Development of Microreactor System for *in situ* investigation of rock-brine-CO_2 interactions

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Abstract of the Thesis

Development of Microreactor System for *in situ* investigation of rock-brine-CO_2 interactions

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A microreactor has been developed for *in situ*, high-energy x-ray diffraction investigations of reaction process between carbon dioxide, brines and rocks. Our design is an evolution of a previous existing reaction cell developed by Diefenbacher *et al* [1]., Several changes and improvements have been made to the new cell design: (i) the reactor chamber will be accessible through two points, whereby any combination of gases, liquids or fluids can be injected and investigated,(ii) the CO_2 flow and pressure will be controlled through a supercritical fluid pump which allows the cell to operate under a well-controlled pressure and flow conditions, and (iii) sintered polycrystalline diamond will be initially employed as X-ray transparent window material. The microreactor should allow investigation of reactions in the rock-brine-CO_2 system in the pressure-temperature range of 400 bar and 600℃. The new microreactor system will increase our capabilities to perform *in situ* investigations of the reaction processes in

between rock-brine and CO_2, relevant for potential carbon storage applications in geological formations.

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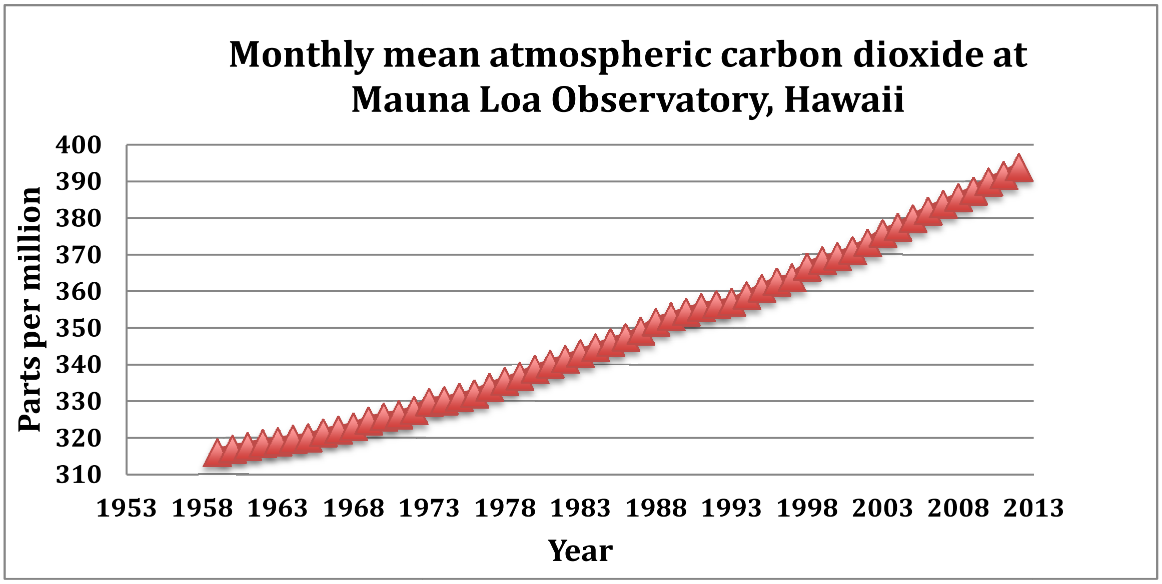
CHAPTER 1. INTRODUCTION

1.1 - Motivation

Carbon dioxide (CO_2) is a major greenhouse gas that contributes to global warming (Friedmann, 2007). It occurs naturally in processes such as photosynthesis and respiration (2010). Carbon dioxide accounts for 0.03 vol. % of the atmosphere (White et al., 2003). CO_2 can also be produced through the combustion of fossil fuels (2010). The use of fossil fuels adds about 600 billion metric tons of CO_2 per year and may remain in the atmosphere for as long as 200 years (McKibbin and Wilcoxen, 2002). The largest source of CO_2 emissions is power generation, followed by transportation, and industrial exhausts (Anderson and Newell, 2004). Of direct carbon emissions, about 40% are from



(Fig. 1.1.1) Monthly mean atmospheric carbon dioxide at Mauna Loa Observatory, Hawaii. This graph displays the seasonally corrected data of the carbon dioxide that was measured as a mole fraction in dry air. Mauna Loa constitutes the longest record of direct measurements of carbon dioxide in the atmosphere. Dr. Pieter Tans, NOAA/ESRL (www.esrl.noaa.gov/gmd/ccgg/trends/) and Dr. Ralph Keeling, Scripps Institution of Oceanography (scrppsCO$_2$.ucsd.edu/).

the generation of electricity, 32% from transportation and 15% from industry (Anderson and Newell, 2004).

Atmospheric carbon dioxide is increasing every year (e.g. see Fig. 1.1.1) (Solomon et al., 2009). At present day, the carbon dioxide concentration is at 394 ppm (Tans and Keeling, 2013). Figure 1.1.1 shows the steady increase of the mean atmospheric CO_2 concentration at Mauna Loa Observatory Hawaii, in the time period from 1958 to 2013. C. David Keeling of the Scripps Institution of Oceanography first took these measurements in March of 1958 at a facility of the National Oceanic and Atmospheric Administration (Priem, 2013). Since May of 1974, NOAA started its own recordings of CO_2 measurements, and these have been conducted in parallel with those made by Scripps (Tans and Keeling). According to Intergovernmental Panel on Climate (IPCC) Fourth Assessment Report, “Carbon dioxide is the most anthropogenic greenhouse gas” and “Most of the observed increase in global average temperatures since the mid-20th century is very likely due to observed increase in anthropogenic greenhouse gas concentrations” (Tans and Keeling). For this reason, technological solutions, such as, Carbon Capture and Storage (CCS), are being investigated worldwide as possible solutions to decrease the CO_2 emissions in the atmosphere (McKibben, 2007).

1.2 - Carbon Capture and Storage

CCS is a technology that prevents carbon dioxide emissions from entering the Earth’s atmosphere by three main processes. The primary involves capturing the gas at large combustion sources, transporting it to a storage site, and storing the CO_2 in order to isolate it from Earth’s atmosphere and environment (McKibben, 2007).

1.2.1 - Capture - The most difficult step in CCS is capturing the CO_2 (McKibben, 2007). The gas must be captured from stationary sources such as oil refineries, fossil-fuel-based power generation, iron and steel plants, etc. (Singh, 2013). Carbon dioxide can be captured through three different processes: post-combustion capture, pre-combustion capture, and oxy-combustion (White et al., 2003). Post-combustion capture occurs after the combustion of fossil fuels and the carbon dioxide is captured from the flue gas (Singh, 2013), whereas in pre-combustion capture the fuel is reacted with oxygen in air, or with steam, to produce hydrogen and carbon monoxide (Olajire, 2010). The pre-combustion process is known as gasification (Olajire, 2010). In this process coal is gasified with oxygen to produce a mixture mainly composed of H_2 and CO (Figueroa et al., 2008), and this mixture is passed through a shift converter, in which the

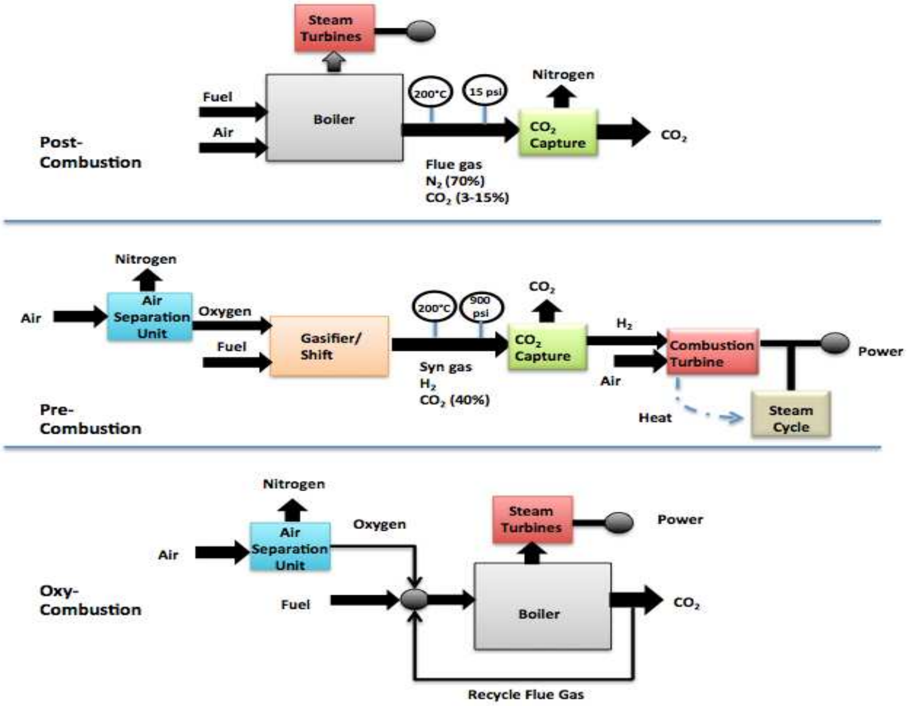


Fig. (1.2.1) Block diagrams illustrating post-combustion, pre-combustion, and oxy-combustion processes steps in carbon capture and storage technology.

CO reacts with steam to produce CO_2 and more H_2 (Olajire, 2010). The CO_2 is then separated and the H_2 is used as fuel in a gas turbine combined-cycle plant (Olajire, 2010). Oxy-combustion is when the fuel is burned in a stream of oxygen that contains little or no nitrogen (Edge et al., 2011). Figure 1.2.1 is a diagram that illustrates the basic concept of the three different capture processes.

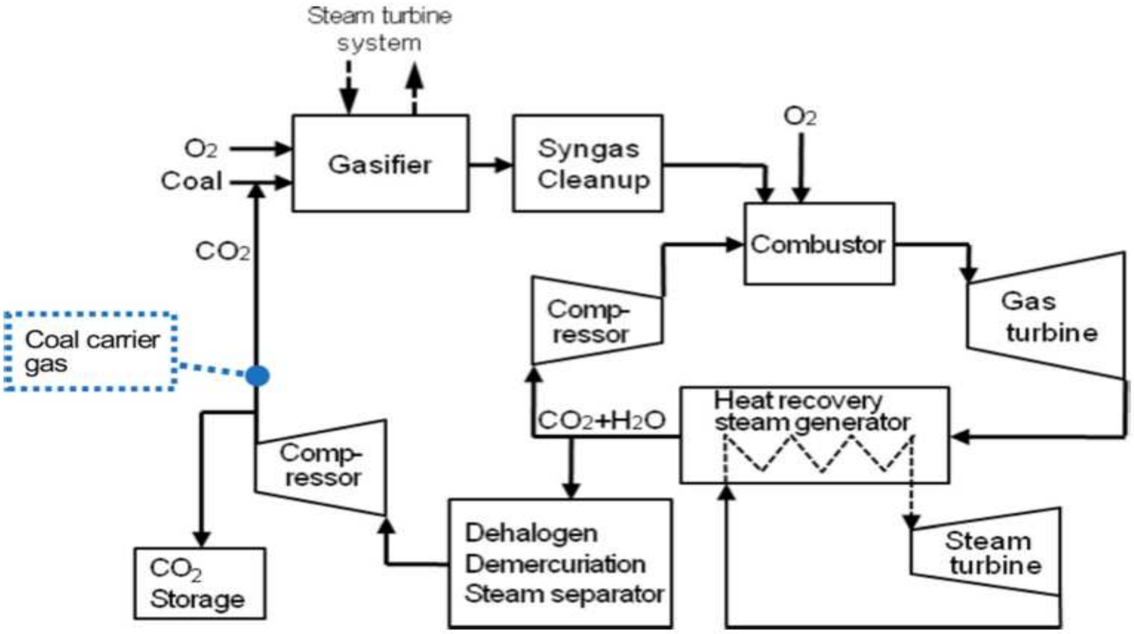
Post-combustion capture mainly is used in coal-fueled power generators that are air fired (Figueroa et al., 2008). Pre-combustion capture can be used in gasification plants and oxy-combustion can be applied in new plants or by modifying existing plants (Figueroa et al., 2008).

1.2.1.1 - Advantages of different capture systems - The advantage of using post-combustion capture is it can be applied to majority coal-fired power plants and it can be retrofitted to existing units that generate two-thirds of the CO_2 emissions of power (Figueroa et al., 2008). Pre-combustion capture is advantageous because the CO_2 concentration is high and the pressure is elevated above atmospheric pressure (Figueroa et al., 2008). This results in an increased driving force for separation, more technologies available for separation and the potential for reduction in compression costs/loads (Figueroa et al., 2008). In oxy-fuel combustion the product minimizes sequestration costs due to the CO_2 concentration in flue gas being very high (Palmer, 2012). During the combustion of oxy-fuel, over 95 vol% purity of flue gas is recycled and is used for combusting a gas purely carbon dioxide and water vapor after which the gas is ready to be stored once purified and compressed (Scheffknecht et al., 2011)

1.2.1.2 - Disadvantages of different capture systems - The disadvantages of post-combustion capture is that the flue gas stream contains a weak CO_2 concentration and is at ambient pressure causing a low CO_2 partial pressure (Figueroa et al., 2008). The low CO_2 partial pressure leads to significantly higher performance or circulation volume required for high capture levels; thus the CO_2 will be produced at lower pressures in conflict to sequestration requirements (Figueroa et al., 2008). One barrier to implementation of pre-combustion capture arises because this process is applicable mainly to new plants, as few gasification plants are currently in operation (Figueroa et al., 2008). Also there are barriers to commercialize the application of gasification due to availability new plants, cost of equipment, and requirements of extensive supporting systems (Figueroa et al., 2008). Employing oxy-combustion capture has its downsides also. When it comes to this process, there is little experience and therefore developing this technique will likely be financially expensive and the risk will be high (Palmer, 2012).

1.2.1.3 - Examples of Separation technologies of carbon capture systems - The most well-established method for capturing carbon dioxide is post combustion chemical absorption method with alkanolamine solvents (Palmer, 2012). When amines react with carbon dioxide, water-soluble compounds are formed (Arachchige and Melaaen, 2013). Alkanolamines can be classified as primary, secondary or tertiary amines (Figueroa et al., 2008). Monoethanolamine or MEA is categorized as a primary amine; it is the most applicable amine because of low partial pressure of CO_2 in the flue gas (Arachchige and Melaaen, 2013). A few other examples of separation technologies that can be used during post combustion are carbonate-based systems in which a soluble carbonate reacts with CO_2 or aqueous ammonia where ammonia-based wet scrubbing is used (Arachchige and Melaaen, 2013)

Some developmental separation technologies that can be used during pre-combustion capture are integrated gasification combine cycle (IGCC), state-of-the-art physical solvent processes or pre-combustion sorbents (Figueroa et al., 2008). Integrated gasification combine cycle is considered to be a very promising approach (Figueroa et al., 2008). Present IGCC concepts that incorporate CO_2 capture give an opportunity for recovering waste heat at levels suitable for district heat production including the usage of classical heat sources [e.g. tap-steam turbine (Figueroa et al., 2008)]. The physical solvent process selectively absorbs the carbon dioxide without a chemical reaction and pre-combustion sorbents, a method involving highly active lithium silicate-based (Li_4SiO_4) sorbent material for high temperature CO_2 removal (Liszka et al., 2013).



(Fig 1.2.2) Diagram of an oxy-fuel integrated gasification combine cycle and semi-closed cycle gas turbine (Güler and Güler, 2013)

An example of a new oxy-combustion separation technology that was designed and under development by the Central Research Institute of Electric Power Industry is an oxy-fuel IGCC power generation system integrated with a combination of CO_2 recovery processing and a semi-closed cycle gas turbine (Figueroa et al., 2008). This new system consists of an oxygen-CO_2 blown gasifier, a hot or dry synthetic gas cleanup system, a semi-closed cycle oxygen-fired gas turbine, and a CO_2 recovery process; a diagram of this system is shown in Figure 1.2.2 (Hasegawa, 2012). Oxy-fuel IGCC could simplify CO_2 recovery systems, reduce station service power, and achieve higher thermal efficiency (Hasegawa, 2012).

Another example of an oxy-combustion system is an oxy-fuel combustion regenerative steam superheater for a power generation system (Hasegawa, 2012). It is based on a previous system called combined cycle power generation system (CCPS) (Pak, 2008). In both systems pure oxygen burns fuel, but the steam superheater utilizes an oxygen-combusting regenerative steam superheater instead of the gas turbine combustor (Pak, 2008).

1.2.2 Transport - Once CO_2 is capture, it must be transported to a storage site (Pak, 2008). The carbon dioxide can be transported via pipelines, ships, railways or trucks (Singh, 2013). The most effective way to transport carbon dioxide is through high-pressure ground pipelines (Singh, 2013). Internationally, there are more than six thousand kilometers of CO_2 transport pipelines in existence (Rusin and Stolecka, 2013). The majority of these pipelines are of no threat to humans because they are located in poorly populated or completely uninhabited areas (Rusin and Stolecka, 2013). New pipelines being planned for carbon dioxide transport will have to travel through densely populated areas and therefore the need to have a risk assessment becomes very crucial (Rusin and Stolecka, 2013). Once the carbon dioxide is transported, can then be injected into a geological formation since it is one of the different options. There are several different injection techniques that can be used.

1.2.2.1 - Injection Techniques – The injection of CO_2 into deep geological formations involves many similar technologies that have been developed in the oil and gas exploration and production industry (Rusin and Stolecka, 2013). Injection technology, well-drilling technology, computer simulation of storage reservoir dynamics and monitoring techniques from existing applications are being further refined for design and operation of geological storage [specifically, from operations such as Enhanced Oil Recovery (EOR) or Enhanced Geothermal Systems (EGS)]. Before CO_2 can be injected and stored into a deep geological formation, it is important to understand the properties and solubility of CO_2 and the local geological and mineralogical setting of the storage site (McKibben, 2007).

1.2.3 Geological Storage - 1.2.3.1 Chemical and Physical Properties of CO_2 - For effective estimation of storage potential we must be able to predict the behavior of the carbon dioxide that is injected into the geosphere in order to understand the conditions required for storage (White et al., 2003). Carbon dioxide exists as a somewhat inactive compound at ambient conditions in the Earth's atmosphere and at its critical point, 304 K and 7.4 MPa (White et al., 2003). Below the critical point, carbon dioxide can be easily compressed into a liquid, which is how CO_2 is transported (White et al., 2003). Above the critical point, CO_2 exists as a supercritical fluid (White et al., 2003). Supercritical fluids are unable to become liquefied under extreme pressure and when changing the density this supercritical fluid can transform from gas-like state to a liquid-like state (White et al., 2003). For the purposes of geological storage CO_2 will be gaseous or supercritical because the critical temperature exceeds conditions of the deep geosphere (Gupta and Shim, 2007).

Liquid dense gaseous CO_2 is an excellent solvent for small hydrocarbons and aromatics (White et al., 2003). Therefore, the CO_2 injected into a geological storage site has the ability to draw out small molecules that are trapped within the macromolecular arrangement inside the pore space of the geological media (White et al., 2003). Natural brines are characterized by high salinity, which can possibly impact the solubility of carbon dioxide (White et al., 2003). For example, lower salinity aquifers will have a higher capacity for solubility trapping of $CO_{2,}$ while higher salinity aquifers will have a lower capacity for solubility trapping (White et al., 2003). These different chemical and physical properties of CO_2 are the stepping-stones defining how and why carbon dioxide interacts with different geological media.

1.2.3.2 - Nature of Trapping/Storage Options - The first chemical reaction with the brine elements upon injection of CO_2 is the dissolution of CO_2 in water (White et al., 2003). When CO_2 dissolves in water, it forms carbonic acid, which lowers the pH level of the solution. Note that as temperatures rise, the pH level will rise, and as pressures rise, the pH level decreases. Increased acidity leads to greater solubility of minerals and in turns leads to increased porosity and permeability of the rock formation. The solubility of carbon dioxide in water depends on the pressure of carbon dioxide and the temperature of the underground water mineralization (White et al., 2003). Some types of interactions or trapping mechanisms that take place between the geologic media and carbon dioxide are static trapping of residual gas, which is classified as physical trapping. Solubility, ionic, mineral and adsorption trapping are categorized as chemical trapping (Drobek et al., 2008). Another type of trapping method is hydrodynamic (Bachu et al., 2007). CO_2 will interact differently with its surroundings depending on the storage option (Bachu et al., 2007).

For example, oil and gas reservoirs, in which stratigraphic and structural trapping can occur before cessation of injection, are not limited by time. Adsorption, which can be applied to coal beds, is not of a temporal nature either (Drobek et al., 2008). However, the investigation of deep saline aquifers is very complex due to the various trapping mechanisms involved that depend on different time scale [specifically, dissolution and mineral precipitation] when it comes to the estimation of storage capacity of CO_2 (Bachu et al., 2007).

In general, oil and gas deposits, unmineable coal seams, saline aquifers, organic-rich shales, and basalts have all been suggested as long-term storage sites for carbon dioxide (Bachu et al., 2007). Oil and gas reservoirs in geologic formations are better understood due to the injection techniques such as EOR or EGS, that have been used by the oil and gas industries for many years (Wang et al., 2013). Therefore the best near-term storage options for CCS are depleted oil or gas reservoirs; however, aquifers represent the best long-term option (Anderson and Newell, 2004). In the United States (US), saline aquifers exists within sedimentary basins that contain large storage capacities which them a viable option of geologic carbon sequestration (Anderson and Newell, 2004). Deep saline aquifers are believed to have the most storage potential on the order of 2,000− 20,000 Gt (Breunig et al., 2013). Although there are many factors that influence the storage of carbon dioxide, these options are very appealing; but there is more than one solution of CCS.

1.2.4 - Alternative Storage Options – There are other options such as opportunities for direct economic use of the capture CO_2, but they are very limited (Wang et al., 2013). Carbon dioxide could be used as inorganic carbonates or as a feedstock for plastics, and new discoveries in chemistry and bioprocessing could lead to additional uses (Anderson and Newell, 2004). Although, the market for these uses is potentially accessible, they remain relatively small compared to the large quantities of CO_2 that would become available upon the nationwide application of CCS (Anderson and Newell, 2004). The conversion of CO_2 for the most part is energy intensive, and in most cases will generate more net CO_2 emissions than would be released absent conversion (Anderson and Newell, 2004). Additionally, CCS is already commercially available for large point sources of CO_2 emitters, such as power plants (Kirchsteiger, 2008). Therefore, the conversion of CO_2 would, in principal, defeat the purpose for an alternative solution of CCS.

Alternative underground injection procedures also provide appropriate operational lessons and experience (Anderson and Newell, 2004). Notably, the deep injection of liquid wastes and acid gas disposal (mixtures of CO_2 and H_2S) have been administered on the megaton scale (McKibben, 2007).

1.2.5 - Pilot, Demonstration, and Commercial Projects – Several pilot, demonstration, and commercial projects have been deployed and provided some insight concerning geological storage in deep saline aquifers (McKibben, 2007). Saline aquifers, depleted hydrogen reservoirs, and un-mineable coal seams are the three major geological storage options of carbon dioxide, but deep saline aquifers have the highest potential capacity globally for CO_2 storage (Michael et al., 2010). Pilot projects have been demonstrated in Frio, Texas; Nagaoka, Japan; and Ketzin, Germany (Michael et al., 2010). The purpose of these pilot projects was to research testing of injection and monitoring technology (Michael et al., 2010). In Decatur, Illinois and Cranfield, Mississippi demonstration projects have been implemented for the sole purpose of analyzing the verification of CCS technology and safety levels at commercial injection rates (Michael et al., 2010). Commercial projects, solely for reducing greenhouse gas emissions from stationary industrial CO_2 sources, are underway at Gorgon, Australia; Sleipner, Norway; and Snøhvit, Norway (Michael et al., 2010).

Although this technology is underway and poses environmental benefits, there are potential risk factors that are associated with the transport of carbon dioxide and storage of carbon dioxide.

1.2.6 - Risk Factors - 1.2.6.1 - Transport Issues - When pipelines will be in densely populated areas and the important elements that will help to prevent adverse effects of uncontrollable CO_2 leakage are:

- Ensure a way to dry the CO_2 to prevent corrosion (Rusin and Stolecka, 2013) Avoid elastomeric seals in the CO_2 installation because CO_2 cannot dissolve such materials (Rusin and Stolecka, 2013)
- Make sure compressors and pumps consists of proper lubricants to

withstand carbon dioxide (Rusin and Stolecka, 2013)

- Account for the possibility of crack propagation in the pipeline at the designing stage and brittle cracking (Rusin and Stolecka, 2013)
- Correct placement of safety valves together with automatic gas leak detection systems (Rusin and Stolecka, 2013)
- Use of a carbon dioxide odorization (Rusin and Stolecka, 2013)

The most important element that helps aid in the reverse effects of uncontrollable CO_2 leakage is the determination of the hazard zones around the pipeline; this will be based on the likely concentration of carbon dioxide (Rusin and Stolecka, 2013).

1.2.6.2 - Reservoir issues – There are two different types of risks due to leakage from storage of CO_2 in geological reservoirs: global risks and local risks (Michael et al., 2010). Global risks include the release of carbon dioxide into the atmosphere that may contribute significantly to climate change once leaked (McKibben, 2007). Additionally, local risks involve possible local hazards for humans ecosystems and groundwater if CO_2 leaks out of a storage formation and produces quantifiable effects (McKibben, 2007). Local risks depend on three things: volume, rate, and surface topography (Wilson et al., 2003).

It is difficult to calculate the available capacity in a sedimentary rock that has a specific volume at a given depth-pressure-temperature for a specific region (Wilson et al., 2003). The nature of geological settings, rock characteristics, and reservoir performance combine to make some estimates unreliable when they are made with methodologies that generalize the inputs for evaluating potential storage capacity

(Bradshaw et al., 2007).

Capacity estimates made by scientists are lacking (Bradshaw et al., 2007):

- Coherent and explicit definitions (Bachu et al., 2007)
- Acknowledged and legitimate use of different scales and assessments (Bachu et al., 2007)
- Acknowledgment of time scales and the effectiveness of various trapping methods (Bachu et al., 2007)
- Consistent guidelines and techniques for capacity estimations (Bachu et al., 2007)
- Appropriate documentation with reference to data, constraints, and techniques (Bachu et al., 2007)
- Appropriate reporting methods and practices (Bachu et al., 2007)
- Recognition of that with each storage option, estimates of capacity changes as technology advances and economic conditions change (Bachu et al., 2007)

A key concern for geologic CO_2 sequestration (GCS) in saline formations is the likelihood for CO_2 leakage through a penetrable or porous fault (Lu et al., 2012). A few things can occur when storage capacity is limited and the storage formations are filled up with saline water. The increased reservoir pressure activates mechanical stresses and deformations around and in the injection site; if this pressure becomes too extravagant, then this will result in new fractures or reactivation old ones (Bachu et al., 2007). Consequently, the pressure buildup caused by the injection of CO_2 within saline formation needs to be alleviated (Rutqvist et al., 2008). The extra pressure can be alleviated through the expansion of reservoir pore space and compression of fluid, or if reservoir boundaries are open, by pressure-driven migration of native brines into neighboring formations (Birkholzer et al., 2012).

As a result of brines being more dense than CO_2, the intended storage reservoir should be overlain by low-permeability caprock formations that are able to adequately restrict upward buoyancy-driven flow of the injected CO_2; depending on the composition, this will force lateral movement, creating a larger CO_2 plume than that of an neutrally buoyant fluid (Birkholzer et al., 2012). The strong buoyancy of CO_2 added to the lengthy time scales appropriate for geological sequestration are challenging issues (Wilson et al., 2003). Therefore, if caprock layers are discontinuous and dissimilar, they will contain deficiencies [for example fracture zones or faults] leading to a bigger problem and possibly causing permeable conduits for CO_2 migration towards the surface (Wilson et al., 2003). There is also the potential for induced seismicity due to undetected faults and pressure build up inside the reservoir (Rutqvist et al., 2008). Earthquake faults can allow gas to escape towards the ground surface (Mazzoldi et al., 2012).

Experiments are being performed to study reservoir performance under different conditions. For example, an experiment was done to investigate the evolution of a fractured carbonate cap rock during the flow of CO_2 acidified brine (Brian Ellis et al., 2011, 248). The objective of this experiment was not only to understand how complex interplay of CO_2-water-rock interactions and fluid transport will impact fracture evolution, but also to aid in the prediction of the type of environment needed for long-term sealing integrity (Ellis et al., 2011).

The experiments results showed that for a carbonate caprock significant fracture erosion is possible when CO_2-acidified brine is able to flow continuously through the fracture; with respect to geological sequestration, this would increase the chances of leakage carbon dioxide through the caprock (Cappa and Rutqvist, 2011). Predicting the amount of time or impact on fracture permeability is difficult due to the fact that fracture geometry can evolve under reactive flow conditions (Ellis et al., 2011). This is just an example of one of the many experiments that place emphasis on the vulnerability of carbonate formations as caprocks and the need to carefully evaluate their sustainability (Ellis et al., 2011).

Predicting the capacity or lifetime of CO_2 in these geological reservoirs is not the only issue, but the bigger problem lies in the uncertainty about the political and regulatory goals of geological storage (Ellis et al., 2011). For example, what should the median lifetime of stored CO_2 be set at or what fraction of early failures are we willing to accept (Wilson et al., 2003)? Some leaks will be unavoidable upon deployment of CCS on a large scale (Wilson et al., 2003), but even with this uncertainty there is a demand for the ability to monitor and verify the behavior of geologically stored CO_2 (Wilson et al., 2003).

1.2.6.3 - Monitoring – Despite the ongoing pilot demonstration and commercial projects allowing for more realistic data, there are limited data from past injection monitoring, which are needed for storage affirmation, model calibration and long-term assessment of monitoring strategies (Michael et al., 2010). If monitoring of these projects is not executed properly, we will not be able limit or avoid further risks. Several ways to monitor CO_2 geological sequestration are through chemical tracers, isotopic ratios of CO_2, and geophysical monitoring; the simplest way to monitor movement of stored CO_2 is through pressure measurements at the surface or *in situ* downhole (Matthes, 2008). Every step of Carbon Capture and Storage is vital to the success of this technology as a whole and taking into account the amount of risks involved, it is appropriate to compare CCS to other alternative solutions.

1.2.7 - Alternative Solutions - Energy dependency, nationally, is one of the most important obstacles faced today and governments are being encouraged to develop game plans in various fields in order to reduce their external dependency (Rodrigues et al., 2013). A few other technological options consist of: lessening energy demand (either by developing more efficient energy conversion and/or utilization devices); decarbonizing energy supplies, or by increasing the use of nuclear energy and/or renewable energy sources; decreasing non-CO_2 greenhouse gases; and sequestering CO_2 through the enhancement of natural sinks by biological fixation; (White et al., 2003). Although there are other alternatives to CCS, “CCS in conjunction with other measures could significantly reduce the cost of achieving stabilization and would increase flexibility in achieving these reductions” (McKibben, 2007).

1.3 - Goals

There still remains limited knowledge and experience on geological storage, as demonstrated in the risks section 1.2.6.1. There is a need for more development and improved understanding of the requirements of sequestration activities, which is needed to define the gap in permitting requirements for large-scale deployment of CCS (Litynski et al., 2008). These gaps of knowledge and different risks associated with the immaturity of geological storage, mentioned in section 1.2.6.2, illustrate why we need more in situ investigations. We utilize a synchrotron source and an externally pressure and temperature controlled microreactor for *in situ*, high-energy x-ray diffraction investigations of reaction process between CO_2, brines, and minerals to further our knowledge on the subject. Using this technique we will learn about the mineral phases and their initial amounts, lending one puzzle piece in the big puzzle of reservoirs.

The goals of this development of the enhanced microreactor system are:

(i) To make the reactor chamber accessible through two points, so that any combination of gases, liquids or fluids can be injected and investigated.

(ii) To better control the flow and pressure of CO_2 through a supercritical fluid pump which will allow the cell to operate under well-controlled pressure and flow conditions.

(iii) To enable the use of a large variety of X-ray transparent windows, initially that of sintered polycrystalline diamond.

(iv) To exceed the capabilities of previously developed microreactor systems in achievable pressure and temperature. Our target was to allow investigation of reactions in the rock-brine-CO_2 system in the pressure temperature range of 400 bar and 600℃.

(v) To use X-ray diffraction to identify mineral phases and their initial amounts.

By improving the previous microreactor design of Diefenbacher (Diefenbacher et al., 2005), we will be able to help further enable the studies of CCS for climate change mitigation.

CHAPTER 2. TECHNICAL SUMMARY

2.1 High Pressure - Temperature Cells:

In this section we give a brief overview of various high-pressure and temperature cells in order to discuss the advantages and disadvantages of each cell and to make a comparison to the microreactor and delivery system we have designed and assembled.

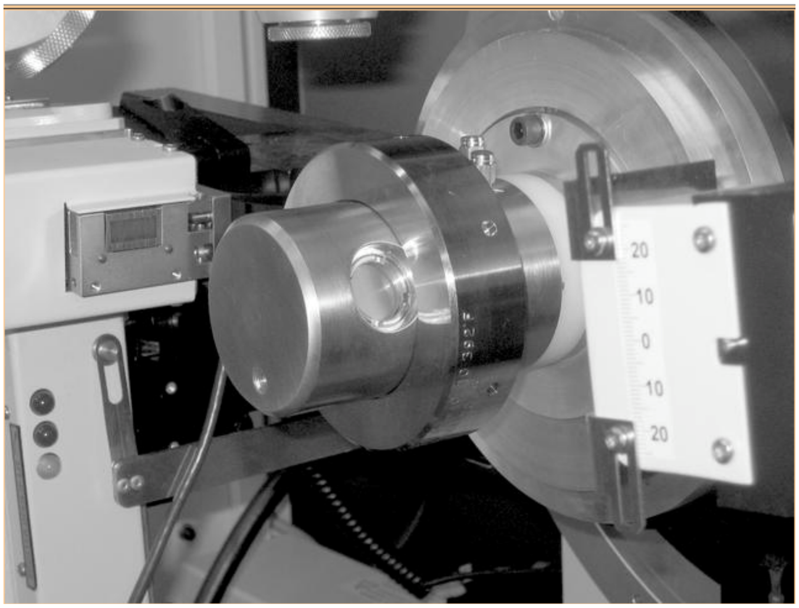
2.1.1 - Hydrothermal Diamond Anvil Cells - Hydrothermal Diamond Anvil Cells are diamond anvil cells with a hydrothermal pressurizing system using aqueous fluids as the pressure medium (Bassett, 2009). These cells are similar to a microreactor, in that, they are appropriate for high pressure-temperature studies in solid-fluid or fluid-fluid systems (Burchard et al., 2003).

(Fig. 2.1.1) In 1993, this Hydrothermal Diamond Anvil Cell, called the Bassett-type Cell, was invented (Bassett et al., 1993)

The most popular HDAC design presently in use is called the Bassett-type cell (Bassett et al., 1993). This cell design resembles that of a Merrill-Bassett diamond anvil cell (Bassett et al., 1993). A picture of the cell is shown above (e.g. see Fig. 2.1.1), and can be illustrated as two adjoining diamond anvils, mounted at their centers, on tungsten carbide (WC) seats in a vice comprised of two metal plates (Bassett et al., 1993). Two metal plates are drawn together, in order to apply pressure to the sample between the diamond anvils, through the tightening of three screws (Burchard et al., 2003). The sample is easily x-ray and visually accessible through holes in the center of the plates (Bassett et al., 1993). In order to avoid the effect of thermal expansion, the belleville springs were aligned between the screw heads and the upper plate (Bassett et al., 1993). The Basset-type cell has attained pressures and temperatures of 2.5 GPa and 1200 ℃ (Bassett et al., 1993).

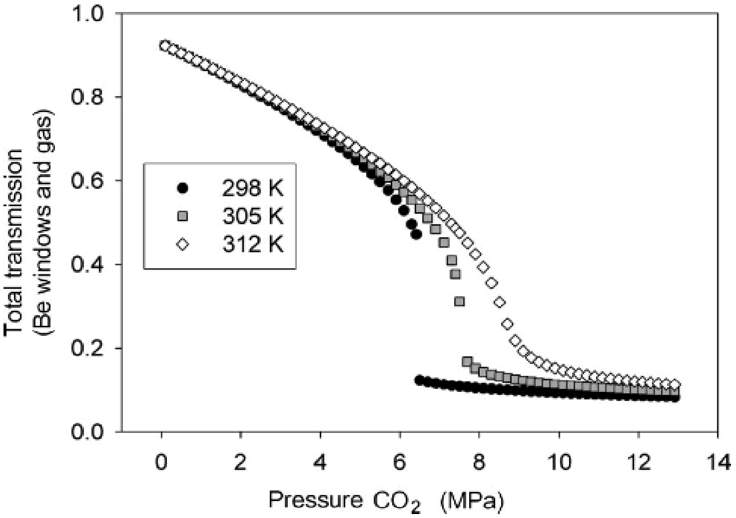
Since the Bassett-type cell, a new modified hydrothermal diamond anvil, designed by Burchard and Zaitsev and Maresch, has proven to be more successful and has reached pressure and temperature conditions exceeding 4.5 GPa and 1000℃ (Burchard et al., 2003). Although the use of Hydrothermal DACs have proven to be successful in such studies, Hydrothermal DACs are limited very diminutive volumes, which convolutes accurate control of some critical experimental parameters (Burchard et al., 2003). Besides volume, the major issue lies in the fact that once the liquid sample has diminished, there is no replenishing it. If the sample is nonexistent, after the experiment is complete, then there is no way to assess the interactions between the rock-brine-CO_2.

2.2 Environmental Chamber A modified design and use of a high-pressure environmental stage, from former design by Koster (shown in figure 2.2.1) (Whitfield et al., 2008), was invented for high-temperature high-pressure (MPa) diffraction work conducive for those studying gas hydrates and materials processing (Diefenbacher et al., 2005). Unlike that of the Diamond Anvil Cell, this cell design is not limited to the dilemma of weak reflections and powder averaging on laboratory diffractometers that are without two-dimensional detectors (Whitfield et al., 2008). This system was specifically used for the study of supercritical and subcritical CO_2 processing of bio-based polymers (Whitfield et al., 2008). In order to reach these supercritical conditions of CO_2, a maximum pressure of 12.4 MPa (1800 psi) was required (Whitfield et al., 2008). A line-focus X-ray tube and parafocusing optics was most appropriate for the reflection geometry (Whitfield et al., 2008). A gas reservoir and transducer were used to balance and keep track of the gas pressure in the gas cell (Whitfield et al., 2008). The maximum pressure available in a commercial stage is 6 MPa and in consequence it was important to build a stage suited for a Bruker D8 diffractometer (Whitfield et al., 2008).



(Fig. 2.2.1) Photograph of the stage assembled and mounted on the Burker D8 diffractometer (Whitfield et al., 2008).

It is predicted that as CO_2 pressures continue to rise, during crystallization of the polymer, obtaining real time data will be difficult due to instantaneously rising gas density and beam attenuation (Whitfield et al., 2008). A major contribution to attenuation at higher pressures is due to the absorption of CO_2 (Whitfield et al., 2008). The structural grade of the beryllium windows (98% Be) also plays a small factor in the lower transmission (Whitfield et al., 2008). The effects of attenuation can be seen in Figure 2.2.2. Rapid data collection with a sufficient time resolution is affected owing to beam attenuation at high CO_2 pressures (Whitfield et al., 2008).



(Fig. 2.2.2) Theoretical transmission of the sample under three different CO_2 temperature/pressure conditions for 30° 2θ with Mo $K\alpha$ (Whitfield et al., 2008). Attenuation caused by the beryllium windows and pressurized CO_2 are accounted for (Whitfield et al., 2008).

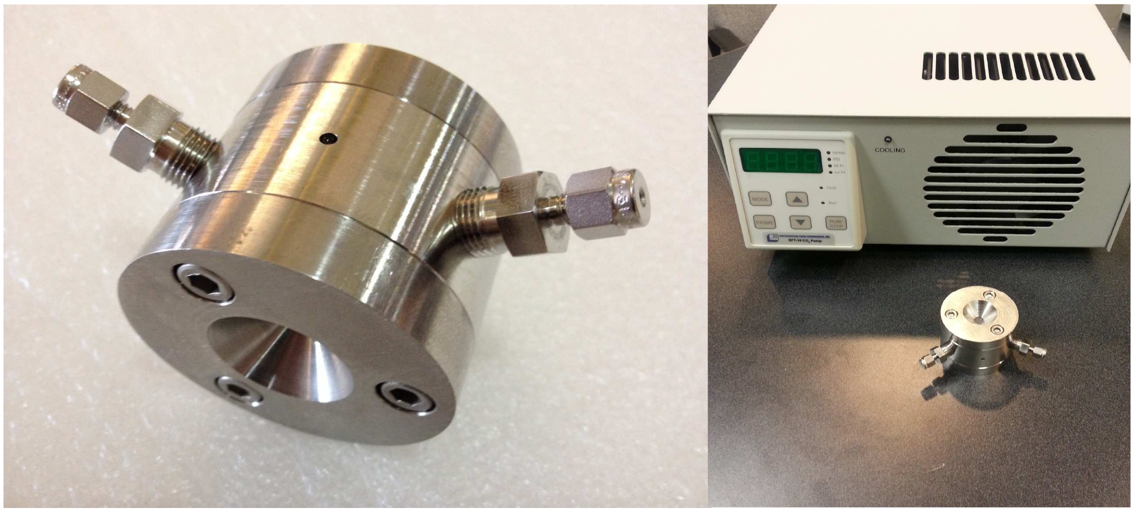
2.3 - Diefenbacher’s Cell Design

Diefenbacher’s microreactor design has been developed in order to bypass the difficulty of the reactant becoming completely consumed during the reaction in closed systems (Whitfield et al., 2008). A picture and diagram can be seen in Figure 2.3.1. It has the capability to monitor heterogeneous reactions, while providing spectroscopic and optical access to the sample chamber, allowing the investigation of fluid–fluid, solid–fluid, solid–gas and fluid–gas systems (Diefenbacher et al., 2005). Through the use of single crystal moissanite (silicon carbide) windows, there is visual access to sample chamber, to allow for spectroscopic investigations such as x-ray diffraction, x-ray radiography, and more (Diefenbacher et al., 2005). The cell provides means to collect data continuously during both subcritical and supercritical ranges over a wide range of pressures and temperatures (Diefenbacher et al., 2005). These different ranges allow for in situ investigations of a wide variety of systems, including, mineralogical reactions, geochemical reactions, catalytic reaction processes, pharmaceutical materials processing, etc.

(Fig. 2.3.1) A photo of the microreaction cell designed by Diefenbacher (Whitfield et al., 2008). It was designed to for reactions involving any combination of fluid-fluid, solid-fluid, solid-gas, and fluid-gas systems (Diefenbacher et al., 2005)

The cell uses a CO_2 pressure ballast as external activity control to broaden the capabilities available for *in situ* reaction (Diefenbacher et al., 2005). Using the CO_2 pressure ballast allows for total pressure to be fixed and the CO_2 to be constantly replenished (Diefenbacher et al., 2005). Although this is a great concept, the CO_2 pressure ballast is subject to pressure changes when the temperature changes (Diefenbacher et al., 2005). The pressure and temperature ranges of the cell are 310 bar and 400 ℃ (Diefenbacher et al., 2005).

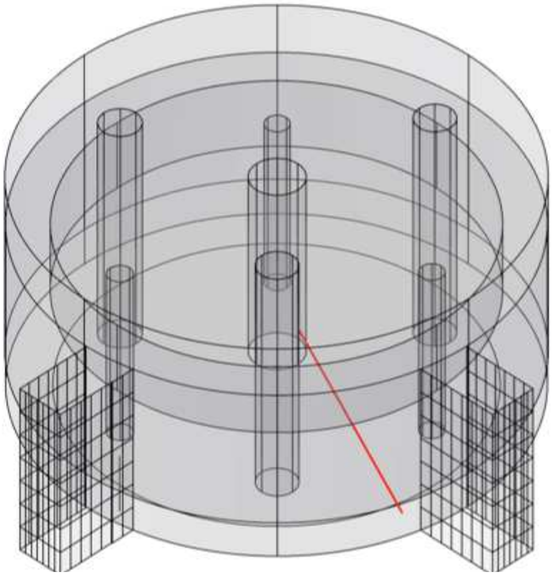
2.4 - Our Modified Microreactor



(Fig. 2.4.1) Modified version of previous cell designed by Diefenbacher. It was designed to for reactions involving any combination of fluid and gas systems .

A modified design, of Diefenbacher's externally pressure and temperature-controlled microreactor, has been created to increase our ability to perform and investigate *in situ* high-energy diffraction of any combination of gases or liquids. Several adjustments have been made to the previous cell design. The reactor chamber is accessible through two points instead of one, whereby any combination of gases, liquids or fluids can be injected and investigated. The CO_2 flow and pressure will be controlled through a supercritical fluid pump, which allows the cell to operate under a well-controlled pressure and flow conditions. In Diefenbacher's design, a CO_2 ballast tank was used as the external pressure control of the system. The disadvantage of using a CO_2 ballast tank to control the pressure is the system's pressure has a tendency to fluctuate once the temperature changes. Another beneficial change is sintered polycrystalline diamond will be initially employed as X-ray transparent window material instead of the silicon carbide. Sintered polycrystalline diamond is as hard or harder than a single-crystal diamond (Diefenbacher et al., 2005), with a hardness of 10 (Irifune et al., 2003). Crystal Moissanite, when sold as an abrasive has a hardness of 9.5 and is the most common out of the natural carbides (Hock, 2009). Moissanite is not cost efficient and has a higher absorption than the sintered polycrystalline diamond. The modified cell design can be seen in Figure 2.4.1, above. We expect to reach pressure and temperature ranges of 400 bar and 600℃.

2.4.1 - The reactor - The reactor, the core of the microreactor, is comprised of Hastelloy B-3. We use this material because it is highly resistive to heat and corrosion. The toughness of this material was shown through the machining. It was very difficult to cut through the Hastelloy B-3. The reactor is a cylindrical shape, with an inlet and outlet for connection to the external pressure system. The interior of the core has a 6 mm diameter and a path length of 23 mm, which yields approximately 650 µl of internal volume. The sample volume is greater than the Diefenbacher cell, which was 100 µl. The ends of the cylindrical core are cut to a depth of 0.5 mm and 10 mm recesses to accommodate the sintered polycrystalline windows, which have a 9 mm diameter. The sintered polycrystalline windows are very appropriate for synchrotron x-ray diffraction studies because optically transparent. The windows are interchangeable, ranging from 1 mm thickness to 3 mm. The



(Fig. 2.4.2) AutoCAD drawing displaying the inlets and outlets of the microreactor, the thermocouple hole (in red), the three pin holes (smaller size cylinders that do not cross the top of the frame), and placement of the three screws (medium sized cynlinder that extend to the top of the frame).

thinner windows will support less pressure in the reactor, but the thinner the widows are the higher the beam transmission of the x-ray. Thus, this will provide a stronger signal for the studies of x-ray diffraction.

Using the preceding information we calculated the amount of stored energy as an appropriate hazard criterion. This value was calculated using the equation for frictionless adiabatic flow of an ideal gas:

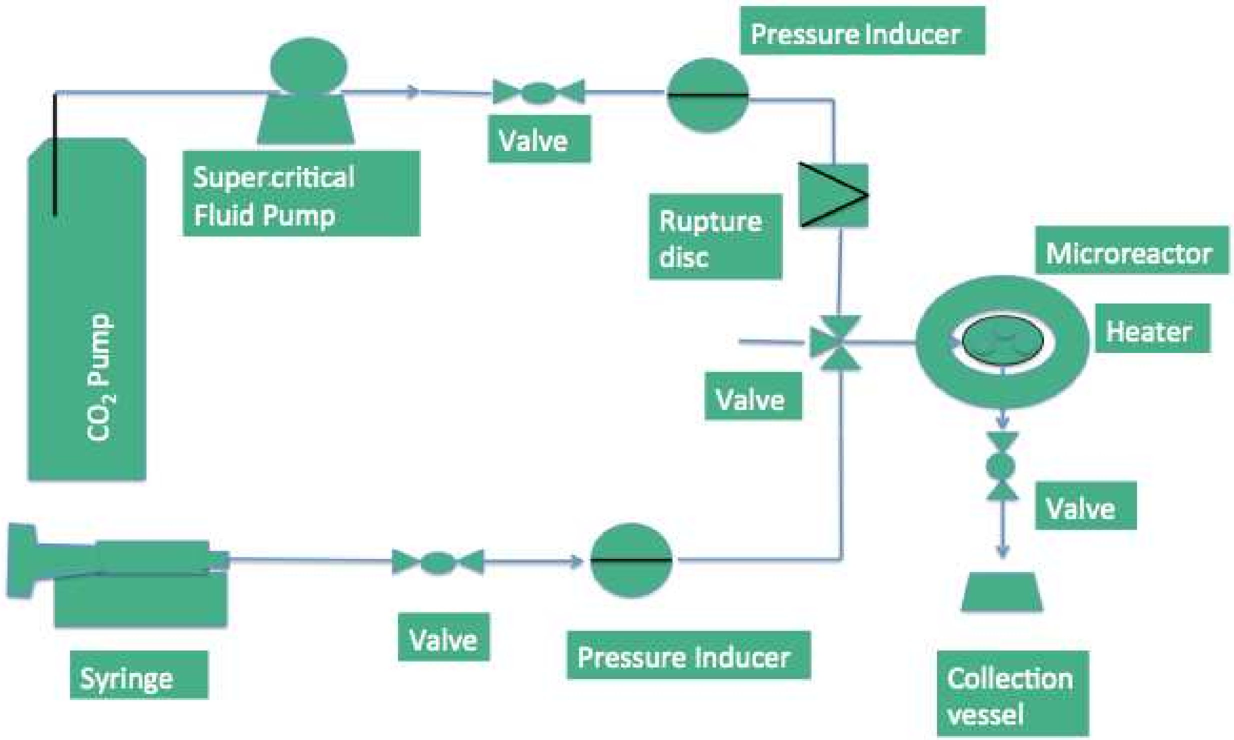
$$U = 101.3\ {}^{(p_s V)}\!\big/_{(\gamma - 1)} \left[1 - \left(\frac{p_a}{p_s}\right)^{\frac{\gamma-1}{\gamma}}\right]$$

Where U is stored energy; P_a is the absolute pressure (≅103 atm); P_s is the absolute pressure to which the vessel would drop if it burst (≅394.77 atm); V is the volume of the vessel (≅650 μl); γ is the adiabatic exponent for that of a diatomic gas (γ = 1.4).

The level or risk or threshold value of this pressurized system is E = 53.27 J. This value is calculated and must comply with the guidelines set forth by national, local laws, and national laboratories, in this case Brookhaven National Lab, before the operation or testing of this pressurized vessel (Hazen et al., 2013). This microreactor was constructed and assembled at Brookhaven National Laboratory in the National Synchrotron Light Source. Thus, there were minimum safety requirements concerning the planning, procuring, identifying, handling, transporting, installing, using, storing, and disposing of compressed gas cylinders and related equipment (BNL).

2.4.2 - The frames - The microreactor incorporates the use of three guideposts and three pinholes containing pins, for the alignment of the core and frames. Furthermore, these three guideposts are used to help manage assuring seal, similar to that of the diamond anvil cell. Gold (Au) gaskets are used for the windows because of its stable nature over a wide range of temperatures and pressures and is soft, allowing deformation and therefore a good seal (BNL). The gasketing of windows and the faces of the frame provide enough support to the windows, to hold them snuggly in place. X-ray access is maintained through the angled inserts on the outside faces of the frame. The material of frames is Vascomax C-300, which is a nickel-based alloy. An AutoCAD drawing of the microreactor is shown in Figure 2.4.2.

2.4.3 - Delivery system - The external pressure system is controlled through the use of a Supercritical Fluid pump (SFT-10) manufactured by SUPERCRITICAL FLUID TECHNOLOGIES, INC. This dual pump is used because it provides constant flow of carbon dioxide and constant pressure throughout the microreactor system. The flow rate can be set in 0.01 mL/min increments from 0.00 to 24.0 mL/min. The constant pressure is reliable from 0 to 10,000 psi in 10 psi increments. High-pressure fluids and gases will flow through 316 stainless steel capillary tubing. Stainless steel valves and fittings are used throughout to ensure that the system is applicable for high-pressure performance and a corrosive environment. Pressure Inducers are used to help monitor the pressure ranges of the experiments. Figure 2.4.3 shows a three-way valve, positioned before the microreactor, which can be used as another access port into the microreactor. A syringe is situated on the opposite side of the system from the SFT-10 pump, for fluid injection. The syringe will contain brine. Relief valves have been placed in between the two pumps and cell to keep the system from over pressurizing. A rupture disc is positioned on the same side as the SFT-10 pump and in between the relief valve and the cell in order to protect the cell from being damaged if the system over pressurizes.



(Fig. 2.4.3) Diagram displaying the delivery system of a modified design of Diefenbacher's microreactor. A Supercritical Fluid Pump is utilized to ensure constant flow of carbon dioxide and pressure.

CHAPTER 3. SUMMARY

3.1 - Summary and Outlook

The work outlined in this thesis enables further experimental study of geological storage options of carbon capture and storage. Different processes, such as the capture of CO_2 for geological sequestration, enhanced coal bed methane production, or enhanced oil recovery are not yet technologically mature to implement nationally (Figueroa et al., 2008). Therefore, it is important to improve instruments and techniques that allow for the investigation CO_2 capture and storage technology.

Our new microreactor was designed in order to make improvements upon previous cell design and delivery system by Diefenbacher, by changing the windows that were used, the type of CO_2 pump used, and by designing an inlet and outlet of the cell. We hope these amendments make for a new and improved microreactor and delivery system. The final steps will be to design and build a copper block for heater, assemble the delivery system, and commissioning of the system.

The copper block is just one part of the whole heating system. It will be used to enclose the heater and the cell. It is necessary to design and build the heater in a way that will not exclude any part of the X-ray beam. Therefore the bevel openings (on the copper block) that overlie the faces of the cell will need to be larger than the bevels openings on the cell itself. Assembly of the delivery system includes the fulfillment of the required safety documentation that will incorporate safety testing of the cell and other instruments incorporated in the delivery system. This documentation can be found on Brookhaven National Lab's website at www.sbms.bnl.gov/committee.cfm (BNL) and can be found in Subject Areas under Pressure Safety. The previous steps are done in order to satisfy all guidelines set forth by the government and Brookhaven National Laboratory and to ensure a safe environment when running experiments with the microreactor. Assembly of the delivery system is the most critical step before commissioning of the system and must be completed before we can begin the final step.

REFERENCES

Anderson, S., and Newell, R. "Prospects for Carbon Capture and Storage Technologies." *Annual Review of Environment and Resources* 29 (2004): 109-42.

Arachchige, U. , and Melaaen, M. "Alternative Solvents for Post Combustion Carbon Capture." *International Journal of Energy & Environment* 4.3 (2013): 441-48.

Bachu, S., Bonijoly, D., Bradshaw, J., Burruss, R., Holloway, S., Christensen, N. , and Mathiassen, O. "Storage Capacity Estimation: Methodology and Gaps." *International Journal of Greenhouse Gas Control* 1.4 (2007): 430-43.

Bassett, W. "Diamond Anvil Cell, 50th Birthday." *High Pressure Research* 29.2 (2009): CP5-186.

Bassett, W. , Shen, A., Bucknum, M., and Chou, I. "A New Diamond Anvil Cell for Hydrothermal Studies to 2.5 GPa and from −190 to 1200□℃." *Review of Scientific Instruments* 64.8 (1993): 2340.

Birkholzer, J. , Cihan, A., and Zhou, Q. "Impact-Driven Pressure Management Via Targeted Brine Extraction-Conceptual Studies of CO_2 Storage in Saline Formations." *International Journal of Greenhouse Gas Control* 7 (2012): 168-80.

Bnl, Brookhaven National Laboratory. "Pressure and Vacuum Systems Safety." 2013.

Bradshaw, J., Bachu, S., Bonijoly, D., Burruss, R., Holloway, S., and Christensen, N. "CO_2 Storage Capacity Estimation: Issues and Development of Standards." *International Journal of Greenhouse Gas Control* 1.1 (2007): 62-68.

Breunig, H. , Birkholzer, J. , Borgia, A., Oldenburg, C. , Price, P. , and Mckone, T. "Regional Evaluation of Brine Management for Geologic Carbon Sequestration." *International Journal of Greenhouse Gas Control* 14 (2013): 39-48.

Burchard, M., Zaitsev, A. , and Maresch, W. "Extending the Pressure and Temperature Limits of Hydrothermal Diamond Anvil Cells." *Review of Scientific Instruments* 74.3 (2003): 1263-66.

Cappa, F., and Rutqvist, J. "Impact of CO_2 Geological Sequestration on the Nucleation of Earthquakes." *Geophysical Research Letters* 38 (2011).

Colour Publications Pvt, Ltd. "What Is Carbon Dioxide and How Is It Discovered?" *Chemical Business* 24.2 (2010): 49-51.

Diefenbacher, J., Mckelvy, M., Chizmeshya, A. , and Wolf, G. "Externally Controlled Pressure and Temperature Microreactor for in Situ X-Ray Diffraction, Visual and Spectroscopic Reaction Investigations under Supercritical and Subcritical Conditions." *Review of Scientific Instruments* 76.1 (2005).

Drobek, L., Bukowska, M., and Borecki, T. "Chemical Aspects of CO_2 Sequestration in Deep Geological Structures." *Gospodarka Surowcami Mineralnymi-Mineral Resources Management* 24.3 (2008): 425-38.

Edge, P., Gharebaghi, M., Irons, R., Porter, R., Porter, R. , Pourkashanian, M., Smith, D., Stephenson, P., and Williams, A. "Combustion Modelling Opportunities and Challenges for Oxy-Coal Carbon Capture Technology." *Chemical Engineering Research & Design* 89.9 (2011): 1470-93.

Ellis, B., Peters, C., Fitts, J., Bromhal, G., Mcintyre, D., Warzinski, R., and Rosenbaum, E. "Deterioration of a Fractured Carbonate Caprock Exposed to CO_2-Acidified Brine Flow." *Greenhouse Gases-Science and Technology* 1.3 (2011): 248-60.

Figueroa, J. , Fout, T., Plasynski, S., Mcilvried, H., and Srivastava, R. "Advancesn in CO_2 Capture Technology - the Us Department of Energy's Carbon Sequestration Program." *International Journal of Greenhouse Gas Control* 2.1 (2008): 9-20.

Friedmann, S. "Geological Carbon Cioxide Sequestration." *Elements* 3.3 (2007): 179-84.

Güler, E., and Güler, M. "Geometry Optimization Calculations for the Elasticity of Gold at High Pressure." *Advances in Materials Science and Engineering* 2013 (2013): 5.

Gupta, R., and Shim, J.-J. *Solubility in Supercritical Carbon Dioxide*. Boca Raton, Florida: CRC Press, 2007.

Hasegawa, T. "Combustion Performance in a Semiclosed Cycle Gas Turbine for Igcc Fire with CO-Rich Syngas and Oxy-Recirculated Exhaust Streams." *Journal of Engineering of Gas Turbines and Power* 134 (2012).

Hazen, R. , Downs, R., Jones, A. , and Kah, L. "Carbon Mineralogy and Crystal Chemistry." *Reviews in Mineralogy and Geochemistry* 75.1 (2013): 7-46.

Hock, R. *The Perfect Edge: The Ultimate Guide to Sharpening for Woodworkers*. Ohio, Cincinatti: Popular Woodworking Books, 2009.

Irifune, T., Kurio, A., Sakamoto, S., Inoue, T., and Sumiya, H. "Materials: Ultrahard Polycrystalline Diamond from Graphite." *Nature* 421.6923 (2003): 599-600.

Kirchsteiger, C. "Carbon Capture and Storage-Desirability from a Risk Management Point of View." *Safety Science* 46.7 (2008): 1149-54.

Liszka, M., Malik, T., Budnik, M., and Ziębik, A. "Comparison of IGCC (Integrated Gasification Combined Cycle) and CFB (Circulating Fluidized Bed) Cogeneration Plants Equipped with CO_2 Removal." 2013. 86-96. Vol. 58.

Litynski, J. , Plasynski, S., Mcilvried, H., Mahoney, C., and Srivastava, R. "The United States Department of Energy's Regional Carbon Sequestration Partnerships Program Validation Phase." *Environment International* 34.1 (2008): 127-38.

Lu, C. , Sun, Y. , Buscheck, T. , Hao, Y., White, J. , and Chiaramonte, L. "Uncertainty Quantification of CO_2 Leakage through a Fault with Multiphase and Nonisothermal Effects." *Greenhouse Gases-Science and Technology* 2.6 (2012): 445-59.

Matthes, F. "Climate Change 2007. The Physical Science Basis, Impacts, Adaptation and Vulnerability Mitigation of Climate Change." *Internationale Politik* 63.4 (2008): 130-32.

Mazzoldi, A., Rinaldi, A. , Borgia, A., and Rutqvist, J. "Induced Seismicity within Geological Carbon Sequestration Projects: Maximum Earthquake Magnitude and

Leakage Potential from Undetected Faults." *International Journal of Greenhouse Gas Control* 10 (2012): 434-42.

McKibben, B. "Climate Change 2007: The Physical Science Basis: Summary for Policymakers (Vol 54, Pg 44, 2007)." *New York Review of Books* 54.8 (2007): 58-58.

McKibbin, W. , and Wilcoxen, P. "The Role of Economics in Climate Change Policy." *Journal of Economic Perspectives* 16.2 (2002): 107-29.

Michael, K., Golab, A., Shulakova, V., Ennis-King, J., Allinson, G., Sharma, S., and Aiken, T. "Geological Storage of CO_2 in Saline Aquifers-a Review of the Experience from Existing Storage Operations." *International Journal of Greenhouse Gas Control* 4.4 (2010): 659-67.

Olajire, A. "CO_2 Capture and Separation Technologies for End-of-Pipe Applications - a Review." *Energy* 35.6 (2010): 2610-28.

Pak, P. "Characteristics Evaluation of a CO_2-Capturing Power Generation System with Reheat Cycle Utilizing Regenerative Oxygen-Combustion Steam-Superheater." *Electrical Engineering in Japan* 165.1 (2008): 35-41.

Palmer, B. "An Overview of Carbon Capture Technology." *A Qatar Foundation Academic Journal*.Carbon Capture and Storage Workshop:13 (2012).

Priem, H. "Climate Change and Carbon Dioxide: Geological Perspective." *Energy & Environment* 24.3-4 (2013): 361-80.

Rodrigues, C., Dinis, M. , and De Sousa, M. "Unconventional Coal Reservoir for CO_2 Safe Geological Sequestration." *International Journal of Global Warming* 5.1 (2013): 46-66.

Rusin, A., and Stolecka, K. "Environmental Hazards Caused by Carbon Capture and Storage (CCS) Technologies." *Polish Journal of Environmental Studies* 22.1 (2013): 205-11.

Rutqvist, J., Birkholzer, J. , and Tsang, C. "Coupled Reservoir-Geomechanical Analysis of the Potential for Tensile and Shear Failure Associated with CO_2 Injection in

Multilayered Reservoir-Caprock Systems." *International Journal of Rock Mechanics and Mining Sciences* 45.2 (2008): 132-43.

Scheffknecht, G., Al-Makhadmeh, L., Schnell, U., and Maier, J. "Oxy-Fuel Coal Combustion-a Review of the Current State-of-the-Art." *International Journal of Greenhouse Gas Control* 5 (2011): S16-S35.

Singh, U. "Carbon Capture and Storage: An Effective Way to Mitigate Global Warming." *Current Science (00113891)* 105.7 (2013): 914-22.

Solomon, S., Plattner, G. , Knutti, R., and Friedlingstein, P. "Irreversible Climate Change Due to Carbon Dioxide Emissions." *Proceedings of the National Academy of Sciences of the United States of America* 106.6 (2009): 1704-09.

Tans, P., and Keeling, R. "Monthly Mean Atmospheric Carbon Dioxide at Mauna Loa Observatory, Hawaii." (2013).

Wang, Z., Small, M. , and Karamalidis, A. "Multimodel Predictive System for Carbon Dioxide Solubility in Saline Formation Waters." *Environmental Science & Technology* 47.3 (2013): 1407-15.

White, C. , Strazisar, B. , Granite, E. , Hoffman, J. , and Pennline, H. "Separation and Capture of CO_2 from Large Stationary Sources and Sequestration in Geological Formations - Coalbeds and Deep Saline Aquifers." *Journal of the Air & Waste Management Association* 53.6 (2003): 645-715.

Whitfield, P. , Nawaby, A. , Blak, B., and Ross, J. "Modified Design and Use of a High-Pressure Environmental Stage for Laboratory X-Ray Powder Diffractometers." *Journal of Applied Crystallography* 41 (2008): 350-55.

Wilson, E. , Johnson, T. , and Keith, D. "Regulating the Ultimate Sink: Managing the Risks of Geologic CO_2 Storage." *Environmental Science & Technology* 37.16 (2003): 3476-83.

Appendix

Parts Name	Part Number	Description	Supplier
Seamless Tubing	SS-T1-S-020-6ME	316/316L SS Seamless Tubing, 1/16 in. OD x 0.02 in.	Swagelok
2-Way Medium-Pressure Ball Valve	SS-6FKBF4-H	316 SS 3-Piece 2-Way Medium-Pressure Ball Valve, 1.3 Cv, 1/4 in. Female NPT, HNBR O-rings	Swagelok
Seamless Tubing	SS-T4-S-035-20	316/316L SS Seamless Tubing, 1/4 in. OD x 0.035 in. Wall x 20 Feet	Swagelok
Tube Fitting, Male Elbow	SS-400-2-4	SS Swagelok Tube Fitting, Male Elbow, 1/4 in. Tube OD x 1/4 in. Male NPT	Swagelok
Pressure Gauge	PGI-63B-PG5000-CAQX	Industrial Pressure Gauge, Bayonet Ring, 63 mm, 0 to 5000 psi, bar secondary, Center-Back Mount, 1/4 in. Tube Adapter	Swagelok
3-Way Ball Valve	SS-42GXS4	SS 1-Piece 40 Series 3-Way Ball Valve, 0.35 Cv, 1/4 in. Swagelok Tube Fitting	Swagelok
Tube Fitting, Reducing Union	SS-400-6-1	SS Swagelok Tube Fitting, Reducing Union, 1/4 in. x 1/16	Swagelok

		in. Tube OD	
Series Ball Valve	SS-41GS1	SS 1-Piece 40G Series Ball Valve, 0.1 Cv, 1/16 in. Swagelok Tube Fitting	Swagelok
Tube Fitting, Union	SS-100-6	SS Swagelok Tube Fitting, Union, 1/16 in. Tube OD	Swagelok
Rupture Disk Tee	SS-RTM-F4-2	316L Stainless Steel Rupture Disk Tee,1/4 in. Male NPT x 1/4 in. Female NPT, 2850 psig (196 bar) Rupture Disc	Swagelok
Relief Valve	SS-4R3A-KZ	SS High-Pressure Proportional Relief Valve, 1/4 in. Swagelok Tube Fitting, Kalrez Seal	Swagelok
Tube Fitting, Male Connector	M-400-1-4	Alloy 400/R-405 Swagelok Tube Fitting, Male Connector, 1/4 in. Tube OD x 1/4 in. Male NPT	Swagelok
Tube Fitting, Male Connector	SS-100-1-4	SS Swagelok Tube Fitting, Male Connector, 1/16 in. Tube OD x 1/4 in. Male NPT	Swagelok
Tube Fitting, Female Connector	SS-400-7-4	SS Swagelok Tube Fitting, Female Connector, 1/4 in. Tube OD x 1/4 in. Female NPT	Swagelok
Tube Fitting, Male Connector	SS-100-1-2RT	SS Swagelok Tube Fitting, Male Connector 1/16 in. Tube OD X 1/8 in. Male ISO Tapered Thread	Swagelok

Windows		PCD Poly Cylinder Htc: 1.00 X: 9.00	Almax Industries
Heater	PM6C1CH-3AAAAAA		Watlow
Gasket	VGG8	Gold gasket-6.95mm I.D. x0.020”	Scientific Instrument Services, Inc.
Supercritical Fluid Pump	SFT-10	Constant Flow/Constant Pressure. Pressure ranges 0 to10000 psi	Supercritical Fluid Technologies