Mineralization of Carbon Dioxide: Literature Review

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Abstract

CCS research has been focused on CO_2 storage in geologic formations, with many potential risks. An alternative to conventional geologic storage is carbon mineralization, where CO_2 is reacted with metal cations to form carbonate minerals. Mineralization methods can be broadly divided into two categories: in situ and ex situ. In situ mineralization, or mineral trapping, is a component of underground geologic sequestration, in which a portion of the injected CO_2 reacts with alkaline rock present in the target formation to form solid carbonate species. In ex situ mineralization, the carbonation reaction occurs above ground, within a separate reactor or industrial process. This literature review is meant to provide an update on the current status of research on CO_2 mineralization.

1. Introduction

Addressing the continuous rise of atmospheric carbon dioxide levels has become a focus of global efforts. Research in carbon capture and storage (CCS) has increased substantially in the last decade [1, 2]. Current carbon storage research has been primarily concentrated on sequestering CO_2 in underground geologic formations such as saline aquifers, depleted oil and gas fields, and unmineable coal seams. These methods of geologic sequestration have the advantage of being relatively low cost when separated from CO_2 capture, separation, and transportation. However, potential issues associated with sequestration in geologic formations include: permanence, long-term monitoring, and verification, with many unknown effects and potential risks still to be determined [3, 4]. An alternative to conventional geologic sequestration is carbon mineralization, where CO_2 is reacted with metal cations such as magnesium, calcium, and iron to form carbonate minerals. Mineralization methods can be broadly divided into two categories: in situ and ex situ. In situ mineralization, or mineral trapping, is a component of geologic sequestration, in which a portion of the injected CO_2 reacts with the alkaline minerals present in the target formation to form solid carbonate species. In ex situ mineralization, the carbonation reaction occurs above ground, within a separate reactor or industrial process. Mineral CO_2 sequestration seeks to mimic the natural weathering process [5] in which calcium or magnesium silicates are transformed into carbonates via reaction with CO_2 gas and/or aqueous CO_2

$$(Ca,Mg)SiO_3\,(s) + CO_2\,(g) \rightarrow (Ca,Mg)CO_3\,(s) + SiO_2\,(s) \quad \ldots \quad (1)$$

Original development of ex situ CO_2 mineralization of calcium and magnesium-bearing silicate minerals occurred at Los Alamos National Laboratory in the mid to late 1990's [6]. Work in this area continued to evolve at the National Energy Technology Laboratory (NETL), where the direct aqueous mineralization method was advanced [7]. Over the course of the last decade the amount of research being performed in this area has increased and spread worldwide. Several comprehensive reviews have been published on both ex situ and in situ CO_2 mineralization, the most recent of which were prepared in Europe [8, 9]. Prior to these, Huijgen and Comans published a very thorough review in 2003 [10], and followed it up with an update in 2005 [11]. Part of the Intergovernmental Panel on Climate Change (IPCC) report from 2005 included an extensive summary of CO_2 mineralization [1]. In 2008, a number of reviews were published by others [12, 13].

The IPCC report [1] suggested that the "highly verifiable and unquestionably permanent" nature of the mineral carbonation storage mechanism is likely to lead to its greater public acceptance. In situ mineralization or mineral trapping has been examined as a potentially stable and cost-effective storage mechanism, but most researchers agree that the fraction of CO_2 mineralized under reservoir conditions will be minor in the first few hundred years. However, less research has been done to evaluate the geochemical interaction between CO_2 with shale and other formations expected to act as natural seals for the injected CO_2. In some cases, these formations may be permeable to/or reactive with CO_2, and could be either mineralization candidates or leakage pathways. A fundamental investigation of the reactivity of clays and/or shale with CO_2 would help define their roles in geologic sequestration. Overall, the in situ mineralization technology is still in its infancy and the costs (\$17/t-CO_2) are higher compared to geological storage in sedimentary basins (\$8/t-CO_2) [9].

A report summarizing eight years of research on ex situ mineralization by NETL, including a feasibility study with a cost analysis was published in 2007 [14]. One of the conclusions reached by the research team was that the scope of mining operations required, and the energy cost of feedstock preparation, made the then (in 2007) current ex situ process unfeasible. This conclusion has been echoed by other researchers [5, 15, 16, 17]. Using the NETL-developed direct aqueous process as a starting point, recent work reported in the literature has been generally focused on economic improvement and the use of alternative feedstock. The latter have the advantage of being a priori suitable for CO_2 uptake by virtue of their mineralogical composition or prior preparation for other industrial processes. These materials include fly ash, steel and iron industry wastes, and mine tailings that contain potentially reactive Fe, Mg, or Ca cations.

If and/or when legislation is enacted that establishes carbon credits and serves to penalize CO_2 producers, smaller point-source generators will also seek cost-effective methods of sequestration to lower their costs. As such processes that sequester CO_2 emissions while remediating industrial waste streams could provide potential carbon offsets, and may prove invaluable to many industrial operations. Notable industries that generate large quantities of both CO_2 and potential mineralization feedstock include the cement, lime, iron and steel industries. Examining total CO_2 emissions from U.S. industries for 2002, iron and steel mills accounted for 126 million metric tons, while the cement and lime industries accounted for 39 and 10 million metric tons of CO_2 emissions, respectively [18]. Current sequestration schemes focus on the potential for large-scale storage of CO_2, in part because of the enormous volume of CO_2 generated by fossil-fuel-fired (predominantly coal) electric generation plants. This has focused much effort on geological storage options. However, some locations such as southeastern Australia or northern Europe do not have significant underground storage capacity and are thus investigating ex situ CO_2 mineralization as a preferred method for sequestering the power plant generated CO_2 [12]. Alternatively, with proper organic waste management, CO_2 emissions could be offset through improved soil productivity and carbon storage [19].

The literature to date indicates that in the coming decades mineral carbonation can play an important role in rebalancing the global carbon cycle and providing a long-term carbon storage solution [9, 16]. This literature review is meant to provide an update on the current status of research on CO_2 mineralization. The status of in situ studies is discussed in the context of storage (mineral trapping) and seals (shale–CO_2 interaction). The ex situ review primarily focuses on potential alternative feed stock materials and various methodologies currently under investigation.

2. Overview of Recent In Situ Mineralization Research

A primary source of current anthropogenic CO_2 emissions is combustion of late Carboniferous coal-bearing Pennsylvanian epoch river delta, swamp, and wetland deposits. These deposits were responsible for the drop of atmospheric CO_2 from around 1,500 ppm in the early Carboniferous Mississippian epoch 360 Ma (million years ago) to around 350 ppm by the end of the Pennsylvanian, around 286 Ma [20]. During the Mississippian, higher CO_2 levels and a mean global temperature of around 20 °C yielded an explosion of terrestrial plant growth, with atmospheric CO_2 being converted through photosynthesis into biomass with an oxygen byproduct, creating an atmosphere of ~30% O_2 by the end of the period. As these plants underwent their life cycles and were continually deposited, the carbon in the plant materials was sequestered as coal and is now a major source of the carbon used today for power generation. This sequestration of biogenic carbon took around 60 million years. While this natural carbon cycle is an interesting corollary to recent research efforts to sequester CO_2, a rapid acceleration of the time scale is obviously necessary for implementation. Geologic sequestration is intended to bypass the atmospheric-photosynthesis component of the natural cycle by direct injection of CO_2 into various geologic formations. In situ mineralization is one aspect of the geologic sequestration method in which injected CO_2 may react with naturally occurring minerals or engineered materials for precipitation as various solid carbonate minerals, which may enhance the long term stability of the injected CO_2. Scientific effort on this technology is still academic-oriented; however, it is and at a more advanced stage of research that at the time of the IPCC report of 2005.

In a 2003 workshop report on greenhouse gases [21], novel approaches to carbon management listed injection of CO_2 into sandstone hosted brine formations as a primary target for geologic sequestration. The report specifically cited basalt-derived sandstone formations, which occur in drainage basins below massive flow regions like the Pacific Northwest and the East Coast of the United States. These formations have an alkaline mineralogy that can contribute the cations necessary to form carbonate species. Other examples of host rocks that may contribute to in situ mineralization include iron-rich sandstone, redbeds, and glauconitic sediments which may provide a source of ferrous iron under reducing environments [22, 23].

Layered flood basalts with porous vesicular and brecciated interflow zones, and off shore deep water layered and pillow basalts are now thought to be potential sinks with mineralization possibilities [24, 25, 26]. In addition to the formations described above, CO_2 injection into magnesium-rich ultramafic deposits of serpentine and peridotite are being explored [27, 28]. Carbonate hosted deep saline formations are also currently receiving attention [29].

Target formations for geologic sequestration are classified either as sedimentary or igneous. Sedimentary formations include marine, fluvial and eolian deposited sandstones, deep sea and evaporative carbonates, gravels, conglomerates, mudstones, and shale. Igneous formations include felsic granitics to mafic basalt, ultramafic peridotite, and ophiolites sequences, containing olivine-rich mantel rock, dunite, peridotite, serpentine, gabbro, basalts and associated fringe carbonates. Porosity and permeability of the target formation are key aspects to injectivity, while solution chemistry, temperature, and pH are critical parameters affecting carbonate formation potential. An illustration of the interplay of these variables during CO_2 storage in sedimentary rocks is provided by Gaus [30].

2.1 Reservoirs

2.1.1 Sedimentary-Hosted Saline Formations

Geologic sequestration has been investigated by numerous authors as a viable option for the storage of anthropogenic CO_2 due to the large areal extent of formations and large potential storage volume [31, 32, 33, 34, 35]. The various forms of stored CO_2 investigated by these authors include: single-phase supercritical fluid ($scCO_2$), gas dissolved into brine, bicarbonate species, and carbonate solids.

Sandstones

Targeted sandstone-hosted saline formations tend to have a quartz content of greater than or equal to 90%, with the remainder being comprised of feldspar, carbonate cements, or clays. These formations are one member in the stratum sequence including basement, reservoir, and caprock sequences. An example is the Mt. Simon sandstone that underlies a large section of the Midwest, from the western slope of the Appalachians in West Virginia and Pennsylvania to the Mississippi River Valley, and north from the Ohio River Valley into Ontario, Canada. The Mt. Simon is high purity quartz-rich sandstone with silica content of ~95% [33]. The Mt. Simon Formation sits atop a granitic basement rock and is primarily overlain by the Eau Claire shale and locally by carbonates of the Knox and additional shale of the Cincinnatian Formations. The Midwest Geologic Sequestration Consortium (MGSC) is in the process of conducting demonstration-scale CO_2 injection into the Mt. Simon within the Illinois Basin of south-central Illinois, as part of the Phase 3 Regional Partnerships sponsored by NETL [36].

Mineralization within quartz sandstone-hosted saline formations will most likely result from the dissolution of alkali feldspar ($NaAlSi_3O_8$) and the precipitation of dawsonite ($NaAlCO_3(OH)_2$). In the case of carbonate-cemented sandstone host rocks, calcite ($CaCO_3$) may form by dissolution of the cement, followed by precipitation of second generation carbonate or bicarbonate. Alkali feldspar, with the general formula $(K,Na)AlSi_3O_8$, varies in crystal structure depending on the formation temperature. The formula actually varies in alkali stoichiometry, ranging from 100% sodium (albite) to 100% potassium (microcline, orthoclase) feldspar. Albite is also one end member in the plagioclase feldspar solid solution series, which trends from the 100% sodium to 100% calcium (anorthite) end members. As an example, the theoretical reaction for the carbon mineralization of albite is as follows

$$NaAlSi_3O_8\ (s) + CO_2\ (g) \rightarrow NaAlCO_3(OH)_2\ (s) + 3\ SiO_2\ (s) \quad \ldots \quad (2)$$

Based on the relatively low concentration of feldspars in high-purity quartz sandstone host rocks, mineral trapping potential in such formations would be low. As such, the predominant forms of CO_2 stored in such formations would likely be as a single-phase super-critical fluid, or as gas dissolved into the brine solution.

Calcite or dolomite-cemented sandstones in which the cement comprises up to 11% of the rock may act quite differently from low carbonate cement sandstones such as the Mt. Simon described above. The carbonate cement may dissolve near the injection site as injected CO_2 lowers solution pH. This dissolution may initially increase porosity, permeability, and injectivity near the injection site, followed by a decrease in all three as the dissolved carbonates re-precipitate at further distances from the injection well. Precipitation of second generation carbonates could result due to a decrease in dissolved CO_2 concentration in the brine at distance, with a coincident increase in pH and decrease in solubility for the basic cations in solution [37].

Mafic or basalt-derived sandstones are rare in the U.S. but do occur in Oregon and Washington State layered with local siltstones, mudstones, and basalts [38]. The mineralogy of basalt-derived sandstones, with higher fractions of the alkaline earth cations, Ca^{2+} and Mg^{2+}, and ferrous Fe^{2+}, make them ideal candidates for natural CO_2 mineralization or mineral trapping. However, a determination has yet to be made regarding whether these formations occur at sufficient depth, have viable storage capacity, and lie near a major point source for CO_2, to consider them promising targets for geologic sequestration.

Ferric iron-rich sandstones, redbeds containing hematite (Fe_2O_3), or glauconitic sediments containing iron-rich micas may provide a source for ferrous iron (Fe^{2+}) ions when a reducing environment is created by the addition of SO_2 or H_2S to the CO_2 injection stream. Reduction of ferric iron (Fe^{3+}) to Fe^{2+} during the dissolution of hematite could result in the formation of siderite ($FeCO_3$) and/or ankerite ($CaCO_3$, $MgCO_3$, $FeCO_3$). Palandri et al. [22, 23] looked at the interaction of CO_2/SO_2 on hematite-rich sandstone formations both numerically and empirically. The results reported suggest that Fe^{3+} is reduced to Fe^{2+}, producing an effective trap for CO_2 as siderite, if partly oxidized sulfur, as SO_2, is present with CO_2 in the injected gas phase. Theoretical equilibrium calculations predict that two moles of CO_2 and one mole of SO_2 will reduce the Fe^{3+} in one mole of hematite to produce the Fe^{2+} in two moles of siderite, effectively mineral trapping the CO_2. However, this work utilized an SO_2 concentration well above the expected concentration (~1.5%) in oxy-fuel combustion or coal gasification flue gases; thus, the impact of lesser SO_2 concentrations in the injected gas stream is not well defined.

Greywacke is rock composed of sand-sized grains in a fine-grained clay matrix, with the clay fraction making up at least 15% of the rock. The sand-sized grains frequently include rock fragments of wide-ranging mineralogies (e.g., pyroxenes, amphiboles, feldspars, and quartz), while the clay minerals are comprised to a large extent of chlorite and biotite. The matrix tends to bind the grains strongly and form a relatively hard rock. The composition of greywacke makes it a more attractive target for mineral trapping of injected CO_2, but the clay matrix limits porosity and permeability and thus injectivity. The extent of such formations and their storage capacity are also not well defined.

Curiously, analysis of the Lafayette meteorite suggested that earlier in Mars' history, when the planet had a much thicker atmosphere and an active hydrosphere, carbonation was likely to have been an effective mechanism for sequestration of CO_2. Tomkinson et al. [39] showed that olivine and a plagioclase feldspar-rich mesostasis in the meteorite have been replaced by carbonate over geological timescales. The susceptibility of olivine to replacement was enhanced by the presence of smectite veins along which CO_2-rich fluids gained access to grain interiors.

Carbonates

Mineralization within carbonate-hosted saline formations is expected to occur as a consequence of the acidification of the brine by the injected CO_2. The acidified brine will dissolve the existing carbonates, thereby liberating Ca^{2+} and/or Mg^{2+} cations that will eventually recombine with the injected CO_2 to again form carbonates and/or bicarbonates [40]. The overall bicarbonate reaction is included below.

$$H_2O + CO_2\ (g) + CaCO_3\ (s) \leftrightharpoons Ca(HCO_3)_2\ (s) \qquad \ldots \qquad (3)$$

Looking more specifically at the process, the initial reaction involves the dissolution of CO_2 into water to form carbonic acid, which dissociates to form HCO_3^- and CO_3^- ions via the following reaction sequence

$$CO_2\ (g) \rightleftharpoons CO_2\ (aq) \qquad \ldots \qquad (4)$$

$$CO_2\ (aq) + H_2O \rightleftharpoons H_2CO_3\ (aq) \qquad \ldots \qquad (5)$$

$$H_2CO_3\ (aq) \rightleftharpoons HCO_3^-\ (aq) + H^+\ (aq) \qquad \ldots \qquad (6)$$

$$HCO_3^-\ (aq) \rightleftharpoons CO_3^{2-}\ (aq) + H^+\ (aq) \qquad \ldots \qquad (7)$$

Carbonate species are then able to form via reaction with the divalent cations of Ca, Mg, or Fe, forming calcite ($CaCO_3$), magnesite ($MgCO_3$), and siderite ($FeCO_3$) as follows

$$HCO_3^-\ (aq) + Ca^{2+}\ (aq) \rightleftharpoons CaCO_3\ (s) + H^+\ (aq) \qquad \ldots \qquad (8)$$

$$HCO_3^-\ (aq) + Mg^{2+}\ (aq) \rightleftharpoons MgCO_3\ (s) + H^+\ (aq) \qquad \ldots \qquad (9)$$

$$HCO_3^-\ (aq) + Fe^{2+}\ (aq) \rightleftharpoons FeCO_3\ (s) + H^+\ (aq) \qquad \ldots \qquad (10)$$

Formation of Ca, Mg, and Fe carbonates is expected to be the primary means by which CO_2 is immobilized [34]. The dissolution and precipitation reactions can increase and/or decrease porosity and permeability within the host rock [41]. The injection of CO_2 into deep carbonate-hosted saline formations is expected to result in changes in rock properties. Changes in porosity and permeability are a result of the dissolution of various minerals within the rock, transportation of the dissolved species, and their eventual precipitation. Continuous dissolution of reactive minerals alters the concentration of the formation fluid, leading to precipitation of secondary mineral phases. While mineral dissolution at the injection site is expected to increase formation porosity and permeability, precipitation of secondary minerals at some distance from the injection point will likely have the reverse effect. At the leading edge of the injected-CO_2 plume, where CO_2 dissolves into brine, minerals such as calcite may dissolve readily, leading to increased porosity and permeability along the flow path. The resultant increased flow rate and dissolution forms what are known as wormholes [42]. These wormholes may then plug due to debris or secondary carbonate precipitation. Changes in formation porosity and permeability, and their resulting impact on the CO_2 injection rate, formation pressure rise, etc., will likely be unique to each injection site.

2.1.2 Igneous-Hosted Saline Formations

Basalts

Mineralization of CO_2 within mafic, generally basalt-hosted saline formations is expected to trap some portion of the injected CO_2 in the form of stable carbonates. Reactions similar to those described previously for the carbonate-hosted saline formations could result in the formation of calcite, magnesite, and siderite. Plagioclase feldspar is a major mineral component in basalts and represents a solid solution series ranging in composition from sodium (albite, $NaAlSi_3O_8$) to calcium (anorthite, $CaAl_2Si_2O_8$) aluminosilicate end members. Each of these minerals and the intermediate phases in the series contain the cations necessary for dawsonite ($NaAlCO_3$) and/or calcite ($CaCO_3$) precipitation. Basalts also contain significant concentrations of pyroxene minerals, such as enstatite ($MgSiO_3$) and augite [$(CaMg(SiO_2)_6$], as well as olivine [$(MgFe)_2SiO_4$)], which is actually another solid solution series between Mg-rich (forsterite) and Fe-rich (fayalite) end members. Each can potentially contribute the cations necessary for carbonate formation. Siderite ($FeCO_3$) and magnesite ($MgCO_3$) can form with the dissolution of olivine, while calcite and magnesite can be produced upon the dissolution of the pyroxene minerals. The Ca, Fe, Mg, and Na cation bearing minerals that occur in basalt have been individually examined for carbonation potential determination [7] in a series of stirred autoclave experiments. Ground whole rock tests also reported carbonate formation from this suite of minerals [26]. The Big Sky Carbon Sequestration Regional Partnership Wallula Gap pilot well has been completed and 1,000 metric tons of food-grade CO_2 is to be injected and studied over a multi-year period to obtain field data on in situ mineralization [43]. The target injection zone within layered flood basalts is the vesicular flow top and overlying brecciated flow bottom, or interflow zone, where the successive flows create zones of high porosity which host saline formations. These interflow zones are isolated by the massive flow sections above and below the high-porosity zone.

Carbon dioxide could also potentially be injected into offshore and deep sea basalt-hosted saline formations and subsea tectonic spreading regions [1, 25], which are highly active geothermally, creating unique geohydrological activity. Seawater flows downward into the sediment at distances of meters to kilometers away from the spreading region, moves toward the spreading region at depth, is heated to high temperatures, and is finally expelled back to the sea [44]. The conditions surrounding these regions have many advantages for mineral trapping of $CO_{2,}$ including improved reaction kinetics due to the increasing heat and pressure in the direction of flow. One theory is that CO_2 could be injected into the geohydrological flow field away from the spreading region and entrained in that flow. This would result in the development of several carbonate species (magnesite, magnesium carbonate, dolomite, and calcite) as the combined flow of seawater and CO_2 is heated, pressurized, and released back to the sea. Distance from CO_2 source point and transport of CO_2 are issues to be addressed however. Assuming a mean porosity of 10%, the global CO_2 storage capacity within basaltic formations falls roughly between 8 to 40 thousand Gt [7]. Including the active ridges described above, this storage capacity could be even greater.

Ultramafics

The concept of injecting CO_2 directly into massive ultramafic formations [7] has concentrated on surface and near surface ophiolite sequences. Kelemen and Matter’s [45] study of the Samail ophiolite in Oman has led to a proposed process to drill and hydro-fracture deep peridotite/ophiolite sequences below an impermeable caprock, heat the rock mass to ~185 °C, and inject water saturated with atmospheric CO_2 to form magnesite and siderite. The carbonation reaction is exothermic, so theories exist predicting that once initiated, the process will self-perpetuate, with no additional heat or energy input. The carbonation of many ultramafic rock minerals has been demonstrated by numerous ex situ CO_2 mineralization research efforts [46] as proofs-of-concept for the in situ reactions.

Peuble et al. [47] study on naturally altered ultramafic rocks suggested that carbonation processes are controlled by local heterogeneities in the structure of rock and fluid transport at the water-rock interfaces. In natural systems, flow of CO_2-rich fluids will induce precipitation of carbonates localized along, and preferentially clogging, vertical flow paths while favoring olivine dissolution along horizontal fluid pathways.

Carbonate growth is systematically oriented normal to the flow, which facilitates the development of chemical gradients with cationic supersaturation conditions for carbonate precipitation near the walls.

2.2 Shale-CO_2 Interaction

2.2.1 Common CO_2-Mineral Reactions

The earlier work in the CO_2 storage literature focused primarily on chemical reactivity, including the mineral precipitation-dissolution reactions, under humid $scCO_2$ conditions and water intercalation in clays as a function of water content in $scCO_2$. CO_2 intercalation had not been sufficiently investigated until recent (2007-2008) findings by the Romanov group (NETL) that it can be very significant [48, 49] and even irreversible [50]. Mineral precipitation and dissolution reactions under low-water CO_2 conditions have received much less attention than those of the aqueous-phase-dominated (CO_2 dissolved in water) systems [30], although the water-bearing CO_2 (water dissolved in liquid or supercritical CO_2) phase can mediate important geochemical reactions as well [51]. No short-term CO_2-induced mineralogical changes have been reported so far for dry shale or pure minerals. However, rapid mineralogical changes, predominantly transformation of illite into smectite, were observed in moist samples with small particle sizes (< 200 um) after exposure to supercritical CO_2, likely from the swelling of the clays due to CO_2 adsorption. No carbonation was noted [29]. Alemu et al. [52] observed changes in mineral grains in the shale seal rock after six weeks in closed reactors with CO_2-brine mixtures, which were consistent with results of their analysis of major ions in the solution samples. Maitra et al. [53] studied the effects of gas environment on dolomite thermal decomposition. The authors observed that CO_2 pressure affected both the temperature of initial direct decomposition into MgO and $CaCO_3$ (bypassing the formation of intermediary phase Mg-calcite) and the temperature of the final decomposition of $CaCO_3$, but in opposite directions. The seal integrity could decrease through dissolution of labile minerals such as feldspar or calcite. The isotopic analysis of the Fizzy and Orwell fields (Rotliegend Group) of the southern North Sea (UK) indicated that feldspar remained stable in the presence of high CO_2 concentrations [54]. However, the isotopic analysis of the Kimmeridge Clay Formation (mudrock) seal around the Miller field of the northern North Sea (UK) indicated feldspar dissolution, attributed to initial acidifying effects of the CO_2 infiltration, which resulted in oversized pore space filled with authigenic kaolin. The overall quantity of subsequently re-precipitated carbonates (euhedral calcite and dolomite growing in secondary pores) derived from prior dissolution of rock fragments was similar to those dissolved, which suggests cation preservation [55].

The quantity of CO_2 trapped via mineralization is limited by cation availability. Estimates indicate that 0.5–30% of CO_2 in the natural Fizzy field accumulation was sequestered in mineral form [55]. Appropriate chemical conditions accompanying CO_2 infiltration into the seal rock may result in seal integrity improvement. Isotopic evidence [27] showed that availability of Fe^{2+} cations resulted in mineral trapping of CO_2 via siderite precipitation in fractures and pore spaces at the Pine Lodge Field within the Belfast Mudstone, Otway Basin, Australia.

2.2.2 Physical Sorption of CO_2 in Shale Caprock

Reports on high-pressure CO_2 sorption isotherms on shales are sparse. In the earlier adsorption studies on the interstitial minerals from sandstone formations [56], B.E.T. surface areas [57] were observed to depend on the nature of the clay and water content. The author of the report [56] concluded that the internal micropores in kaolinite, pyrophyllite, illite, and sodium bentonite aggregate particles were not accessible for low temperature (–183 °C) van der Waals adsorption; in halloysite and calcium bentonite, internal pore accessibility varied with the state of hydration. Recent studies on CO_2 adsorption on shales [29] provided evidence of significant storage potential of shaly caprock that could not be attributed to CO_2 dissolution in water or sorption on organic matter alone. The main CO_2 uptake was most likely related to adsorption on clay minerals. The processes and mechanisms of such adsorption are not quite understood yet [50, 58]. For example, water molecules usually compete with CO_2 for surface sorption sites. Yet, the maximum CO_2 sorption capacity of kaolinite and of certain shales tended to decrease with decreasing moisture content [59]. Additionally, CO_2 adsorption onto kaolinite surface initially increases with increasing CO_2 density, reaching a peak near 0.4 g/cm^3, before declining rapidly due to competition between the surface kinetics and energetics of the CO_2–mineral surface and CO_2–CO_2 interactions; DFT (density functional theory) studies confirmed that CO_2 adsorption at kaolinite surface is favored over CO_2 clustering up to the density of $\sim$0.34 g/cm^3 [60]. For black shales, Nuttall et al. [61] found a positive correlation between CO_2 sorption capacity and organic carbon content, whereas no correlation with the clay mineral content was observed.

2.2.3 External Surface Area

Mineral surface areas play important role in geochemical water–rock–CO_2 simulations [62]. External (micropore) surface areas are typically determined by the B.E.T. method [57] using chemically inert gas sorption isotherms [63, 64, 65]. Surface area available for sorption of gas molecules can be significantly affected by cation exchange, which tends to occur at edge sites and the outer layer flat surfaces of the clay aggregates before interlamellar sites [66, 67]. Edge sites have been proposed to make up roughly 20% of the total exchange capacity of montmorillonites [68], although that claim is also subject to debate [66]. Similar claims regarding edge exchange sites preference have been made for Cs^+ and K^+ exchange on illite and vermiculite [69]. Multivalent cations could bind the edges together to give wider clay aggregates with correspondingly smaller external surface area. Also, the available surface area was reported to dramatically decrease for ordering of the clay platelets orientation, such as when forced by aqueous dispersion [70] or by smaller cations [71] such as sodium and barium. Surface areas internal to such “quasi-crystalline” regions are generally inaccessible to non-polar molecules [72]. However experimental evidence has led to arguments suggesting that CO_2 molecules were sufficiently polarized to be able to penetrate between some overlap montmorillonite [72] as well as non-swelling illite [73] crystals, through a separation of these regions by residual water molecules.

2.2.4 Interlayer Penetration

Upon exchange of smaller cations for larger ones ($(CH_3)_2NH_2^+$ or even Co(en)3,3^+) in montmorillonite, exchange in the clay interlayers results in expansion of interlayer spacing of the aggregate, which may permit penetration by the sorbing gas molecules [66, 70]. The cation exchange appears to be enhanced on those surfaces where exchange had already begun, resulting in a tendency toward segregation [66]. Large lamellar separations are a necessary but not sufficient condition for interlamellar penetration of gas molecules. Large exchangeable cations such as alkylammonium cations [74] may clog the clay interlayer and even some of the aggregate pores. If the separation between the lamellae is not sufficiently wide, penetration of a gas molecule into the interlayer region is determined by its ability to do mechanical work in expanding the basal spacing of the quasi-crystalline regions. Contrary to the findings for montmorillonite, increasing the size of the interlayer cations does not weaken the forces between layers in vermiculite sufficiently for penetration by non-polar gas molecules. This is attributed primarily to the stronger interlayer forces resulting from substitution of Al for Si in the outer tetrahedral sheets of this mineral, which is structurally similar to montmorillonite [75]. The presence of even a few residual water molecules, coordinated with the interlayer cations, greatly facilitates the entry of CO_2 into a quasi-crystalline region of montmorillonite [73]. In vermiculite, coordinated water does facilitate slight edge penetration between the platelets [75]. X-ray experiments [76, 77, 78] indicate that CO_2 can become intercalated into hydrated clays under conditions proposed for geologic sequestration. Recent molecular dynamics studies [79, 80, 81] showed the possibility of intercalation and retention of CO_2 in smectites at conditions relevant to geological storage [82].

In another study by the Romanov group, accelerated carbonation was observed in smectites exposed to dry, high-pressure liquid and supercritical CO_2, predominantly, within the first two days of the exposure [83]. Romanov [58] observed a combination of the manometric sorption isotherm hysteresis, diffuse reflectance infrared spectroscopy ‘trapped CO_2’ fingerprints, irreversible X-ray diffraction pattern changes for the clay interlayer in intermediate hydration state, and HF acid digestion resulting in formation of non-extractable $F{:}CO_2$ adducts; the observations corroborated a hypothesis that carbon dioxide molecules become irreversibly trapped via anomalous extreme confinement in the galleries associated with montmorillonite interlayer, which results in formation of carbonates in the longer term. The subsequent validation on montmorillonite lumps suggested that such processes may occur in natural clay deposits at a different rate [58].

The most recent, DFT-based molecular dynamics simulations [84] have provided a model confirming the intercalation of CO_2 into a montmorillonite clay interlayer based on the red-shift in asymmetrical stretch vibration of CO_2 trapped in montmorillonite [58]. The origin of the shift was attributed to asymmetric distortion of the CO_2 molecules induced by the water molecules. The molecular simulations using classical force fields were carried out to study the structural and transport properties of clay mineral–water–CO_2 systems at elevated pressures and temperatures relevant to geological carbon storage. The simulations showed that the degree of swelling caused by intercalation of CO_2 strongly depends on the initial water content in the interlayer space and that CO_2 intercalation stimulates inner-sphere adsorption of the positively charged interlayer ions on the internal clay surfaces, which modifies the wetting properties of the surfaces.

The same group continued this research effort by investigating energetic and structural properties of rotationally disordered clay mineral–water–CO_2 systems. The simulations [85] showed that turbostratic stacking of hydrated Na- and Ca-montmorillonite and hydrated montmorillonite with intercalated carbon dioxide is an energetically demanding process accompanied by an increase in the interlayer spacing.

On the other hand, rotational disordering of dry or nearly dry smectite systems can be energetically favorable. The distributions of interlayer species were calculated as a function of the rotational angle between adjacent clay layers.

2.2.5 Organoclays

In such clays (e.g., with bentonite or hectorite base), gas molecules adsorb to essentially external surfaces or to those surfaces which they can access without appreciably separating the individual clay platelets. Thermal decomposition and carbonization of the organic groups strongly affects their hydrophilic-hydrophobic character. Since carbon is relatively hydrophobic, the increase in hydrophobicity is attributed to increased exposed clay surface (oxygen populated) as the hydrocarbon chains are dehydrogenated. Hydrophobic character of organoclay is preserved up to 300 °C. Montmorillonite's activation energy for the dehydrogenation step is higher than hectorite's systems [86] and hectorite structure slightly favors the hydrogenation step over the montmorillonite [74]. Carbon resulting from the hydrogenation separates the clay platelets enough to permit gas molecules to penetrate the interlayer region. Surprisingly, in some organoclays (e.g., dimethylaryloctadecylamine-exchanged bentonite) preheating up to 100 °C results in sharp increase in the nitrogen surface areas [74].

2.2.6 Reactive CO_2 Transport in Low Permeability Shale

Shale lithotypes of various compositions occur abundantly in sedimentary basins and act as natural seals for oil and gas reservoirs. Efficiency and long-term integrity of the seal (caprock) formations is one of the central issues for CO_2 transport in geological storage reservoirs. Caprock is generally characterized by low reactivity, low permeability, and high elasticity/plasticity [87]. Leakage through caprock is generally described in terms of: (i) gas flow through fractures, (ii) long-term permeability after the capillary breakthrough pressure is exceeded, and (iii) diffusion of dissolved gas through the water-saturated pore space. Simulations of the mass transfer and geochemical behavior in bedded sandstone-shale sequences was performed with the reactive fluid flow and geochemical transport code TOUGHREACT, assuming that alteration of the host rock aluminosilicate minerals is very slow under the deep-aquifer conditions [88]. WoldeGabriel et al. [82] investigated the decades-long effects of CO_2-flooding on the shale caprock from SACROC unit wells. They found no evidence of CO_2 diffusion into the caprock. Recent findings provide a new look at the issue of the shale caprock integrity. For short-term (30 days) experiments [87], dolomite and calcite minerals partially dissolved, and new carbonate precipitates formed after longer times (360 days). In the same experiments, kaolinite dissolved entirely whereas illite and smectite became destabilized in the long term. Due to CO_2 chemical reactivity and the resultant swelling and mineralogical changes induced in shales, CO_2 is expected to differ from natural gas in terms of coupled transport and interaction with the mineral-water systems [29]. The steady state diffusive flux is controlled by the effective diffusion coefficient of CO_2 in pore water, which is affected by tortuosity of the shale pore system, as well as the CO_2 sorption capacity in the water-saturated rock. That flux may change over time due to changes in surface area and porosity [59].

2.3 Models

Scientific understanding of CCS is vital to earn support of all stakeholders and to reduce public concerns, which may otherwise block this technology. Reactive transport models [89, 90], developed in support of the ANR-PICOREF CO_2 sequestration project [91] at Saint Martin de Bossenay, Paris Basin, France, were used to gain better understanding of physico-chemical reactivity of clay-like materials. Michel et al. [92] used cluster analysis phase mapping to populate the model with fixed initial and final mineral phases and to force specific compositional reaction paths. For the carbonates, two calcite-type, and two dolomite-type phases were identified as corresponding to initial and final phases. For illite-smectite mixtures, three phases were identified to represent the initial mixture, the final phases defined as the mean-composition of Fe-rich, and the mean-composition of K-rich clays. Solid solution models [93] were used to characterize the fixed phases using modified thermodynamic properties of pure known phases, and the USGS (U.S. Geological Survey) kinetics laws for the pure phases were applied to the slightly modified model phases. The coupled reaction-transport code Crunch [94] used by Credoz et al. [87] to identify geochemical phenomena and to calculate the carbonates and illite/smectite mineral dissolution rates relies on kinetic laws based on transition-state theory developed by Aagaard and Helgeson [95] and Lasaga [96, 97]. The model was populated by the data from the kinetics compilation of Palandri and Kharaka [22] and the EQ3/EQ6 database [98].

Predicting carbon dioxide fate in geological storage reservoir requires understanding interfacial tension, mineral surface wettability, and the capillary pressure dependence on saturation, for interactions between scCO_2, brine, and reservoir mineral surfaces. Many models for CO_2 transport in reservoirs rely heavily on the better understood capillary characteristics of immiscible fluid pairs [99]. The most recent research on CO_2 intercalation, however, provides an accurate molecular description of CO_2 for evaluating surface tension, contact angles, capillary flow, snap-off (or the disconnection of a continuous stream of the non-wetting CO_2 when it passes through pore constrictions, a form of residual trapping), and related phenomena associated with CO_2 trapping [84]. Intercalation could provide additional storage capacity for CO_2 in clay layers on reservoir rock coatings and in the caprock [50, 58], and could also be a mechanism for controlling potential leakage [58, 100, 101]. Investigations into these aspects of scCO_2 behavior, at elevated pressures and temperatures characteristic of geologic carbon sequestration, have only recently begun [99, 102].

Geological structures that do not provide the dome-shaped geology required for a CO_2 storage reservoir may provide long flow paths, which allow sequestration of the injected CO_2 via mineralization or groundwater dissolution. Modeling of CO_2 injection into the White Rim Sandstone (Colorado Plateau, Central Utah) using the ChemTOUGH reactive chemical simulator showed that 1,000 years after injection, approximately 21% of CO_2 was sequestered in form of minerals and 17% leaked to the surface [103].

Results of numerical simulations for CO_2 injection in the US Gulf Coast sediments, with the reactive fluid flow and TOUGHREACT geochemical transport code, indicated that the CO_2 mineral-trapping capacity reaches 90 kg/m^3 of the medium over 100,000 years and depends on primary mineral composition. The major trapping minerals were found to be dawsonite (with reaction controlled by Na^+ provided by initial oligoclase dissolution) and ankerite/siderite (with reaction controlled by Fe^{2+} supplied by chlorite and hematite dissolution and reduction) [104].

Palandri et al. [22] performed thermodynamic calculations for sequestration of CO_2 in ferrous carbonate, using the computer programs CHILLER [105] and GAMSPATH [106]. The simulations with SO_2 or H_2S at 120 bar and 50 and 100 °C showed that iron can be reduced by SO_2 and transformed almost entirely to siderite, thereby trapping CO_2.

Gunter et al. [42] used a computer model, PATHARC.94, to interpret a large increase in alkalinity after a one-month exposure of Glauconitic Sandstone core (Alberta Sedimentary Basin, Canada) in synthetic formation water to CO_2 at 90 bar and 105 °C. Carbon dioxide-trapping reactions were predicted to take 6 to 40 years under conditions of the above experiment and hundreds of years under the aquifer conditions (54 °C, up to 260 bar), resulting in formation of siderite, calcite and aqueous bicarbonate ions. Potential errors were estimated to be as high as two orders of magnitude based on examination of the kinetic data used in the modeling.

PHREEQC geochemical modeling was able to simulate the observations of mineral reactions induced by carbonized brine, at Werkendam and Barendrecht-Ziedewij gas fields, CO_2- and CH_4-bearing stratigraphic equivalents in the Netherlands [107]. The results showed that the difference in paragenetic sequence between the two fields was partially due to different temperature evolutions and fluid influxes. However, a sensitivity study on the type of illite used in the model, and the inclusion of minor minerals showed that careful selection of initial mineralogy and an expert opinion on diagenetic processes were required to guide the model towards the proper mineral reactions.

3. Overview of Recent Ex Situ Mineralization Research

Unlike in situ mineral carbonation, ex situ technology has been demonstrated on larger scales [108], which helps in reducing the fundamental knowledge gaps; however, the slow reaction rates and material handling issues are still hindering its commercial application due to the relatively higher costs ($50–300 per t-CO2 sequestered) [9]. The most recent comprehensive literature reviews on ex situ carbon dioxide mineralization were published by Kelly et al. [109], Khoo et al. [110], Sanna et al. [9] and by Zevenhoven group [8, 12]. Prior to these, a number of reviews have been published by Lackner [111] and, later, by Huijgen and Comans [10, 11] and by Stephens and Keith [13]. These reviews provided two primary reasons for continuing research in CO_2 mineralization, both of which are still applicable: the fact that mineralization provides a stable, leakage-free method for fixation of CO_2 that requires minimal to no long-term monitoring, and that the available feedstock, namely Ca and Mg-based silicate minerals such as olivine, serpentine, and wollastonite, are abundant and relatively accessible. The following section updates these previous reviews by summarizing much of the work that has been conducted in this area in the last few years.

A feasibility study based on the research performed in this field at NETL was published in 2007 [14]. The conclusion of the NETL study was that large-scale ex situ CO_2 mineralization using silicate minerals was impractical due to the high cost estimate of about $54/t-$CO_2$ sequestered as well as the scale of the mining operations, requiring about 55,000 tons of mineral to carbonate the daily CO_2 emissions from a 1 GW coal-fired power plant.

The high energy requirement and cost are major obstacles that are still in place, as the aqueous method developed at NETL currently remains the preferred method for large-scale carbonation of Ca and Mg silicate minerals [11, 12]. The main barrier to large-scale application of the carbonation of silicates using the aqueous method remains the energy associated with feedstock preparation, including mining, grinding, and in the case of serpentine, dehydroxylation. Slow kinetics associated with the cation extraction step and acid/base makeup or recoveries are two major issues that still need to be addressed. However, possibilities have been proposed for reducing these energy requirements and identifying cost-effective niche CO_2 mineralization methods. One area of recent investigation involves examining substitute materials for the typical silicate mineral feedstock, such as industrial waste streams containing significant quantities of available carbonation reactants, predominantly Ca and Mg oxides.

The potential CO_2 mitigation associated with low-cost mineral carbonation of common industrial-sourced alkaline byproducts, including coal fly ash [14, 50], represents a small share (0.1%) of U.S. total CO_2 emissions [112].

Current research is primarily directed towards three main issues: reduction of feed activation energy requirements, improvement of the slow chemical kinetics of the process, and alternative feedstock exploration. The following section is broken down into two sub-sections. The first discusses alternative feedstock utilization, and the second provides an overview of kinetic and economic improvement of carbon mineralization via a variety of alternative process methods.

3.1 Alternative Feedstock

There has been a marked increase within the last few years in research into utilizing industrial waste streams as a source of Ca and Mg cations available for carbonation. Interest for using industrial residue materials and byproducts as reactant mineral carbonation sources has arisen because they are readily available, cheap, and often generated near large CO_2 emission sources. Fly ash and bottom ash from furnace operations typically contain a significant amount of lime (CaO) and magnesium oxide (MgO), which are more readily carbonated than the silicates. Their small particle sizes also facilitate rapid reaction rate. Cement kiln dust and waste concrete, mining waste, slags from iron and steel-making operations, and alkaline paper mill waste are also promising feedstock material for carbonation. The capacity to sequester CO_2 with these alkaline residues depends directly on the proportion of divalent cations bound in oxides (CaO and MgO) and/or hydroxides ($Ca(OH)_2$ and $Mg(OH)_2$) present in the waste matrix.

3.1.1 Municipal Incinerator Ash

Among the solid residues generated by municipal solid waste incineration (MSWI) bottom ash accounts for 20–30% by mass of the original waste and tends to have lower CaO and higher SiO_2 content compared to fly ash. Accelerated carbonation has been proposed as an application for this ash prior to its final disposal. There are multiple advantages to carbonating MSWI ash. First, the ash contains a high CaO content. Secondly, MWSI ash already consists of fine-size particles and thus is ready for carbonation with no pre-treatment. Thirdly, the incineration process generates a significant amount of CO_2, so alternately sequestering a portion of the CO_2 along with the waste products would be advantageous. Fourthly, carbonating the ash tends to decrease the leaching of potentially hazardous heavy metals contained within the ash. Presently, MSWI ash at some locations undergoes a natural weathering process prior to disposal, of which natural, atmospheric carbonation is an important step.

Baciocchi et al. [113] reported the study of accelerated carbonation of varying size fractions of bottom ash from refuse-derived fuel (RDF) incinerator. Accelerated aqueous carbonation batch experiments were performed to assess the influence of temperature (30 to 50 °C), CO_2 pressure (1 to 10 bar) and liquid-to-solid ratio (0 to 0.6 L/kg) on reaction kinetics. Five size fractions with Ca content from ~26% to ~35% along with one fraction (0.150–0.425 mm) having only ~3% Ca were tested. Pressure and size fraction were found to be the most relevant parameters affecting the carbonation yield. The amount of CO_2 uptake ranged from 4% by weight for the coarse fractions to 14% for the finest fraction of the bottom ash. The three larger size fractions (0.425–12 mm) make up ~89% of the feed, indicating some size reduction would be beneficial. The subsequent leaching behavior of the material was found to be mainly related to the decrease upon carbonation in the natural pH of the ash. The carbonated ashes displayed reduced heavy metals mobilization. An estimation of maximum CO_2 sequestration potential of 2% of the total CO_2 emitted from the incineration plant could be achieved using the bottom ash generated by the incineration process if the carbonation could be advanced to 90%.

Wang et al. [114], Li et al. [115], and Rendek et al. [116] studied the influence of reaction time and liquid-to-solid (L/S) ratio on high CaO (~53%) content fly ash and bottom ash carbonation. The optimum L/S ratio of the fly ash was found to be 0.03 to 0.25 for accelerated, room temperature, ambient pressure CO_2, carbonation. A weight gain of ~12% was achieved with these conditions in all three studies. The effects of increased CO_2 partial pressure and/or temperature on the carbonation rate were not investigated. The tests evaluated the effect of carbonation on the mobilization of some hazardous heavy metals. These results were compared to the non-carbonated material subject to the same leaching conditions. The leaching potential of Pb, Zn, and Cu was found to significantly decrease whereas the As leaching only slightly decreased. Conversely, leaching of Cd and Sb increased. Based on the de-mobilization of heavy metals, the optimum pH of the fly ash was determined to be 9.5–10.5, down from a starting pH of around 12 with a required reaction time of about 7 hrs. The likely reaction sequence is as follows

$$CaO\ (s) \rightarrow Ca(OH)_2\ (aq) + CO_2\ (aq) \rightarrow CaCO_3\ (s) + H_2O \qquad (11)$$

Li et al. [115] studied the accelerated carbonation of municipal solid waste incineration fly ashes in the U.K. The study found an optimum water-to-solid ratio of 0.3 for accelerated carbonation under ambient temperature conditions. This study also reported lime, portlandite, and calcium chloride hydroxide removal and calcite formation. The leaching properties of carbonated ash were also examined. Release of soluble salts, such as SO_4^{-2} and Cl^- was reduced after carbonation, but was still higher than landfill limits for hazardous waste.

Rendek et al. [116] explored using bottom ash for CO_2 mineralization by a gas–solid reaction method. An average mineralized CO_2 volume of 12.5 L/kg bottom ash was reported using a high pressure vessel at room temperature. The reaction proceeded faster with higher CO_2 partial pressure, although the total volume of sequestered CO_2 did not increase. An ash moisture content of 15% (w/w) seemed to optimize CO_2 mineralization. This moisture content was achieved by partially drying the ash, since the initial moisture content of the ash was 25% (w/w). Carbonation decreased the pH from 11.8 to 8.2 and reduced leaching of Pb, Cr, and Cd. The authors concluded that this process could be used to sequester 0.5 to 1% of the CO_2 emissions from an MSWI.

Gunning et al. [117] studied the accelerated carbonation treatment of industrial and municipal wastes from the U.K., where the oven-dried samples were mixed with water, to form a smooth paste, and then carbonated in 2 bar CO_2 atmosphere for 72 hours. Cement dusts and paper incineration ashes were identified as the most reactive due to free lime (CaO) resulting from calcination of calcite in the waste during incineration. Carbonation of bauxite, pulverized fuel ashes, sewage sludge ash, clinical waste incineration ash, and steel wastewater sludge showed little or no reaction. The authors reported that carbon dioxide reactivity was related to total calcium content as well as the mineralogy, as some calcium-bearing minerals were discovered to be not reactive, accounting for the low reactivity of some wastes with high calcium contents. With the selection of specific waste streams and optimization of the process, the sequestration of large amounts of CO_2 as carbonate material was believed to be achievable. Carbonation proved effective in reducing the mobility of lead and barium, while increasing antimony and chromium mobility. Arsenic, copper, molybdenum, nickel, and most anions were largely unchanged.

3.1.2 Combustion Fly Ash

Bauer et al. [118] conducted mineral carbonation of lignite fly ash at ambient temperature and pressure in a semi-dry reaction system. They reported that the carbonation reaction depends on three factors: dissolution of CO_2 in the liquid phase, mobilization of Ca and Mg from the mineral surface, and precipitation of the carbonate solids.

Uliasz-Bochenczyk [119] studied CO_2 sequestration via mineral carbonation in coal fly ash from lignite combustion in Poland. Three types of fly ash with CaO contents up to 29% were studied in an aqueous suspension system with various ash-to-water ratios ranging from 0.6 to 1.5. The average CO_2 absorption of 5.5 g CO_2/100 g of ash was observed at a reaction temperature of 35 °C, corresponding to 19% conversion of available CaO within the ash.

Montes-Hernandez et al. [120] conducted a CO_2 mineral sequestration study at lower temperatures (20 to 60 °C), using an aqueous process to carbonate a coal combustion fly ash that contained a high content of CaO. The carbonation of the fly ash was carried out in two steps. First, the hydration of lime:

$$\mathrm{CaO\ (s) + H_2O \rightarrow Ca(OH)_2\ (s)} \qquad (12)$$

Second, the spontaneous carbonation of calcium hydroxide in suspension:

$$\mathrm{Ca(OH)_2\ (s) + CO_2\ (g) \rightarrow CaCO_3\ (s) + H_2O} \qquad (13)$$

The carbonation efficiency of CaO in the fly ash, calculated at ~82% after two hours at 30 °C, was discovered to be independent of CO_2 partial pressure (10, 20, 30 and 40 bar) and was not significantly affected by reaction temperature or by fly-ash concentration in the slurry (5–15% S/L). This experiment demonstrated that one ton of fly ash, an industrial waste that usually contains about 4 wt% of lime (CaO), could sequester up to 26 kg of CO_2, or 38.2 tons of fly ash per ton of CO_2 sequestered. The release of other toxic metallic ions initially present in the fly ash was not observed with leaching tests, indicating that those ions could also be safely sequestered by the carbonation process. While the authors note that fly ash has less sequestration capacity than steel slag, fly ash is more readily available, with about 600 million tons annual production.

Soong et al. [121] proposed the use of coal combustion fly ash and brine solutions (waste from oil and gas production) to sequester CO_2 via a multi-step aqueous mineral carbonation process. For the study, Ca-rich fly ash (29% CaO) was added at 18 ºC to increase the pH-level of the reactant brine (also containing Ca) from a pH of about 3.0 to above 9.0. This produced slurry amenable to the carbonation process. Calcium oxide rich industrial waste (Class C and GFD fly ash) was used as the alkaline agent for the brine carbonation reaction under relatively mild conditions (20 °C, 13.6 bar CO_2). The CaO within the fly ash was found to contribute to the carbonation reaction. The authors proposed that after the fly ash was mixed with the brine, most of the CaO was converted to $Ca(OH)_2$, which was readily ionized to Ca^{2+} and OH^- ions. The CO_3^{2-} in the solution reacted with the Ca^{2+} in the brine/ash slurry, resulting in precipitation of $CaCO_3$. Calcium originally from both the brine and fly ash contributed to the formation of calcium carbonate.

Liu and Maroto-Valer's study [122] aimed to promote formation of carbonates by using a buffer solution in the presence of coal fly ash and brine, under ambient as well as high temperature and pressure (100 °C, 103 bar) conditions.

Grace et al. [123] applied statistical technique to study the factors affecting carbonation of fly ash impacted by brine. Nyambura et al. [124] studied carbonation of fly ash in brine as well. Jo et al. [125] evaluated the factors affecting mineral carbonation of fly ash in aqueous solution. Uliasz-Bochenczyk [126] utilized fly ash for aqueous carbonation reaction.

Various methods of accelerating the aqueous carbonation of alkaline coal fly ash were studied by Ukwattage et al. [127]. Their results indicated that increasing the pressure increased the carbonation rate but not the overall carbonation, and that a solid-to-liquid ratio of 0.2 yielded the highest overall carbonation gain. The authors further noted that increased CO_2 separation from flue gas was a major limitation to overcome for this process. He et al. [128] were able to synthesize 97–98% pure calcium carbonate via indirect carbonation of coal fly ash by extracting Ca from the ash using recyclable ammonium salts, followed by carbonation using NH_4HCO_3 as a substitute for CO_2. NH_4HCO_3 is an on-site byproduct of the ammonia-water CO_2 capture process, and would thus eliminate costs associated with the CO_2 compression and transportation. Furthermore, utilization of NH_4HCO_3 as a carbonate ion source for calcium was found to increase the carbonation efficiency compared to the bubbling CO_2, from the range of 41–47% to 90–93%.

Rao et al. [129] conducted a study on the carbonation of fluidized bed combustion (FBC) ash by sonochemical treatment. Tests were performed treating four FBC ashes at temperatures ranging from 20 to 80 °C. Their results confirmed that carbonation only occurs after the CaO has been hydrated to form $Ca(OH)_2$. Experiments with NaCl and seawater additives were carried out; these additives were found to enhance the hydration step, but not the level of carbonation. The ash reactivity displayed a strong temperature dependency, with nearly complete carbonation achieved within minutes at higher temperatures.

Dilmore et al. [130] studied the mineralization of CO_2 using mixtures of caustic byproduct and saline waste water. Three caustic industrial byproducts were examined:

flue gas desulfurization (FGD) spray dryer ash, Class C fly ash from coal combustion, and bauxite residue. Flue gas desulfurization spray drier ash exhibited the highest CO_2 sequestration capacity, followed by the bauxite residue, and then the Class C fly ash. This process had the added advantage of neutralizing the acidic brine when mixed with the caustic solids. Carbonation results of a bauxite and saline waste water mixture were confirmed by x-ray diffraction, with a mixture of calcite ($CaCO_3$) and magnesite ($MgCO_3$) composing 35% of the product. This result was achieved for a slurry mixture comprised of 53% bauxite liquor by mass to 47% Oriskany brine, at room temperature (~21 °C) and 6.9 bar CO_2 for 30 minutes.

Uibu et al. [131, 132] proposed using oil shale ash for CO_2 mineral carbonation. Estonian oil shale ash contains 10–25% free lime and has been carbonated at the laboratory scale for CO_2 sequestration. The aqueous carbonation of CaO-bearing oil shale ash in both a batch and continuous stirred tank reactor system (CSTR) was studied by Uibu and Kuusik [131]. During the carbonation process, CaO hydrated to $Ca(OH)_2$ before forming the final $CaCO_3$ product. Particle surface area was found to strongly affect the reactivity. Carbonation products $CaCO_3$ and $CaSO_4$ precipitated at the pores and acted as surface diffusion barriers, slowing the carbonation rate. The carbonate and sulfate ions themselves also acted as a mass transfer barrier, inhibiting further carbonation at elevated ion concentrations. The cascading CSTR reactor system significantly increased carbonation efficiency compared to the batch reactor system, in part by optimizing pH and concentration of dissolved salts at each step and thus prolonging the contact time of the reactants. Two mineral feed materials were utilized: pulverized firing cyclone ash (PF) and circulating fluidized bed combustion ash (CFBC). The CFBC ash was more porous, less affected by sulfate and carbonate ion levels, and more reactive than the PF ash. The state of the aqueous ions affected PF ash kinetics more strongly. The authors noted that PF ash would likely require feed treatment before carbonation.

Muriithi et al. [133] compared the carbonation processes of fresh fly ash and of weathered fly ash. Fresh fly ash can capture up to 6.5 wt% CO_2 with a 60% conversion from calcium to $CaCO_3$ via accelerated carbonation within 2 hours under 90 °C and 4MPa conditions; while, for comparison, 6.8 wt% CO_2 was found to have been captured by natural carbonation of wet disposed fly ash, in situ over a period of 20 years.

3.1.3 Steelmaking Slag

Steelmaking slag typically contains about 25–55 wt% CaO, making it a good candidate for carbonation. In one study, blast furnace slag was treated with the pH swing method for calcium carbonate formation in a batch reactor over a temperature range of 30 to 70 °C and pressure range of 1 to 40 bar [134]. The effect of solution pH, temperature, and CO_2 partial pressure on the precipitation of carbonates was studied. Acetic acid was used for the calcium leaching step, but had to be evaporated away for recovery. Carbon dioxide was then bubbled through the resultant calcium salt solution while the pH was controlled via the addition of sodium hydroxide. Greater pH values led to an increase in the amount of calcium carbonate conversion, although temperature had little effect on conversion efficiency. A thermodynamic analysis of the reaction verified the observed conversion improvement with NaOH addition. The thermodynamic simulations also predicted some carbonate formation without NaOH addition; however, experiments without NaOH addition did not result in significant carbonate formation. Observed trace impurity precipitations were theorized to interfere with the NaOH-free carbonate precipitation, as those impurities were not taken into account in the simulations. Approximately 4.4 kg of blast furnace slag, 3.6 L of acetic acid, and 3.5 kg of NaOH would be required to bind 1 kg of CO_2. Energy requirement calculations indicated that the electricity required for NaOH regeneration would make the process unsuitable for CO_2 sequestration. Two major improvements were suggested: a cheaper NaOH substitute and the use of waste heat for the acid evaporation and recovery.

Doucet [135] studied South African steel slag leaching behavior for industrial mineral carbonation. Rapid extraction of Ca and Mg from Basic Oxygen Furnace (BOF) and Electric Arc Furnace (EAF) slag was successfully performed in HNO_3 at ambient temperature. However, the resulting acidity of the Ca-rich leachate (pH ~4.0) was problematic. The pH of the leachate must be adjusted for subsequent carbonation. Modeling was used to examine the theoretical carbonation potential and the formation of calcite ($CaCO_3$) and dawsonite ($Na_3Al(CO_3)_3$).

Stolaroff et al. [136] studied CaO and MgO-rich industrial waste streams (concrete waste and steel slag) for carbon dioxide sequestration. Both $Ca(OH)_2$ and CaO from concrete waste or steel slag was dissolved in water and reacted with CO_2 at ambient temperature and pressure to form carbonate. An industrial process was proposed that was estimated to sequester 32 kilotons CO_2 yearly, requiring: 97 kilotons of steel slag, 680 kilotons of concrete or 200 kilotons of high-cement fines, and an estimated 23 million gallons of water/day. The operating cost was estimated at \$8/t-CO_2 sequestered, although the significant crushing and grinding costs were not taken into account during that value estimation. However, these particular waste products would require crushing for non-sequestration applications, such as concrete filler or road aggregate, so a portion of grinding and crushing costs would exist with or without sequestration via mineralization.

Chang et al. [137] evaluated various steel-making slags for carbonation reaction in a slurry reactor. Eloneva et al. [138] investigated precipitated of calcium carbonate with steelmaking slags. Sun et al. [139] applied NH_4Cl as a leaching solution for CO_2 mineral sequestration with steelmaking slag. Van Zomeren et al. [140] studied the changes in mineralogical and leaching properties of steel slags at low CO_2 pressure and temperatures between 5 and 90 °C. Said et al. [141] produced calcium carbonate from steelmaking slags high in Ca and Fe. Ammonium salts were used to selectively extract calcium from the slags–CO_2 was then bubbled through the resultant calcium-rich solution, thus precipitating the carbonate. Reducing slag particle size was found to enhance the extraction efficiency. Decreasing the extraction solid-to-liquid ratio was also found to increase efficiency, while greatly increasing total cost due to the larger reactor sizes required for these low-solids-fraction reaction conditions.

Salman et al. [142] studied the effects of accelerated carbonation on argon–oxygen decarburization of stainless steel slag as a means of mineral sequestration of CO_2.

Two alkaline waste streams from the same plant (steel slag from a basic oxygen furnace and metal working waste water) were utilized by Pan et al. [143] for hot-stove flue gas carbonation within a rotating packed-bed reactor (RPB). The centrifugal forces within a RPB reactor allowed for the formation of thin liquid films and tiny droplets whose micro-mixing properties greatly enhanced gas mass transfer rates through the liquid, thus enhancing overall carbonation rates. Carbon dioxide removal efficiencies of 96–99% were obtained within one minute at ambient conditions, and the pH of the waste water stream was reduced from 12 to 7.

3.1.4 Paper Mill Waste

Perez-Lopez et al. [144] experimentally investigated the aqueous carbonation mechanism of an alkaline paper mill waste containing about 55 wt% portlandite ($Ca(OH)_2$). The overall carbonation reaction includes the following steps: 1) Ca release from portlandite dissolution, 2) CO_2 dissolution in water, and 3) $CaCO_3$ precipitation. The authors estimated that one ton of paper mill waste could sequester 218 kg of CO_2 in calcite form. The total capacity is independent of temperature (within the range of 30 or 60 °C) and CO_2 partial pressure.

3.1.5 Mining and Industrial Waste

Jacobs and Hitch [145] conducted mineral carbonation study to accelerate the carbonation of mine waste materials. Power et al. [146] utilized a microbial method for mineral carbonation. Pronost et al. [147] used ultramafic mineral waste for mineral carbonation study. Vögeli et al. [148] reported an investigation of the potential for mineral carbonation of the Platinum Group Metals' processing tailing in South Africa. The major cations in the tailings were those of Ca, Fe and Mg. While carbonation was possible, the overall conversions were low (3–30%) predominantly due to the low Mg extraction levels during the acid leaching step [149]. Much of the Mg was contained within orthopyroxene, which was fairly unreactive and thus ultimately responsible for the low conversion values. Various additives and pH adjusters failed to increase the Mg extraction levels, and so the authors concluded that more work is required on Mg extraction from pyroxene materials.

The aqueous carbonation of nickel mining residues from the waste stream of a Ni–Cu mine pilot plant was studied by Assima et al. [150]. The sensitivity of the carbonation reaction to temperature and oxygen content was investigated. While a 10-times increase in reaction rate was observed from 10–40°C, the presence of oxygen within the CO_2 gas led to the formation of iron (III) hydroxide and other passivating surface oxides, thus reducing both the carbonation rate and total potential. The introduction of a dilute solution of trans-1,2-diaminocyclohexanetetra acetic acid (CDTA) was able to slightly mitigate the negative carbonation effects of oxygen by reducing hydroxide precipitation. Assima et al. [151] also compared the direct gas-solid carbonation of five specific Québec mining residues using a fixed-bed diffusion cell, in an effort to predict residue properties advantageous for carbonation. While successful carbonation was observed, the carbonation rate and yield were both increased and highly dependent upon the presence of brucite and chrysotile, due to the ease of dissolution for Mg production.

Dilmore et al. [152] studied the use of a bauxite residue and brine mixture for CO_2 sequestration. The experiments were conducted to explore the concept of utilizing a mixture of caustic bauxite residue slurry (pH 13) and produced oil field brine for CO_2 sequestration from flue gas. The CO_2 sequestration was augmented by adding bauxite residue as a caustic agent to acidic brine solutions, and CO_2 trapping was accomplished through both mineralization and solubilization. The product mixture solution was neutralized following carbonation in nearly all mixtures. Yadav et al. [153] also studied CO_2 sequestration using bauxite residue at ambient temperature. Calcium bearing mineral phases (cancrinite and chantalite) resulted from carbonation of the bauxite residue. The carbonation capacity was estimated to be 5.3 g of CO_2/100 g of residue.

Bobicki et al. [154] studied the alkaline industrial wastes, Cardenas-Escudero et al. [155] used phosphogypsum industrial wastes, Morales-Florez et al. [156] investigated the calcium-rich industrial waste, and Renforth et al. [157] utilized industrial waste from silicate production, for various mineral carbonation studies under different reaction conditions. Alkaline industrial wastes can be utilized in CO_2-mineralization fuel cell systems producing valuable $NaHCO_3$ concomitantly with electricity generation [158]. Using phosphogypsum and natural insoluble K-feldspar for production of soluble potash, Wang et al. [159] reported CO_2 mineralization ratio of ∼7.7% with potassium extraction ratio of ∼87%. Bodenan et al. [160] evaluated the application of ex situ mineral carbonation technology to mafic/ultramafic mining and industrial wastes. They concluded that the region of New Caledonia, France, with its insularity and local abundances of "carbonable" (suitable for carbonation) rocks and industrial wastes, and with significant greenhouse gas emissions, stands out as a strong candidate for application of ex situ mineral carbonation.

3.2 Process Routes and Technologies

Process routes for CO_2 mineralization of silicate ores are generally divided into direct and indirect methods. Simply put, direct carbonation consists of directly reacting CO_2 with the mineral source in one step, whereas for indirect carbonation the process is broken down into multiple steps. Other mineralization process aspects recently investigated seek to increase reaction rates via feed activation [161], utilize different reactor technologies, and explore possibilities for the industrial use, resale, and/or recycling of carbonation products. Economic improvement of the overall mineralization process is an additional goal for these studies.

3.2.1 Direct Carbonation

Two general schemes for accomplishing direct carbonation exist: dry gas–solid and aqueous. A better understanding of the carbonation rate limiting mechanisms, including exploration of the reaction at the particle–reactant interface, is important for lowering processing costs. A key factor repeatedly discussed in the literature is that the carbonates are thermodynamically favored over silicate minerals so that the overall reaction is exothermic [162].

Dry Gas-Solid Carbonation

The dry gas–solid direct carbonation process involves reacting gaseous carbon dioxide with a solid mineral cation source. Advantages of this process include simplicity and the ease of heat recycle from the exothermic reaction, but reaction rates are generally too slow to be industrially viable [11]. Despite this fact, research has continued on various aspects of this process. Larachi et al. [163] performed in situ tracking of the gas–solid carbonation of chrysotile in dry and 10% H_2O atmospheres. Reactions took place at atmospheric pressure and in the temperature range of 300–1200 °C. The final product was magnesium carbonate hydrate with both environments. In general, the presence of water resulted in increased carbonation rates. A four-step mechanism was proposed incorporating this water effect. Trace amounts of cesium feed impurities were also able to significantly increase the chrysotile carbonation capacity.

The kinetics of gas–solid carbonation of air pollution control residues (mainly CaO and $Ca(OH)_2$) from 300–500 °C was investigated by Prigiobbe et al. [164]. The morphology of the particles changed from layered to round during reaction. The study concluded that an initial rapid nucleation and growth mechanism was followed by slower reaction controlled by diffusion through the carbonation product. Temperature was found to have a minimal effect on the carbonation. The CO_2 concentration was also found to have a minimal effect, indicating that this type of process could be satisfactorily operated with CO_2 concentrations of the order of 10%, thus eliminating the need for an additional CO_2 capture step from flue gas. The maximum reported conversions were 60–80%, but the authors believe that water vapor presence in flue gas should act as a catalyst, thereby increasing those conversion levels [165].

The gas–solid carbonation of Ca or Mg oxide or hydroxide could prove to be more energetically and economically feasible. This is considered an indirect carbonation method since the Ca- and Mg-silicate minerals are not directly carbonated. Rather, an oxide or hydroxide intermediate product is derived from the silicate in an initial step. This multi-step method is discussed in the indirect carbonation section.

Aqueous Carbonation

Aqueous mineralization schemes take advantage of the increased carbonation reaction rates that occur in aqueous mineral slurry. An aqueous carbonation process route advanced by NETL [7] has generally been accepted as a well-defined mineral carbonation route [10, 11], and is thus often used as a baseline process when studying other aspects of carbonation. Recent research has focused on more closely inspecting the chemical processes during dissolution of the silicates and precipitation of carbonates and optimizing these conditions. Maroto-Valer et al. used an aqueous method similar to that of NETL to investigate feedstock activation on serpentine reaction kinetics [166]. Another study of aqueous olivine carbonation investigated the reaction surface and interface, as well as the formation of a silica passivation layer that limits further carbonation [167]. The study concluded that agitation, or addition of abrasive particles such as quartz, increased particle-to-particle collisions that were effective in exfoliation of the silica passivation layer, leading to an increase in carbonation.

Klein and Garrido [168] also studied the thermodynamic constrains on mineral carbonation of serpentinized peridotite. Back et al. [169] conducted the reaction with alkaline earth metal oxide CaO and MgO. A life cycle assessment of CO_2 sequestration in serpentine via NETL mineralization process was conducted by Nduagu et al. [170].

Kinetics of aqueous wollastonite carbonation was measured at supercritical conditions of 90 °C and 25 MPa of CO_2 by Daval et al. [171]. The data was used along with published rate laws to develop a kinetic model for the process. The supercritical carbon dioxide was introduced into three wollastonite-containing systems: pure wollastonite, wollastonite plus water, and wollastonite plus 0.44 M NaOH. The dissolution of the CO_2 into the water solution resulted in acidic experimental conditions, while CO_2 dissolution into the NaOH solution resulted in a nearly neutral pH solution, referred to as pH circum-neutral by the authors. The pH circum-neutral medium (NaOH) yielded greater initial aqueous supersaturation levels, which resulted in elevated formation of smaller, passivation calcite crystals on the wollastonite surface and the slowest kinetic rates. In the more acidic conditions (wollastinite plus water), wollastonite dissolution was found to be the rate limiting step, with SiO_2 passivation playing only a minor role on the kinetics. The kinetic model showed good agreement when the carbonation reaction took place in water (acidic), but poor agreement when performed in the NaOH solution (pH circum-neutral). Lack of fundamental silicate dissolution and carbonate precipitation data for water activities much smaller than unity prevented kinetic modeling under the supercritical CO_2 condition. The authors stated that looking at the secondary precipitation reactions of calcite and silica on the wollastonite surface would be critical for determining the “true reaction surface area”, and that more understanding of rate and chemical affinity relationships would be critical for developing a more coherent model.

Other research has explored altering the reactant solution pH for carbonation rate improvement. A kinetic study and examination of the optimum conditions for olivine, wollastonite, and serpentine aqueous carbonation was reported by Gerdemann et al. [14]. The carbonation rate for wollastonite was the greatest, followed by olivine, then serpentine. The carbonation rate was enhanced by increasing CO_2 partial pressure and by the presence of an alkaline buffered saline solution consisting of 1 M NaCl and 0.64 M $NaHCO_3$, which is stable at ambient pressure and temperature, allowing for easy separation of the solids and solution recycle. An economic feasibility review was also part of this study. One of the conclusions presented was that the large scale of mining operations required to sequester significant CO_2 emissions is problematic, but that the mineralization process could be a valuable means for reclaiming industrial waste material utilized as the mineral feedstock.

Enhancement of the olivine aqueous carbonation rate at 185 °C and 13.5 MPa via the addition of bicarbonates was investigated by Jarvis et al. [172]. The most effective additive was determined to be a 5.5 M $KHCO_3$ solution. The added bicarbonates increased the H^+ activity, leading to increased SiO_2 passivation layer exfoliation and increased overall carbonation. The aqueous carbonation efficiency at 150°C and 280 bar of Stapafell (Iceland) basalt rocks containing olivine was compared to separate olivine by Sissman et al. [173]. While the dissolution of the separate olivine sample was hindered by silica layers on the olivine surfaces, this effect appeared to be mitigated in the basalt samples, perhaps due to favorable redox conditions found in the more chemically complex basalts. The cation presence of both Fe and Al, within the basalt, was also theorized to potentially increase driving force for breakdown of those silica passivation layers or modifying the porosity around those layers.

Olivine reactivity with CO_2 and H_2O on a microscale was studied with CO_2 pressure up to 80 bars, at temperatures of 25 °C and 120 °C, with and in the absence of oxygen [174]. The dissolution of olivine in the presence of oxalate, citrate, and CO_2 at 90 °C and 120 °C was also studied [175]. Kwon et al. [176, 177, 178] conducted a series of kinetics studies to convert the olivine into carbonate.

Serpentine dissolution enhancement in weakly acidic salt solutions was investigated by Krevor and Lackner [179] with the impetus being a reduction in the energy demand of the grinding step by enhancing dissolution kinetics, thus allowing for the use of coarser ground reactants. The study found that 0.1 M sodium citrate, sodium oxalate, or sodium EDTA solutions improved the dissolution rate while having only a small effect on the pH. Initially, a rapid dissolution rate was observed (>60% dissolution within the first 2 hours and >80% in 7 hours) followed by a region with a slower dissolution rate as complete conversion was approached (complete dissolution in 10 to 20 hours). The salt additions were found to have a large effect on the initial dissolution rate, but less on the slower rate that followed. The authors were not able to specifically determine the mechanism for the increase in initial dissolution rate, although slight pH changes at higher added salt concentrations were thought to be partially responsible. These results were compared to dissolution experiments under identical conditions (120^{o}C and 20 bars of CO_2 pressure) with no added salts, and solutions with 1 M NaCl, 1 M NH_4Cl, or 0.5 M sodium acetate. Because of the increase in initial dissolution rates, the additions of sodium salts of citrate, oxalate, and EDTA led to an increase in the overall dissolution when compared to solutions with no added salts. The experiments with NaCl, NH_4Cl, and sodium acetate also increased the initial rate, but not as drastically as the sodium salts of citrate, oxalate, and EDTA.

Zhao et al. studied the aqueous carbonation of natural brucite in both 0.39 M HCl and H_2O at room temperature and pressure [180]. While brucite generally has better carbonation reactivity than other minerals, it is not as readily found in nature. Instead of the typical magnesium carbonate product generally achieved, the product from this study was the less thermodynamically stable hydrated carbonate, likely a result of the low reaction temperature as phase transition potential is limited at room temperature. Due to more rapid dissolution in HCl, the carbonation reaction is initially faster in HCl, however, the carbonation rate in HCl is eventually surpassed by that in H_2O. Overall, carbonation in H_2O results in a higher conversion than in HCl. The authors posit that product crystals form a diffusion barrier in the presence of HCl, although they were not able to confirm that statement through imaging analysis. The acidic environment results in lower concentrations of HCO_3^- (and CO_3^-), thus resulting in lower carbonation conversion. The authors note that this brucite method could be used as an effective flue gas scrubber.

Other

A modified direct aqueous carbonation route where a magnesium-rich brine solution ($MgCl_2$) was flushed with carbon dioxide gas was proposed by Ferrini et al. [181]. Proposed sources for the magnesium brine include seawater, artificial saltpans, evaporated saline deposits, or waste streams such as desalination byproducts and produced water from oil and gas production. The authors note that many of these potential sources exist further than desired from CO_2 emission sources. The kinetics of this method were studied and described as fast, although no rate law or mechanism was proposed. The pH was controlled with NH_3 and was regenerated by treating product NH_4Cl with activated carbon.

A well-known strategy for enhancing metal dissolution kinetics is to decrease the pH. However, a more acidic solution also decreases the driving force for subsequent carbonate precipitation in a single step mineralization process. Therefore, direct carbonation generally requires a solution with a pH close to neutral, which balances the optimal conditions of the two steps of the reaction – metal dissolution and carbonate precipitation. Kinetics of olivine dissolution and subsequent magnesium carbonation at 120 °C were studied by Prigiobbe et al. [182, 183]. The olivine dissolution was performed in a flow-through reactor with varying pH from 2 to 8 and three olivine particle sizes fractions: below 90 µm, 90–180 µm, and 180–355 µm. Dissolution rate was found to increase as the pH was reduced, but decrease with increased particle size. More specifically, the dissolution rate log correlated linearly and negatively with pH. Additive salts and carbon dioxide did not have a measureable effect on the dissolution rate. Carbonation batch reactor kinetics was monitored with online Raman spectroscopy while varying the magnesite supersaturation ratio (S_M). For $S_M < 3$, no magnesite precipitation occurred. Direct magnesite precipitation was observed when S_M was in the range of 3–9.

Simultaneous precipitation of magnesite and hydromagnesite was observed when $S_M > 9$, although the hydromagnesite presence slowed further growth kinetics. The authors also discussed appropriate operating conditions for conducting both the dissolution and carbonation in one step, although no specific work was undertaken towards this one step process.

A magnesium silicate source well below 100 μm in particle size was shown to be crucial for achieving effective carbonation. Eikeland et al. [184] reported one of the fastest to date complete conversions for the carbonation reaction of Mg-rich olivine under supercritical conditions, with the addition of $NaHCO_3$ and NaCl to catalyze the reaction. A 70% conversion was achieved in 2 hours, using 10 μm olivine particles, while a 100% conversion was achieved within 4 hours. The CO_2 sequestration rate was found to be highly dependent on the applied temperature and pressure, as well as the addition of $NaHCO_3$.

Ryu et al. [185, 186] studied carbonation of chrysotile and tremolit and observed morphological changes.

3.2.2 Indirect Carbonation

Direct carbonation methods are generally kinetically slow [11]. The speed of the carbonation process can be increased by breaking the process up into multiple, kinetically faster steps. There are a variety of indirect methods being studied, most of which involve varying the pH of the solution [187, 188]. Generally, indirect carbonation involves a minimum of two steps: extraction of the Ca or Mg reactive components, and reaction with carbon dioxide to form carbonates. Since the dissolution of the silicates requires a low pH, while the precipitation of the carbonates requires a higher pH, the key to success could be to keep the two reactions separate. This phenomenon has led to the development of indirect carbonation techniques, e.g. two-stage or pH swing routes.

Acid Ion Extraction

Use of acidic solutions can enhance the rate and extent of leaching of divalent cations (Ca/Mg) from their mineral hosts. The cations can then be carbonated when reacted with carbon dioxide gas. Thus, the overall carbonation rate can be increased simply by the addition of an acidic species before the carbon dioxide is introduced to the metallic species. Baldyga et al. [189, 190] used bicarboxylic acid to accelerate the mineralization process. An additional step for neutralizing the solution is necessary to bring the pH into range for carbonate formation.

Alexander et al. studied the effect of particle size (median size 61–163 µm), residence time (1–6 hours), and acid concentration (1–5 M sulfuric acid) on leaching efficiency [191]. These conditions were chosen to be milder than found in most studies so that their detailed effects would not be masked by operating under strong conditions (e.g. concentrated acid use). Even at these milder experimental conditions, acid strength was still the dominant factor affecting leaching potential. Leaching rate increased for particle sizes at and below 125 µm. The serpentine elemental composition changed as the particle size was reduced due to differing grinding effects upon varying elements. For example, the smallest particle size fraction contained the least amount of iron, and magnesium content varied between the particle size fractions. Stronger acidic conditions were found to remove more water from the serpentine, although the net effect of the water removal was undetermined. In previous work the dehydroxylation of the serpentine proved critical to carbonation [7]. The authors theorized that under milder acidic conditions, longer tests (than were performed) would be required in order to observe any residence time effect.

Van Essendelft and Schobert focused on serpentine leaching, testing four acids as leaching agents [192]. They performed a kinetic study of magnesium leaching with concurrent grinding. The grinding action was found to increase the degree of leaching, but high levels of mixing action actually reduced the grinding contact area and were a leaching hindrance. The authors found that surface reaction was limiting during the initial stages while diffusion through the silica layer surrounding the unreacted core governed the reaction at later stages. The grinding action increased magnesium leaching by breaking down and effectively thinning the silica layer that forms on the outside of the particles, thus increasing diffusion through the silica as opposed to exposing fresh surface area. The study also attempted to fit the data obtained based upon the reactivity of the surface groups and a shrinking core kinetic model. Experimentally measured particle size distributions were used as a model input, but poor agreement between predicted and observed conversion data resulted when those distributions were implemented. The discrepancy was attributed to the model algorithm assuming spherical serpentine particles when in fact the particles were highly non-spherical and fibrous in shape. The model fit was improved when the semi-empirical Rosin-Rammler bimodal particle size distribution was used to more accurately represent the serpentine feed material.

pH Swing

Magnesium and calcium leaching is generally more effective in acidic conditions, while the desired final carbonate production precipitates more easily under basic conditions. Thus, mineral carbonation rates can be further enhanced by treating the system with two separate, successive addition steps: an acid followed by a base, referred to as the pH swing method. For example, Li et al. studied the carbonization of serpentine with an HCl magnesium leaching step followed by precipitation of magnesium carbonate with NaOH using a simulated flue gas [193]. The best results were heat treated serpentine at 650 °C prior to acid leaching with a 98.8% conversion of the Mg^{2+} in the liquor. Reaction temperature was 90 °C and hydro-magnesite ($Mg_5(CO_3)_4(OH)_2(H_2O)_4$) was produced which was found to be stable with respect to CO_2 release up to 450 °C. Gas pressure was not mentioned. For this study, the acid and base material came from electrolysis of ocean water.

Kodama et al. used a strong acid – weak base solution ($HCl/NH_4Cl–NH_3$) for carbonation of steelmaking slag at reaction temperatures of 40 °C, 60 °C, 80 °C, and 90 °C and atmospheric pressure. The ammonium chloride promoted calcium leaching, with conversions up to 60% and a liquid ammonia byproduct [194]. As leaching continued and the chloride ion concentration dropped, the ammonia dissolved into the water, elevating the pH and promoting calcium carbonate precipitation. The temperature of the precipitation step was found to strongly control the extent of conversion and morphology. The precipitation reaction also regenerated NH_4Cl, offsetting the need for an acid evaporation step, although NH_3 recovery and feed preparation costs remain high for the process. The total energy consumption of the process was estimated to be about 300 kW·h/t-CO_2 converted, with feed grinding comprising the majority of that demand. The cost would be \$60/t-CO_2 sequestered for a \$0.20/kW·h electricity rate. The authors also suggest that this particular method could be extended to silicate minerals and other industrial byproducts.

Wang and Maroto-Valer [195, 196] used ammonium salt for dissolution of serpentine to further mineralization reaction. A serpentine mineralization process using a mixture of concentrated nitric and hydrochloric acids as the magnesium leaching agent was studied by Teir et al. [197]. After leaching at 70^{o}C, a magnesium salt was precipitated by filtering out the silica precipitate, then boiling away the acid, which could then be reused. Carbon dioxide was then bubbled through the resultant magnesium salt solution, resulting in the final hydromagnesite product. During the final mineralization step, the pH was controlled via sodium hydroxide addition. Although the process was able to successfully convert most of the carbon dioxide to hydromagnesite, the cost of the large amounts of acid and sodium hydroxide prevent the process from being economically viable. The authors postulated that the overall costs could be reduced by finding a market for the product materials (hydromagnesite, copper, and chromium extracted from the original serpentine) or finding cheaper acid/base alternatives. The same group continued this research effort by investigating lower cost reduced acid concentration (0.1–0.5 M) leaching agents [198]. However, the magnesium leaching potential was greatly reduced with these acids. The study also looked at replacing the energy intensive acid solvent evaporation step using excess serpentine in an attempt to neutralize the acid, however, no improvement of magnesium leaching was observed. The study concluded that the acid evaporation step is necessary and that future efforts should focus on development of a method to recycle the acid and base materials to lower operating costs.

Magnesium hydroxide feed materials have better carbonation kinetics compared to magnesium silicate materials, so a new method for $Mg(OH)_2$ preparation from serpentine using a pH swing method was proposed by Lin et al. [199]. Magnesium ions were first leached with HCl, and then SiO_2 was precipitated by the addition of NaOH to a solution pH of 8. Further addition of NaOH to pH 11 precipitated $Mg(OH)_2$. Hydroxide conversion greater than 90% with high surface area product was reported. This method was followed up with a TGA study of the gas–solid CO_2–$Mg(OH)_2$ carbonation reaction. The formation of a carbonate monolayer on the particle surface was found to hinder further reaction. The amount of carbon dioxide fixation was governed by the crystal domain size (domain boundary area).

Fagerlund et al. are investigating the production of magnesium hydroxide (brucite, $Mg(OH)_2$) from the addition of ammonium sulfate to serpentine [200]. In the proposed process, magnesium sulfate precipitates out and is then reacted with ammonium hydrate to form magnesium hydroxide and regenerated ammonium sulfate. Current efforts for this process are focused on the optimization of reaction conditions as well as near 100% recovery of the ammonium sulfate, ammonia, and sulfur dioxide byproducts. A process for Mg^{2+} extraction using a high temperature fluidized bed reactor is being explored as an alternative to aqueous carbonation.

Azadarpour et al. [201] reviewed the mineral carbonation with minerals rich in calcium and magnesium, via pH swing process for the formation of calcium and magnesium carbonates.

Wollastonite carbonation at ambient conditions utilizing sulfuric acid leaching of calcium, followed by ammonia salt treatment, was used by Ding et al. [202]. The crystal structure of the wollastonite was destroyed during the acid leaching stage, resulting in fibrous and sheet-line basanite and granular calcium carbonate. Grinding the wollastonite to 20 µm particle size and utilizing ammonium salt during the carbonation were the key parameters that increased the maximum carbonation conversion up to 91.1%.

Indirect Gas–Solid Carbonation

The carbonation of calcium or magnesium oxide/hydroxide proceeds much faster than direct carbonation of the base silicates. However, the Ca and Mg still need to be extracted from the matrix, requiring high temperatures (600 °C) and/or pressures (100 bar) or the use of a pH-altered solution. There has been considerable recent effort by a group in Finland exploring an indirect method for gas–solid carbonation of calcium or magnesium oxide/hydroxide [162]. The energy efficiency of the serpentine carbonation processes was evaluated by calculating the exergy of product process gas streams. The formation of both of the reactants was included in the energy analysis: the oxide was produced directly from serpentine and the hydroxide resulted from hydration of the oxide. The study concluded that the process route utilizing magnesium hydroxide (a three-step process) was more energy efficient. The researchers claim that since the carbonate minerals are thermodynamically more stable than the silicates and the overall chemical reaction is exothermic, the process can in theory be carried out with low or even negative energy input. The authors are continuing this work by optimizing a fluidized bed reactor for magnesium hydroxide carbonation at elevated temperature and pressure [200].

In situ kinetic measurements of $Ca(OH)_2$ carbonation using an infrared microscope coupled to a reaction cell were performed by Montes-Hernandez et al. [203]. The hydroxide ion consumption and production of water and calcium carbonate were monitored as a function of time. They observed the passivation effect of a dense layer of carbonate forming around the $Ca(OH)_2$ particles. The study discovered that the adsorption of water onto the surface of the reacting particles served to enable the carbonation of the particles at lower temperatures than usual, down to 30 °C. A pseudo-second order model was applied to the carbonation in the presence of adsorbed water kinetic data. The model identified three stages of the reaction: an initial fast mass transfer step, a slow mass transfer equilibration step, and a diffusion controlled (or passivation layer) step. When the adsorbed water was removed prior to CO_2 addition, no carbonation was observed at low temperatures (30 °C). In order to activate this dry carbonation route, the authors found that the temperature had to be elevated up to 300 °C. A reaction mechanism was posited for the dry gas–solid carbonation route involving a high temperature requirement that allows for atomic excitation and migration of solid-bound oxygen atoms towards adsorbed gaseous CO_2.

The effect of the presence of water during the carbonation of portlandite [$Ca(OH)_2$] in supercritical CO_2 at elevated temperature and pressure was investigated by Regnault et al. [204]. The thrust of the study was to examine stability of well cements in geologic sequestration of CO_2. Carbon dioxide is a non-polar solvent and is not able to affect the movement of ionic species away from reacting particles. When carbonation took place in dry supercritical CO_2, product $CaCO_3$ tended to form on the portlandite surface, hindering further reaction as a passivation layer. In contrast, the extent of carbonation was increased when water was present, as the polar water molecules attracted ionic species and moved them away from the portlandite surface. Thus, the $CaCO_3$ precipitate formed away from the surface and did not result in a diffusion barrier as others have recently reported [164, 167, 171, 179, 199, 200, 203].

3.2.3 Feed Activation

The reactivity of carbonation reactions can generally be improved via feed activation. The activation can be thermal, mechanical, chemical, or some combination of the three. Many recent carbon mineralization studies have utilized some sort of feed activation method [171, 172, 180, 191, 192, 193, 197, 199, 205] [206, 207, 208] even if the activation effectiveness was not specifically studied. Unfortunately, feed activation methods tend to be costly and energy intensive. A major contribution to the high energy demand of both direct and indirect ex situ mineralization processes is the energy required for particle size reduction of mineral feedstock materials, which increases the effective surface area. For example, energy consumed in grinding Ca or Mg silicate feedstock in preparation for mineralization can be as high as 75% of the total energy cost of the carbonation process [179]. Alternative industrial waste feedstock materials such as furnace bottom ash and fly ash can help to reduce this energy requirement as they generally exist as fine particles.

Maroto-Valer et al. conducted various thermal and chemical activations upon serpentine material and subsequently tested the carbonation potential of the activated feed [166]. Thermal activation comprised of heat treatment under air and steam at 300 °C and 650 °C, resulting in water removal with little impact on specific surface area. The lower temperature activation treatments only removed adsorbed water and had little effect on carbonation rate. The higher temperature steam activation also removed surface hydroxyl groups, smoothing out the particle surfaces and exfoliating smaller particles. Carbonation conversion at 155 °C and 126 atm after 1 hour was improved from 7% to 60% with the higher temperature steam activation; although the authors noted that the heat treatment process was still rather costly. Chemical activation involved treating the serpentine feed with various acids and bases. Chemical activation with sulfuric acid increased the specific surface area, from 8 m^2/g to 330 m^2/g, and removed adsorbed water. The acid treatments began to leach magnesium from the serpentine, leaving behind sub-micron pores that contributed to the drastic increase in surface area. These chemical treatments did not necessarily improve the degree of overall carbonation, but resulted in similar conversion levels at a reduced temperature (20 °C), thus reducing the energy requirements for carbonation.

Serpentine feed heat activation treatment at temperatures from 150 to 950 °C was studied by Li et al. [193]. Adsorbed water was removed at lower temperatures. Above 500 °C, the removal of surface hydroxyl groups, which inhibit carbonation by occupying reaction sites, was also observed. Magnesium solubility due to acid leaching was increased with the heat treatment, although the maximum solubility was observed at only 650 °C. Further temperature increase resulted in the formation of a new, stable serpentine crystal structure that slightly reduced magnesium solubility. Overall, serpentine feed heat treatment doubled the carbonation extent.

As part of their evaluation of the aqueous direct carbonation of olivine, wollastonite, and serpentine, Gerdemann et al. investigated the effect of feed treatment on the carbonation rate [14]. Various grinding techniques were used to prepare feed for carbonation tests on particle sizes less than 75 µm, 38 µm, and 4 µm. The reaction rate was found to increase with decreasing particle size (or increasing specific surface area). A significant increase in reaction rate was observed with particles less than 4 µm due to an increase in surface area and the disruption of the mineral crystal structure. Unfortunately, achieving such a small particle size is extremely energy intensive, estimated by the authors to be as high as 230 kW·h/ton for a three stage crushing and grinding process. The effect of heating of the serpentine feed to 630 °C was also investigated. The heating process was able to remove chemically bonded water and increase the carbonation reaction rate. A direct correlation of water content of serpentine feed and carbonation was observed, as lower H_2O content led to greater extent of carbonation. The energy required for the heat activation process was estimated to be roughly 300 kW·h/ton for antigorite and lizardite serpentines. All treatment techniques also allowed the carbonation process to take place at lower temperatures, pressures, and duration.

The presence of steam at high relative humidity caused drastic acceleration in the rate of carbonation of magnesia, MgO and brucite, $Mg(OH)_2$ observed in a small-scale experimental study [209]. The irregular reaction was triggered by spontaneous and repeated condensation and re-evaporation of water micro-droplets. Conversion to magnesite, ($MgCO_3$) and/or hydromagnesite, $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ was achieved within a few hours under very mild conditions (<200 °C, <10 bar). It was observed that carbonation was even possible in simulated flue gas below 45 °C. Pre-dampened brucite seemed to carbonate faster than the dry form, as long as there was no passivation layer due to excess water condensation.

In the aforementioned study by Kodama et al., the effect of steelmaking slag particle size from 63–2,000 µm on carbonation conversion was measured [194]. The conversion was found to increase as the particle size was reduced, but the authors reported that the reaction is not completely controlled by the reactive surface area. The high cost of feed grinding was also addressed. The overall energy consumption of the process was roughly estimated at 300 kW·h/t-CO_2, with more than half of this power requirement stemming from the slag grinding process.

Carbonation kinetics has also been measured where oxalic acid ($H_2C_2O_4$) was utilized as the carbon dioxide source [205]. A supercritical water–carbon dioxide mixture was obtained by decomposing oxalic acid along with various magnesium-rich minerals (orthoproxene, chrysotile, and olivine) at temperatures of 400–500 °C and a pressure of 1 kbar. The authors observed that the carbonation reaction was coupled with the serpentinization of olivine and that the controlling mechanism was the silicate dissolution/magnesite precipitation reactions at the fluid–silicate interface. Olivine was found to be the most reactive; reactions in general were favored in the presence of water and sodium chloride.

Flue-gas desulfurization (FGD) gypsum as a source of calcium was proposed as a potential feedstock in the most recent study by Azdarpour et al. [210]. The purpose of this laboratory study was to investigate the effects of reaction parameters such as CO_2 pressure, reaction temperature, particle size, and ammonia solution concentration on calcium carbonate purity through Merseburg process. High purity calcium carbonate was produced when reaction temperature and CO_2 pressure were increased to 400 °C and 70 bar, respectively. Experimental results showed that reducing particle size was also effective in enhancing the calcium carbonate purity in which the smallest particles produced higher purity calcium carbonates rather than larger particles. The role of ammonia solution on calcium carbonate purity was found to be beneficial.

3.2.4 Other Technologies

Flow Reactor

Huntzinger et al. conducted two studies of gas–solid carbonation of waste cement kiln dust in a packed bed reactor under ambient temperature and pressure [211, 212]. For these studies, the packed bed was compacted core samples of the kiln dust; gas containing carbon dioxide then flowed through the compacted core. The water content and the CO_2 concentration of the flow gas were varied. The carbonation process was a direct route with calcium carbonate the final product. Overall, similar conversions to batch reactor conversions were obtained and the gas flow rate was determined to not be a limiting factor. More experimental work will be required in order to differentiate the effects of feedstock material compositional variation from the effects of the reactor operating conditions.

Kashef-Haghighi and Ghosal [213] proposed using CO_2-containing flue gas for concrete (calcium silicate) carbonation for cement production in a packed bed gas flow reactor. Concrete was utilized as the packing material while the gas flow was a simulated flue gas with 20% CO_2 at ambient pressure and temperature. Conversions were of the order of 18%, comparable to a batch reactor system while consuming less total energy. The authors found that the product carbonate precipitate reduced pore volume, and thus mass transfer to the solid. Another reaction inhibiting effect was the loss of surface area in the concrete columns due to silica–cement bonding.

The dependence of the olivine dissolution rate on factors such as pH, CO_2 pressure, salinity, and grain size has been explored through experiments in a high pressure flow reactor operated from 90–150 °C and modeling [182, 183, 214]. In these experiments, the magnesium and silica reactor outlet concentrations were measured in situ with an ion chromatograph and a spectrophotometer. Temperature, pH, and grain size had a noticeable effect on the dissolution kinetics, however, CO_2 pressure and salinity did not have a significant effect. The dissolution rate was fitted to a linear regression kinetic law, utilizing a population balance equation to account for the particle size distribution. The log of the dissolution rate was found to vary linearly with pH, indicating that the dissolution mechanism is H^+ adsorption on the olivine particle surface, which is in agreement with previous work. The same group also used in situ Raman spectroscopy to measure the effect of supersaturation and solution composition on magnesium carbonate precipitation kinetics from magnesium chloride in a flow-through reactor at 120 °C and 100 bar [183]. The magnesium ion concentration was found to control the carbonate form that precipitated: low magnesium levels resulted in the formation of magnesite while high levels yielded a mix of magnesite and hydromagnesite.

Fluidized Bed

Research into the use of fluidized beds for carbonation is increasing and appears to be a cost effective method for improving reaction kinetics at lower temperatures and pressures. A group at the University of Wyoming is working on a proprietary technique for carbon mineralization utilizing both flue gas CO_2 and combustion fly ash [215]. Experiments were conducted in a fluidized bed of fly ash (predominantly SiO_2 with 10–50% CaO, Fe_2O_3, or MgO) with flue gas flow (mostly N_2 with 2–6% CO_2). This is believed to be the first attempt at simultaneous direct capture and carbonation at the point source of CO_2 emissions. A major cost of implementation of wide-scale carbon capture and storage is in the transportation of CO_2, most likely requiring a network of pipelines to be built. Elimination of the need for transport would serve to decrease costs substantially.

Fagerlund et al. are in the early stages of a study involving the carbonation of magnesium hydroxide in a fluidized bed at supercritical CO_2 conditions (600 °C, 100 bar) [200]. The authors believe that the particle–particle interactions and collisions in the fluidized bed will work to continually expose fresh, unreacted core material to the CO_2 by breaking down and removing the rate limiting diffusion barrier carbonate product layer, thereby increasing the achievable upper conversion level. Fagerlund and Zevenhoven [216] conducted an experimental study of $Mg(OH)_2$ carbonation in a fluidized bed reactor.

Other Methods

Li et al. [193] proposed seawater electrolysis to generate the acid (HCl) and base (NaOH) pair required for the pH swing carbonation of serpentine. The authors posit that the electrolysis process will be more efficient than traditional routes for acid and base synthesis. Bang et al. [217] studied precipitation of calcium carbonate by carbon dioxide microbubbles. López-Periago et al. [218] observed higher rates of conversion from CaO or $Ca(OH)_2$ to $CaCO_3$ using CaO nanoparticles as a solid precursor; the use of ultrasound stirring accelerated the kinetics of the carbonation process, thus increasing the calcium carbonate yield.

Hangx and Spiers used a "beach weathering" method for olivine carbonation where the olivine is spread along beaches and allowed to carbonate by reacting with atmospheric CO_2 [219]. The authors used published kinetic data to develop a model for their proposed system, looking at particle sizes ranging from 10 to 1,000 μm. The authors found that the olivine feed material would need to be ground into the 10–50 μm range to achieve realistic carbonation rates. The model also took into account the energy costs and CO_2 emissions for the grinding process. In order to achieve particle sizes in the desired 10–50 μm range, additional grinding costs were found to reduce process efficiency by 5–20%. Time scales for complete carbonation were computed to be of the order of years, but no further energy input would be required once the olivine was transported to beach areas. However, transportation costs may be too high as carbonation times are too slow for the process to be feasible in colder regions that tend to be closer to olivine deposits. Another disadvantage is the potential dust health hazards existing from the deposited beach olivine. The authors conclude that this method would not be viable for large scale CO_2 sequestration, but could exist as a niche method in certain regions.

Vinoba et al. [220] examined CO_2 absorption and mineralization in the amine–CO_2–organometallic calcium precursor system and observed improved catalytic efficiency (1.07×10^4 $M^{-1}s^{-1}$) for the binding between CO_2 and N-methyldiethanolamine, enhanced by the presence of bovine carbonic anhydrase enzyme.

Value-Added Products

The economics of carbon dioxide mineralization could be improved if the mineralization products could be utilized for other purposes or sold for use in other industrial products. The value of such products is critical to making the mineral carbonation technology economically viable in the same way as conventional CCS benefits when combined with enhanced oil recovery (EOR) [9]. Therefore, reuse or resale of the products for other uses should be taken into consideration, especially since the amount of product generated could be quite significant if CO_2 mineralization is performed on a large scale. For example, mined limestone ($CaCO_3$) is calcined to form lime (CaO or $Ca(OH)_2$) for use in a host of industrial products and other applications, the largest of which is cement manufacturing. While liberation of the carbonate CO_2 during this lime production would be undesirable, using mineralized $CaCO_3$ as the lime precursor would result in carbonate ore mining avoidance, a potential net gain. Calcium carbonate is used extensively in cement clinkers and road construction aggregates, and thus could provide a market for mineralized CO_2 fixed as $CaCO_3$. However, one must also consider the potential for release of CO_2 from the carbonated product resulting from the beneficial use.

In another study by the Zevenhoven group, potential markets for carbon mineralization products were examined, including inorganic carbonates such as $CaCO_3$, $MgCO_3$, $NaCO_3$, KCO_3, etc., along with organic carbonates such as polycarbonate and dimethyl/ethyl carbonates [221]. They state that there is a significant demand for precipitated calcium carbonate (PCC), with worldwide production estimated at more than 7 Mt/year, predominantly resulting from limestone calcination. This volume of PCC could be supplanted by carbonation of silicate ores. The authors estimate a net fixation of 0.34 kg CO_2/kg PCC via the acetic acid route using wollastonite. The previously mentioned study by Kashef-Haghighi and Ghosal [213] examined cement production using flue gas CO_2 for concrete (calcium silicate) carbonation, although the paper focused specifically on the carbonation process as opposed to product cement quality or economics. Ferrini et al. stated that their hydrated magnesium carbonate product generated from flushing magnesium-rich brine with CO_2 gas could be used as an acid-resistant building material [181].

4. Discussion and Conclusions

Concerns with anthropogenic CO_2 emissions have in the last decade or so generated a great deal of research in methodologies designed to store carbon. The methods range from deep saline aquifer injection to direct mineral carbonation of ultramafic rock and industrial byproducts as a means to sequester generated CO_2. Nearly all methodologies will necessitate CO_2 separation and capture at the emission source as an integral part of the carbon mineralization process. The ex situ methodologies using mafic/ultramafic rock types and/or industrial byproducts as the cation source must also deal with the sheer feed volume, and the increased product volume, as carbonation results in a weight and volume gain. An uncertain factor that needs further investigation is the ultimate environmental stability of the formed carbonate material [222, 223]. While large surface deposits of silicate minerals occur worldwide, greatly exceeding available quantities of fossil fuels [13], the scale of mining operations could be problematic. Saline injection will require local CO_2 point sources to minimize transportation costs, as well as long term monitoring after the injection period [6, 12]. As a component of saline injection, mineral sequestration within geologic formations (mineral trapping) will have the same requirements. Mineralogy and structure of selected formations can greatly enhance sequestration success; for example, the favorable mineralogy and layered structure of flood basalts provides an injection target with high mineral trapping potential and apparently well isolated zones of high porosity [7, 25, 26]. However, studies suggest that only a small fraction of the injected CO_2 would be mineralized within a few hundred years. More work is required to more fully understand the CO_2-reservoir environment and issues such as host rock stability and caprock permeability and stability [52, 53, 54, 55].

For CO_2–shale reservoir interaction, cation availability is the key parameter affecting the volume of CO_2 trapped, so chemical analysis of these shale formations will be the key as well. Another potential concern is mineral dissolution from initial acidification from the CO_2 injection. Recent results have in fact suggested that CO_2 injection initiates a mineral dissolution/re-precipitation process in shale caprock that may affect the caprock integrity [87]. Other recent work has indicated the likelihood of CO_2 adsorption to shaly caprock [29]. The sorption mechanism and longevity are not yet well understood and must be further investigated. Various geochemical models are being developed to simulate long term reservoir conditions and reactivity in order to more fully address long term stability concerns.

Ultimately, acceptance and implementation of any carbon sequestration methodology will be a social and political decision.

Studies involving the use of industrial byproducts and/or waste as the cation source include: municipal incinerator waste ash, combustion fly ash, steelmaking slag, bauxite residue, cement dusts, concrete, oil shale ash, and paper mill waste. Carbon mineralization routes utilizing these waste streams are generally considered niche remediation applications having the added advantage of sequestering some portion of plant-emitted CO_2. For example, calculations have shown that 1% [116] to 2% [114] of generated CO_2 from municipal waste incinerators can be sequestered along with all of the incinerator ash. For steel/cement/concrete operation, 6–8% of generated CO_2 can be sequestered along with the generated waste ash/slag [136]. Most of these alternative feedstock routes require feed particle size reduction as well as addition of acidic or basic materials in order to achieve acceptable reaction rates. The process economics are worsened due to the material and recovery costs associated with acidic and basic additions and due to costly feed preparation techniques [14]. However, waste stream utilization and carbonation can also serve a secondary purpose of immobilizing potentially hazardous heavy metals [114, 116, 117, 120].

The fraction of total anthropogenic CO_2 emissions that can be sequestered by use of industrial product streams is relatively small [1] since the amount of available feedstock is much less than the emitted CO_2. Still, ex situ carbonation technologies could be useful in the future as a means for individual industries to derive carbon credits if carbon regulation were to ensue, and to potentially stabilize solid waste streams.

While the direct aqueous carbonation route is generally accepted as a promising method [10, 11], research into other ex situ carbonation routes using traditional Ca and Mg silicate feedstock continues, in efforts to reduce energy consumption and improve economics. Using existing proven process technologies, the best case estimated cost for the direct aqueous method is around \$54/t-CO_2 sequestered [14]. At this price, and in the absence of carbon regulation, large scale ex situ carbonation using mineral feedstock is currently economically unfeasible. Feed preparation costs contribute to a significant portion of the overall cost, with estimates for feed preparation costs ranging from as high as 50% [194] to 75% [179] of the total energy requirement for the mineralization process. Therefore, a key driving force for research into alternative ex situ routes is the search for methods that can reduce process costs.

Some of the alternative routes currently being investigated include: direct and indirect dry gas–solid carbonation, acid ion extraction, and pH swing, as well as the use of alternate reactor technologies such as packed beds and fluidized beds. Many of these routes require significant amounts of strong acid and base materials, leading to the recognized need for cheaper acid/base substitutes and acid/base recovery. However, recovery costs still remain high [194, 197, 198, 200] and carbonization extent is low when utilizing cheaper (i.e. weaker) acid/base components [198]. Measuring ex situ CO_2 mineralization kinetics is another key component of recent research, as the carbonation rate contributes to overall process costs. While these kinetic studies have taken place over a variety of routes, a common finding has been the formation of a product passivation layer or diffusion barrier on the feedstock surface that slows down and/or inhibits continued carbonation [164, 167, 171, 179, 199, 200, 203]. Thus, some work has been directed towards removal of that passivation layer via acid treatment or particle agitation, although those treatments, while increasing reaction rates, also further increase costs.

As evidenced by the literature cited here, CO_2 mineralization continues to be the subject of significant study by researchers world-wide. Whether the investigations follow an industrial (ex situ) format, or consider the potential impact of mineralization within geologic formations (in situ), it is clear that reaction of CO_2 with mineral solids will be a vital component of any and all sequestration methodologies.

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