916	0.44972067
13	1.41	0.76	1.39	0.53900709	0.9858156

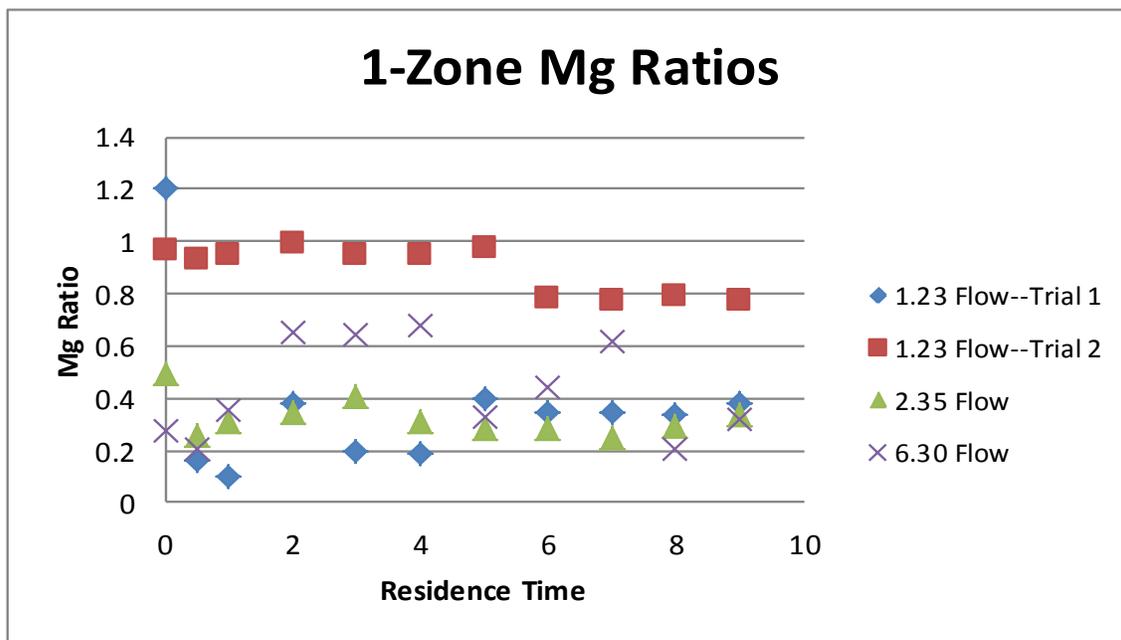


Figure 4-27. 1-Zone Mg Ratios

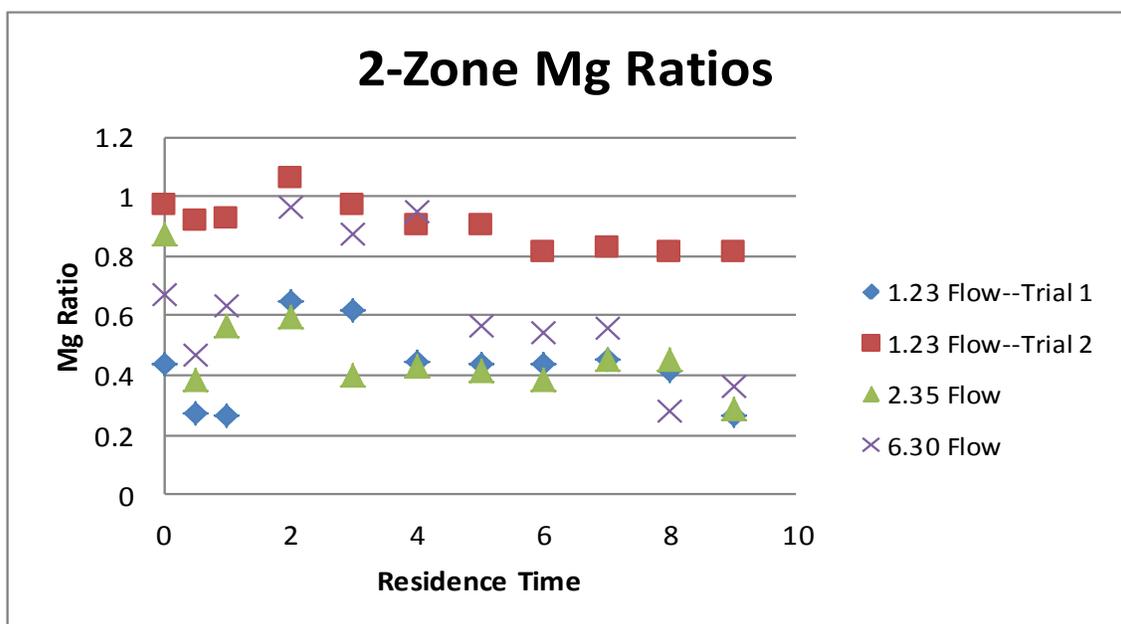


Figure 4-28. 2-Zone Mg Ratios

Mg ratios are generally once again less than one, demonstrating that the highest Mg concentrations can be found within the mixed column. There is most definitely a decreasing trend for all three flow rates, although concentrations of Mg actually increase between residence times 3 and 4 for each flow rate. This may be due to the fact that the inlet solution is just beginning to interact with the magnesium ions, causing a short but dramatic increase in concentration. For the slow and medium flow rates, the concentration of Mg is higher in the 2-zone column than in the 1-zone region for all residence times, demonstrating that dissolution is occurring at a faster rate in the 1-zone region. The fast flow rate also demonstrates the same concept, although the ratios do become closer toward the end of the experiment.

Chapter 5: Discussion of Results

The results presented above clearly demonstrate that the dissolution of magnesite in each case is most definitely affected by flow rate and mineral distribution. However, the extent of how the dissolution rate is affected varies between different columns.

Flow Velocity Analysis

Generally speaking, the most dramatic results were found at the lowest flow rate of 1.23 mL/min, where the concentration of magnesium ions was almost always the highest of all columns. The fact that the slowest flow rate yields the highest concentration makes sense when analyzing the equation $R = C \cdot Q$ where C is the concentration of magnesium (mass/volume) and Q is the flow rate (volume/time). For example, when looking at Figure 4-14 one would think that the 6.30 mL/min trial would yield a higher rate, since Q for this trial is over five times the value of the slower flow rate (1.23 mL/min). However, when plugging in values for concentration for the 1.23 mL/min case we see that $R = (4.35 \cdot 1.23) = 5.35$ ug/residence time whereas the 6.35 mL/min case yields $R = (0.79 \cdot 6.30) = 4.98$ ug/residence time. Therefore, the slow flow velocity does indeed yield a higher rate than the fast flow rate. Considering that the slow flow rate has more time to penetrate each column to dissolve the magnesite, this conclusion makes sense.

One interesting fact to note when analyzing the 1.23 mL/min case is the magnitude of difference of Mg concentration values between the mixed zone column and the 1 and 2-zone columns. Fatemeh observed in her experiment (with larger magnesite grains) that the magnitude of difference of concentration values between these columns

was between two and three (Saleikhoo 2012). However, in this experiment it was observed that the difference in concentration values was on a magnitude of between 3 and 4 in the lowest flow rate trial. The smaller grain sizes likely increased the porosity of the column since it is easier for particles to fill in between the larger grain sizes, decreasing the porosity of the system. The magnitude of difference of Mg concentration values decreased to around 2.0 in the 2.35 mL/min case and decreased yet again to approximately 1.5 in the 6.30 mL/min case. The pH values were always the lowest for the 6.30 ug/mL case and decreased in an almost perfect logarithmic function.

Mineral Distribution Analysis

From the pH and Mg information above, we can also draw generalized conclusions on how dissolution is affected by the distribution of the magnesite in each column. When looking at pH values, it is interesting to note that values do not decrease significantly in the mixed column, but decrease substantially in the 1 and 2-zone columns. As stated previously, this is likely due to the fact that the magnesite is in direct contact with the quartz and inlet solution, which may limit the ability of the magnesite to change its pH. However, it is definitely clear when plotting Mg concentrations that values increase, particularly during the early time region where the unit slope line can once again be found. The 1-zone column contained the most condensed concentration data for all flow rates due to the fact that there is only one outlet for mass transport from the system.

Mg concentration values are highest in the mixed column, which has the most contact area with the quartz matrix and therefore has the most mass transport of

magnesite out of the system. Concentration values on average remain above 4 ug/mL for the mixed system. The 2-zone column has higher concentration values than the 1-zone column which also makes sense considering that the 2-zone column has twice the amount of contact area with the quartz matrix than the 1-zone case. Mg values hover around 2 ug/mL for the 2-zone case while values for the 1-zone case fluctuate between 1.1 and 1.4 ug/mL. It is much harder for the magnesite to transport out of the 1-zone case due to the zonation of the magnesite into one area. Additionally, Mg values obtained during the fastest flow rate are much more random than the slow and medium cases. For example, Figure 4-15 shows Mg values for the 6.30 mL/min trial decreasing below 1 ug/mL after residence time 7 before increasing back to 1.6 ug/mL at residence time 9, then decreasing thereafter. This S-shape graph also occurred in the 1-zone region, demonstrating that the fast flow rate is working very hard to transport magnesite out of the system and may be affecting the reaction.

In each of the graphs for Mg concentration (mixed, 1-zone, and 2-zone), a unit slope line (approximately equal to one) was observed in the early time region before values began to diverge. This unit slope line is not as important as the middle and late time regions since little to no magnesite dissolution has actually taken place. Nonetheless, this line can show us how concentration may change right as the experiment commences, with a greater slope indicating a faster dissolution rate. It is not surprising, therefore, to see that the mixed zone case has the steepest unit slope line while the 1-zone case has the flattest slope. During the middle time regime, the 1-zone column shows that the Mg concentration values for all flow velocities are all within a narrow range (between

0.5 and 1.4 ug/mL), which supplements the fact that this column has the lowest contact area with the inlet solution.

Matrix Acidizing Applications

Applications of this experiment during matrix acidizing processes in the field were discussed at the beginning of Chapter 2, but now specific conclusions can be drawn given the data above. In matrix acidizing, the goal is to dissolve some of the formation rock in order to increase hydrocarbon production, and to clear certain minerals (like magnesite) from flow channels in the reservoir. Therefore, high dissolution rates are preferred in the field in order to maximize the economic potential of the region. From the data above, it appears that the slowest injection rate of 1.23 mL/min yields the highest dissolution rates, making it desirable to have low acidizing rates in the field. If the rate of acid injection is too high, the concentration of Mg ions that dissolve out of the formation rock decrease significantly (by a magnitude of 3-4) resulting in an insufficient tertiary recovery process. Additionally, a flow rate that is too fast may result in damage to the reservoir and the formation rock, making hydrocarbon recovery nearly impossible without the addition of other techniques. The early time region (less than five residence times) is where the concentration of magnesium increases the most, so it is important to closely monitor the rate of dissolution immediately after acidizing commences in order to fully understand how the reservoir changes over time. During the late time region (residence times greater than 15), the concentration of Mg does not change significantly, demonstrating that the acidizing process can be stopped at an earlier time to save money since no further improvement to the reservoir will be experienced.

It is also desirable to utilize matrix acidizing in mixed carbonate reservoirs (heterogeneous distribution of quartz and magnesite) since dissolution rates were the highest in the scheme. However, this scheme is not usually found in the field due to the natural geological deposition of sediment and minerals. The 1 and 2-zone reservoirs are much more common, which is unfortunate considering that Mg concentrations were much lower in these columns. The rate of dissolution in the 2-zone region is higher than the 1-zone region due to the fact that the magnesite can diffuse out of two mass transport regions while the 1-zone can only diffuse out of one. The flow rate of magnesite is also higher in the 2-zone column, but dissolution rates could be increased in the 1-zone column by processes such as hydraulic fracturing and adding more perforations in the wellbore. One would expect multiple-layered reservoirs to experience even lower pH and even higher Mg values because the contact area increases with the addition of each new mass contact area, increasing the flow velocity and dissolution rate of magnesium.

Comments on Mg/pH Relationships

While recording the pH values of different fluid samples throughout the experiment was an important parameter to explore, it cannot tell us for sure how Mg values may change with time. For example, by looking at Figure 4-20 above the results show that all three pH values are extremely close to each other for every residence time during the experiment. If there was a direct correlation between pH and Mg concentration, one could say that all Mg values should form a single increasing line with similar values for each residence time for all columns. However, this is clearly not the case, as Figure 4-24 demonstrates. While this correlation may be roughly used to state

that the concentration of Mg in the 1 and 2-zone columns increases at the same rate as the pH values in these systems decrease, the same cannot be said for the mixed column case. The concentration of Mg during all three flow rates for the mixed case increases much more dramatically, especially during the fast flow rate case. Therefore, we can say that pH can roughly predict dissolution in reservoirs that only have the same characteristics as the 1-zone and 2-zone cases.

Chapter 6: Concluding Remarks

The effects of flow rate and mineral spatial distribution on the dissolution of magnesite and other substances found in nature is vital to understanding subsurface processes, especially when utilizing acidification processes in petroleum engineering. With the information described above, a more generalized approach to modeling dissolution reactions in rock cores can be accomplished, but much still needs to be done in terms of identifying how spatial distribution may affect specific reservoir properties.

At high injection rates, the dissolution rates for all three columns were very similar, indicating that the time to equilibrium for each of the reactions was almost the same. However, at low injection rates the values of Mg concentration and pH were easily distinguishable from each other, especially when analyzing the mixed column case. Additionally, dissolution rates seemed to be very similar for all flow rates in the 1-zone column due to the fact that the mass transport was constricted to the confines of the isolated magnesite zone. By increasing the number of flow boundaries to the reservoir, an increase in flow velocity and magnesium dissolution can be obtained.

Much more information needs to be gathered from mineral distribution and flow velocity effects on different sizes of magnesite grains in addition to different minerals in carbonate reservoirs such as dolomite and calcite. This thesis should serve as a precursor to this research and provide a guide toward future dissolution work as acidification processes continue to advance and become more complex in nature.

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