Mineral carbonation for CO₂ storage

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MINERAL CARBONATION FOR CO$_2$ STORAGE

Dissertation submitted to the

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for the degree of

DOCTOR OF SCIENCES

presented by

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Abstract

Anthropogenic greenhouse gas emission contributing to the temperature rise has been scientifically recognized and climate change has become one of the central issues facing our society. Its mitigation is a big technological challenge that must be addressed in the next decades. Among the promptest actions, carbon dioxide capture and storage (CCS) systems are the ones that are considered to be the most promising together with energy conservation and efficiency.

Mineral carbonation of metal-oxide bearing materials such as wollastonite, olivine, serpentine, and industrial alkaline residues ensures the safest CO₂ storage as binds carbon into stable and environmental benign minerals possibly reusable. Based on the reactivity of the starting material, either aqueous carbonation or direct carbonation are recommended.

This work attempted to investigate the thermodynamics and kinetics of the elementary processes (silicate dissolution, carbonate precipitation, and gas-solid reaction) within mineral carbonation by using natural silicate (olivine, (Mg,Fe)₂SiO₄) and industrial alkaline residues (such as air pollution control residues, fly-ash) to finally select optimal operating conditions.

Being silicates less reactive than fly-ash, they must be treated through aqueous mineral carbonation where by releasing cations into water they determine the formation of carbonates upon the reaction of these cations with CO₂. On the other hand, fly-ash can be directly carbonated by a gas-solid reaction.

Aqueous mineral carbonation is a process based on a reaction that is thermodynamically favored and kinetically controlled by mineral dissolution and anhydrous carbonate precipitation such as calcite and magnesite. Mineral dissolution reaction notably favored at high temperature, for small particle size, and low pH can be further enhanced by varying solution composition through the addition of suitable chemicals such as inorganic and organic salts, and CO₂. These additives catalyze the kinetics by modifying the reaction at
the mineral-solution interface. The selection of the chemicals is not straightforward task because their action depends on their composition, the crystal structure of the mineral, and their interaction with the mineral under the applied operating conditions. Inorganic salts such as NaCl and NaNO$_3$ as well as CO$_2$ have been observed to enhance dissolution only through their effect on the pH; whereas organic salts such as sodium citrate and sodium oxalate resulted to accelerate dissolution reaction above pH 5 of one order of magnitude with respect to the same process performed in a organic-free solution. We characterized the thermodynamics as well as the kinetics of mineral dissolution investigating the olivine-salts-CO$_2$ aqueous system modeled with the geochemical software package EQ3/6 and population balance equation model coupled with a mass balance equation. Precipitation reaction of anhydrous carbonates notably enhanced at high temperature, high CO$_2$ partial pressure, and neutral pH is kinetically hindered by the high hydration of the cations and becomes particularly critical in the case of magnesite (MgCO$_3$) precipitation with the formation of unstable and hydrated Mg-carbonates (e.g., MgCO$_3$-3H$_2$O and (MgCO$_3$)$_4$-Mg(OH)$_2$-4H$_2$O). However, these hydrated minerals eventually transform into magnesite, but the water consumption, the sludge volume, as well as the reaction time of the process increase when hydrated crystals form in comparison to a process where direct magnesite precipitation occurs. Therefore, in order to select operating conditions suitable for a direct and a fast formation of magnesite, we undertook a thermodynamics study of Mg-carbonate precipitation using the MgCl$_2$-NaCO$_3$-CO$_2$ aqueous system. We monitored the process with online Raman spectroscopy that allowed to observe the suspension and solution composition over time and we modeled it with the geochemical software package EQ3/6. Moreover, we characterized Mg-carbonate precipitation kinetics by modeling the MgCl$_2$-NaCO$_3$-CO$_2$ aqueous system using population balance equation model (PBE) coupled with a mass balance equation, a geochemical model, and multivariate kinetics modeling.

Direct mineral carbonation is a process based on a reaction that is thermodynamically favored and kinetically controlled by chemical composition of the material. Air pollution control residues such as fly-ash are very reactive and
suitable for a direct carbonation process. In this work, we investigated the kinetics and the extent of the carbonation reaction occurring during direct carbonation of fly-ash with the final aim to evaluate its potential as CO$_2$ storage option. By undertaking a systematic experimental work, we observed that fly-ash converts directly and quickly to stable carbonates such as calcite with the highest reaction extent within a narrow range of temperatures (300-500$^\circ$C), at low partial pressure of CO$_2$ (1 bar), and under 10 vol.% CO$_2$ concentration. This combination of operating conditions would allow to lump capture and storage in a single step process by using flue-gases whose CO$_2$ content is around 10 vol.% directly at a power-plant. However, these residues can only cover a small amount of the total CO$_2$ European storage capacity required to comply with the Kyoto protocol objectives, but the proposed process could be applied to other residues characterized by a high content of free metal oxides and hydroxides, thus increasing the impact of this storage option.
Abstract

E’ stato oramai riconosciuto scientificamente il contributo dei gas serra emessi dall’uomo all’aumento della temperatura terrestre e il cambiamento climatico e’ diventato uno dei problemi centrali che la nostra società deve risolvere. Inoltre, la sua mitigazione e’ una delle piu’ grandi sfide tecnologiche della società contemporanea. Tra le soluzioni di piu’ immediata implementazione le piu’ promettenti sono le tecnologie di cattura e di stoccaggio della anidrite carbonica (CO$_2$) (in inglese, carbon dioxide capture and storage, CCS) nonché’ i sistemi di risparmio energetico e di aumento dell’efficienza.

La carbonatazione minerale di materiali contenenti ossidi di metallo (come wollastonite, olivina, serpentino e residui industriali alcalini) permette uno stoccaggio sicuro della CO$_2$ poiche’ lega il carbonio in minerali stabili e compatibili con l’ambiente come calcite e magnesite possibilmente riutilizzabili. Sulla base della reattivita’ del materiale di partenza, due processi di carbonatazione minerale sono possibili carbonatazione minerale in fase acquosa oppure carbonatazione minerale diretta.

In questo lavoro di tesi, la termodinamica e la cinetica dei processi elementari (dissoluzione dei silicati, precipitazione dei carbonati, e la reazione di gas-solido) che accadono durante il processo di carbonatazione minerale sono stati studiati. Due tipi di materiali sono stati usati: un silicato naturale di magnesio ovvero l’olivina ((Mg,Fe)$_2$SiO$_4$) e dei residui industriali alcalini prelevati da un sistema di controllo delle emissioni inquinanti (fly-ash), Infine, le condizioni operative ottimali per un processo che utilizzi questi minerali sono state selezionate.

Poiche’ i silicati sono meno reattivi delle fly-ash, essi possono essere carbonatati solo mediante un processo che preveda una loro dissoluzione in acqua dove rilasciando cationi determinano la precipitazione di carbonati a seguito della reazione tra questi cationi e l’anidrite carbonica. Diversamente, le fly-ash possono essere carbonatate direttamente mediante una reazione di gas-solido ponendole a contatto con l’anidrite carbonica.
La carbonatazione minerale acquosa è un processo basato su una reazione favorita termodinamicamente e la cui cinetica è controllata dalla dissoluzione dei silicati e la precipitazione di carbonati non idratati come calcite e magnesite. La reazione di dissoluzione dei silicati è un processo favorito ad alte temperature, usando piccole dimensioni delle particelle del minerale, e a pH acidi. Inoltre, la cinetica della dissoluzione può essere ulteriormente migliorata modificando la composizione della soluzione in cui il minerale è disceso aggiungendo sali organici ed inorganici e anidrite carbonica. Questi additivi chimici catalizzano la cinetica modificando il meccanismo di reazione all’interfaccia solido-liquido. La selezione della sostanza chimica più adatta non è facile perché la sua capacità dipende dalla sua composizione, dalla struttura cristallina del minerale, e dalla sua interazione con il minerale alle condizioni operative applicate. L’effetto di sali inorganici come NaCl e NaNO₃ e della CO₂ è stato osservato dipendere solo dalla loro capacità di modificare il pH della soluzione; mentre i sali organici come l’ossalato e il citrato di sodio hanno determinato oltre pH 5 un tasso di dissoluzione di un ordine di grandezza più alto rispetto ad una dissoluzione condotta in una soluzione senza questi sali. In tutti gli studi di dissoluzione, la termodinamica e la cinetica del processo sono state caratterizzate studiando un sistema acquoso del tipo olivina-sali-CO₂ e modellandolo usando l’equazione di bilancio di popolazione associata ad un’equazione di bilancio di massa. La reazione di precipitazione dei carbonati non idrati è un processo favorito ad alte temperature, ad alte pressioni parziali di CO₂, e a pH neutri, ma è inibita cineticamente dall’alta idratazione dei cationi e diventa particolarmente problematica nel caso della precipitazione dei carbonati determinando la formazione di carbonati di magnesio idrati e instabili (come per esempio, MgCO₃·3H₂O e (MgCO₃)₄·Mg(OH)₂·4H₂O). Questi carbonati si possono trasformare in magnesite essendo questo il carbonato di magnesio più stabile, ma il consumo di acqua, il volume dei solidi prodotti nonché’ il tempo di reazione augmentano quando questi cristalli idrati precipitano rispetto ad un processo dove invece avviene la precipitazione diretta di magnesite. Quindi al fine di selezionare condizioni operative che determinino la precipitazione diretta e rapida di magnesite, lo studio della ter-
modinamica della precipitazione dei carbonati di magnesio e’ stato affrontato su un sistema acquoso del tipo MgCl$_2$-NaCO$_3$-CO$_2$. Il processo e’ monitorato mediante spectroscopia Raman che ha permesso di osservare l’evoluzione nel tempo della composizione della soluzione e della sospensione e modellato usando il programma di modellazione geochimica EQ3/6. Inoltre, la cinetica della precipitazione dei carbonati di magnesio e’ stata valutata modellando il sistema acquoso MgCl$_2$-NaCO$_3$-CO$_2$ con l’equazione di bilancio di popolazione associata ad un’equazione di bilancio di massa, ad un modello geochimico, e ad alla modellazione cinetica multivariata.

La carbonatazione diretta e’ un processo basato su una reazione termodinamicamente favorita e cinematicamente controllata dalla composizione chimica del materiale. Residui industriali alcalini derivanti da un sistema di controllo delle emissioni inquinanti (fly-ash) sono molto reattivi e adatti per un processo di carbonatazione diretta. In questo lavoro di tesi, abbiamo studiato la cinetica e la conversione della reazione durante la diretta carbonatazione delle fly-ash con lo scopo finale di valutare la potenzialità di questo processo per lo stoccaggio della CO$_2$. Studiando in maniera sistematica questa reazione, abbiamo osservammo che questo materiale puo’ carbonatare direttamente e convertirsi velocemente in carbonati stabili come la calcite. Il tasso di conversione massimo e’ stato ottenuto a temperature tra 300-500$^{\circ}$C, a bassa pressione parziale di CO$_2$ (1 bar), e utilizzando un gas contenente 10 vol.% di CO$_2$. Questa combinazione di condizioni operative permette di unire cattura e stoccaggio in un singolo stadio di processo usando direttamente emissioni gassose da processi di combustione essendo il loro contenuto di CO$_2$ circa del 10 vol.. Tuttavia, la carbonatazione delle fly-ash coprirebbe solo una piccola frazione della quantità totale di CO$_2$ da stoccare a livello europeo per rispettare gli obiettivi previsti dal protocollo di Kyoto. In ogni caso, il processo di carbonatazione diretta qui proposto potrebbe essere applicato ad altri residui industriali alcalini la cui composizione e’ simile a quella delle fly-ash ovvero con un alto contenuto di ossidi ed idrossidi di metalli. In questo modo, il contributo di questo processo allo stoccaggio della CO$_2$ sarebbe maggiore.
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Chapter 1

Introduction

1.1 Climate Change

It was in the 1830s that the first hypothesis was made about a large change in climate on the Earth (Hulme, 2009). The author was a Swiss scientist, J. L. R. Agassiz. From the variation of the extension of the glaciers on the Alps, he developed the glacial theory of climate change in the 1860s. The idea that variation of CO$_2$ in the atmosphere could induce such a climate change was considered by J. Tyndall 1860s. In his experiments based on the Fourier’s theory of ‘greenhouse gases’, he showed for the first time that if the human activity alters the concentration of these gases it can affect the temperature regulation of the planet. It was then S. Arrhenius in the 1890s the first one that undertook the experiments and the calculations of the sensitivity of the world temperature to CO$_2$ concentration in the atmosphere. He demonstrated experimentally and by simple calculations how changes in the CO$_2$ con-
centration could affect glacial climate, establishing in this way the theory of global climate change based on CO₂ concentration changes. In the 1938, G. S. Callendar linked systematically together the three aspects of anthropogenic climate change: Greenhouse effect, rising concentration of CO₂ in the atmosphere, and the increase in world temperature. Last century, Keeling was the first scientist that started to implement measurement stations of CO₂ concentration in the atmosphere, observing in this way its increase over time; and Manabe was the first scientist to build interconnecting models of the earth to describe climate change. Now these models have become very sophisticated by combining several oceanic and atmospheric phenomena and the Hadley Centre in UK is at the forefront in developing them (Heffernan, 2010).

In 1989 Intergovernmental Panel on Climate (IPPC) was founded by United Nations Environment Programme and the World Meteorological Organization bringing together the most expert scientists about climate change. However, IPPC expressed only in its Forth Assessment Report that a ‘very likely’ connection between rasing temperature and the emission of anthropogenic greenhouse gases exists (IPCC, 2007). In this report, IPPC brings together evidence of climate change by reporting long record of temperature, sea level, snow and ice extent measurements over the globe (Figure 1.1). These are only some of the indicators that together with changes in the human and biological systems, vegetation, and weather extreme events can give an overall picture of the climate change impact.

The most important anthropogenic greenhouse gas (GHG) is CO₂. Its annual emission has grown between 1970 and 2004 by about 80%, from 21 to 38 Gt. The largest growth in GHG emissions between 1970 and 2004 has come from energy supply, transport and industry, while residential and commercial buildings, forestry (including deforestation) and
Figure 1.1: Observed changes in (a) global average surface temperature; (b) global average sea level from tide gauge (blue) and satellite (red) data; and (c) Northern Hemisphere snow cover for March-April. All differences are relative to corresponding averages for the period 1961-1990. Smoothed curves represent decadal averaged values while circles show yearly values. The shaded areas are the uncertainty intervals estimated from a comprehensive analysis of known uncertainties (a and b) and from the time series (c) (IPCC, 2007).
agriculture sectors have been growing at a lower rate over the years. Global increases in CO$_2$ concentrations are due primarily to fossil fuel use and the global atmospheric concentration of CO$_2$ increased from a pre-industrial value of about 280 ppm to 389 ppm in March 2010 (NOAA, 2010). Since fossil fuels are projected to maintain their dominant position in the global energy mix to 2030 and beyond, CO$_2$ emissions from energy use between 2000 and 2030 are projected to grow 40 to 110% over that period.

Global efforts to mitigate climate change are guided by projections of future global surface temperature. Based on climate sensitivity defined as the equilibrium global average surface warming following a doubling of CO$_2$ concentration, global temperature rise should not exceed 2°C from the pre-industrial temperature. Based on that, several emission scenarios (SRES) have been drawn to forecast CO$_2$ concentration and global temperature change. Figure 1.2 shows the Global GHG emissions based on these SRES.

Projections of the global warming as a consequence of these drawn scenarios show that warming is expected to be greatest over land and at most high northern latitudes, and least over the Southern Ocean (near Antarctica) and northern North Atlantic, with the possibility to exceed the 2°C threshold (Figure 1.3).

To reduce the magnitude of change, adaptation by sustainable development and mitigation by decreasing GHG emission must be considered. Mitigation consists in actions to be taken to change the impact of our society on CO$_2$ emissions. Therefore, changes in sectors such as energy supply, transport, buildings, industry, agriculture, forestry and waste are envisaged. Regarding energy supply, mitigation consists in technology and practice changes, e.g., improved supply and distribution efficiency, fuel switching from coal to gas, nuclear power, more use of renewable
1.1 Climate Change

Figure 1.2: Global GHG emissions (in GtCO$_2$-eq per year) in the absence of additional climate policies: Six illustrative SRES marker scenarios (coloured lines) and 80th percentile range of recent scenarios published since SRES (post-SRES) (gray shaded area). Dashed lines show the full range of post-SRES scenarios. The emissions include CO$_2$, CH$_4$, N$_2$O and F-gases. The A1 storyline assumes a world of very rapid economic growth, a global population that peaks in mid-century and rapid introduction of new and more efficient technologies. A1 is divided into three groups that describe alternative directions of technological change: fossil intensive (A1FI), non-fossil energy resources (A1T) and a balance across all sources (A1B). B1 describes a convergent world, with the same global population as A1, but with more rapid changes in economic structures toward a service and information economy. B2 describes a world with intermediate population and economic growth, emphasizing local solutions to economic, social, and environmental sustainability. A2 describes a very heterogeneous world with high population growth, slow economic development and slow technological change (IPCC, 2007).
1. Introduction

Figure 1.3: Left panel: Solid lines are multi-model global averages of surface warming (relative to 1980-1999) for the SRES scenarios A2, A1B and B1, shown as continuations of the 20th century simulations. The orange line is for the experiment where concentrations were held constant at year 2000 values. The bars in the middle of the figure indicate the best estimate (solid line within each bar) and the likely range assessed for the six SRES marker scenarios at 2090-2099 relative to 1980-1999. The assessment of the best estimate and likely ranges in the bars includes the Atmosphere-Ocean General Circulation Models (AOGCMs) in the left part of the figure, as well as results from a hierarchy of independent models and observational constraints. Right panels: Projected surface temperature changes for the early and late 21st century relative to the period 1980-1999. The panels show the multi-AOGCM average projections for the A2 (top), A1B (middle) and B1 (bottom) SRES scenarios averaged over decades 2020-2029 (left) and 2090-2099 (right) (IPCC, 2007).
1.1 Climate Change

Figure 1.4: Cumulative emissions reductions for alternative mitigation measures for 2000-2030 (left-hand panel) and for 2000-2100 (right-hand panel). The figure shows illustrative scenarios from four models (AIM, IMAGE, IPAC and MESSAGE) aiming at the stabilisation at low (490 to 540 ppm CO₂-eq) and intermediate levels (650 ppm CO₂-eq) respectively. Dark bars denote reductions for a target of 650 ppm CO₂-eq and light bars denote the additional reductions to achieve 490 to 540 ppm CO₂-eq. Some models do not consider mitigation through forest sink enhancement (AIM and IPAC) or CCS (AIM) and that the share of low-carbon energy options in total energy supply is also determined by inclusion of these options in the baseline. CCS includes CO₂ capture and storage from biomass. Forest sinks include reducing emissions from deforestation. The figure shows emissions reductions from baseline scenarios with cumulative emissions between 6000 to 7000 GtCO₂-eq (2000-2100) (IPCC, 2007).

heat and power (hydropower, solar, wind, geothermal and bioenergy), and applications of carbon dioxide capture and storage (CCS). Figure 1.4 shows a comparison of these technology mitigation options. Energy conservation and efficiency, adoption of renewable energy, and implementation of CCS are the ones with the biggest impact on the short term.
1.2 CO₂ capture and storage (CCS)

Reduction in CO₂ emissions by fossil fuel combustion requires the implementation of Carbon Capture and Storage (CCS) systems. These first concentrate (capture) CO₂ from diluted sources to a rather pure CO₂ stream, which is then conveyed to storage. The net reduction of emissions to the atmosphere through CCS depends on the fraction of CO₂ captured, the increased CO₂ production resulting from loss in overall efficiency of power plants or industrial processes due to the additional energy required for capture, transport and storage, any leakage from transport and the fraction of CO₂ retained in storage over the long term. A power plant equipped with a CCS system (with access to geological or ocean storage) would need roughly 10-40% more energy than a plant of equivalent output without CCS, of which most is for capture and compression (IPCC, 2005). CCS could reduce carbon emissions from power stations by 80-90%, although after taking life-cycle factors into account, that number could decrease to as little as 67% (Schiermeier et al., 2008). Figure 1.5 shows an overview of the CCS systems.

1.2.1 CO₂ capture

The aim of CO₂ capture systems is to generate an almost pure CO₂ gas stream from deluded flue gases produced from the combustion of fossil fuels (coal, natural gas, and oil) and biomass. In this way, the energy costs of transport to the storage site and storage itself are significantly reduced.

In the case of fossil-fuel combustion plants in air the CO₂ concentration ranged between 3-15 vol.%, it can increase up to 60 vol.% in integrated gasification combined cycles (IGCC), and to 80 vol.% in oxyfuel
1.2 CO₂ capture and storage (CCS)

Figure 1.5: Schematic diagram of possible CCS systems showing the sources for which CCS might be relevant, transport of CO₂ and storage options (IPCC, 2005).
plants (IPCC, 2005). Three are the main capture systems, namely: Post-combustion, oxyfuel, and pre-combustion which all aim at reducing the CO₂ emissions by 80-90%, but with an increase of energy cost between 20 and 85% depending on power-plant technology applied.

In post-combustion systems consist in the upgarding of exist power-plant with CO₂ separation technology. In these plants, CO₂ is captured by absorption based on organic solvents such as monoethanolamine (MEA), adsorption using zeolites and organic carbons, and through separation using polymeric and ceramic membranes. Oxyfuels systems consist in the combustion of fossil fuels in an almost O₂-pure atmosphere generating a CO₂ concentrated stream (e.g., 80-98 vol.%) that can be further treated by applying the same captures technologies used in the post-combustion systems. Pre-combustion systems process fossil fuels usually in IGCC power plant with steam and air or oxygen producing an hydrogen- and carbon monoxide-rich gas stream. Then, CO is reacted with steam in a shift converter to form CO₂ and hydrogen resulting in a high-pressure gas stream containing high CO₂ concentration between 15 and 60 vol.%. The principal chemical component are then separated using physical or chemical adsorption, membrane, and adsorption to produce a carbon-free energy carrier such as hydrogen and CO₂ ready to be transported.

The CO₂-concentrated gas stream is dehydrated (with a relative humidity less than 60 %), pressurized up to 100-800 bar reaching the supercritical state, and transported to the storage site.

1.2.2 CO₂ storage

The most accredited CO₂ storage options rely on in situ technologies, which consist in injecting CO₂ into deep saline aquifers, coal bed seams
(enhanced coal bed methane recovery), oil reservoirs (enhanced oil recovery), and potentially into deep oceans (ocean storage) (IPCC, 2005). CO₂ storage is likely ultimately to be targeted at saline aquifers, which represent by far the largest CO₂ storage capacity. Estimates of global aquifer capacity range from 2,000 GtCO₂ to nearly 11,000 GtCO₂, enough large compared to the facilities worldwide that might be candidates for CCS currently that emit about 15 GtCO₂ annually (Schiermeier et al., 2008). CO₂ storage in saline aquifer consist essentially in injecting CO₂ at depth below 800 m very CO₂ is in supercritical state. By having a density as large as 50-80% of water, it tends to move upwards, therefore the presence of impermeable formations of shale and clay (named, cap rock) must be present to avoid the leakage. Although a few pilot-scale in situ CO₂ storage facilities are running, still many doubts exist on how to assess the fate of CO₂ after injection reliably, and to avoid leakage back to the atmosphere. An alternative to the in situ CO₂ storage approach consists in an ex situ process based on the chemical reaction with alkaline bearing materials such as Ca- and Mg-silicate, and alkaline industrial materials. This process, known as ex situ mineral carbonation, mimics natural weathering, where CO₂ reacts exothermically with alkaline elements present in natural or industrial materials, forming thermodynamically stable and benign carbonates.

1.3 Mineral carbonation

Seifritz (1990) proposed for the first time mineral carbonation process as a technological option for CO₂ storage. Afterwards, several authors, e.g., Lackner et al. (1995); Park et al. (2003); Park and Fan (2004); Wolf et al. (2004b); Huijgen et al. (2005); Bearat et al. (2006); Gerdemann et al.
have studied it using natural silicates such as olivine, serpentine, and wollastonite or alkaline industrial residues such as fly-ash, steel-slag, bottom-ash.

Mineral carbonation is an ex situ (IPCC, 2005) and in situ (Matter and Kelemen, 2009) CCS technology where metal-oxide bearing materials react with CO$_2$ transforming into carbonate minerals that are thermodynamically stable, environmentally benign, and weakly soluble in meteoric water. In particular, ex situ mineral carbonation has the advantage to have, if compared with CO$_2$ storage in saline aquifer and unminable coal seams, a minimal monitoring requirements for the long-term fate control of the carbon dioxide and for land licensing because it produces stable and environmentally benign materials.

There are two process routes (Lackner et al., 1995): Direct mineral carbonation through a gas-solid reaction and aqueous mineral carbonation where silicates react in water with CO$_2$ forming carbonates. If direct carbonation is a straightforward process, it is slower than the aqueous one. However, aqueous mineral carbonation needs a more complex set-up. Faster direct carbonation can be achieved if some kind of alkaline industrial residues are used instead of silicate minerals. As a matter of the fact, some residues from industrial activities have been proposed because they are a valuable source of alkalinity for the carbonation process and more reactive. Suitable alkaline industrial residues for mineral carbonation are the ones with high content of metal oxides and hydroxides (e.g., CaO and CaOH) such as: Pulverized fuel ash produced by coal fired power stations, ground granulated blast furnace and stainless steel slags from the steel manufacturing industry, bottom and fly municipal solid waste incineration ashes, as well as deinking ash, resulting from the waste produced during the recycling of paper (Johnson, 2000). These materials contain alkaline elements in a more readily available form, so
1.3 Mineral carbonation

that carbonation could in principle take place at less severe operating conditions than the ones needed for silicate minerals. The amount of available alkaline residues is of a scale which will allow to store only a few hundreds MtCO$_2$/y. Nevertheless, the process can substantially reduce the CO$_2$ emissions of specific industrial sectors (e.g., cement or steel industry) and might improve the environmental behavior of the residues allowing either for their reuse or make their disposal less expensive (Costa et al., 2007). Contrarily, the quantity of metal oxides in the silicate rocks that can be found in the earth’s crust exceeds the amounts needed to fix all the CO$_2$ that would be produced by the combustion of all available fossil fuel reserves. However, the fraction of silicate reserves that can be technically and economically exploited for CO$_2$ storage is still unknown, but for a large scale implementation of this process, the most suitable source of metal oxides would be magnesium silicate minerals, such as olivine and serpentine, due to their large worldwide availability (e.g., in ophiolite belts) (Goff et al., 2000).

1.3.1 Chemical reactions

Mineral carbonation is a thermodynamically favored reaction that mimics weathering occurs in nature. During this reaction, CO$_2$ reacts with metal oxides and form stable carbonate.

Direct mineral carbonation reactions of metal oxides are given by:

$$
\text{MgO} + \text{CO}_2 \leftrightarrow \text{MgCO}_3 + 118 \text{kJmol}^{-1}, \quad (1.1)
$$

$$
\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3 + 179 \text{kJmol}^{-1}. \quad (1.2)
$$

They are very slow in presence of natural minerals, while become very fast when industrial alkaline residues rich in metal oxides such as the
In aqueous mineral carbonation, CO\textsubscript{2} is initially dissolved into water to form carbonic acid (H\textsubscript{2}CO\textsubscript{3}), which dissociates to H\textsuperscript{+}, HCO\textsuperscript{−}, CO\textsubscript{3}\textsuperscript{2−}. The H\textsuperscript{+} ion hydrolyzes the mineral, liberating metal cations such as magnesium and calcium. The free cations react with the carbonate ions to form the solid carbonate. Metal oxides are rare in nature while silicate and basalt rich in calcium and magnesium oxides are very common. Being Ca- and Mg-silicate such as olivine, serpentine, and wollastonite available worldwide, they are the most suitable candidate rocks to be used in this process.

Dissolution of these minerals is enhanced at high temperature, low pH, and for small particle size. Similarly, carbonate precipitation is kinetically favored at high temperature and at high pH where carbonate ions are the dominant species. High pH can be reached by adding chemicals that allow also to compensate the lower CO\textsubscript{2} solubility at high temperature. The more reactive rock is wollastonite mostly due to the faster calcium carbonate precipitation kinetics in comparison to magnesite.

Aqueous mineral carbonation reactions of these silicate minerals are given by:

**Forsterite** (magnesium end-member of olivine)

\[
\text{Mg}_2\text{SiO}_4 + 2\text{CO}_2 \leftrightarrow 2\text{MgCO}_3 + \text{SiO}_2 + 89\text{kJmol}^{-1}\text{CO}_2 \quad (1.3)
\]

**Serpentine**

\[
\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{CO}_2 \leftrightarrow 3\text{MgCO}_3 + \text{H}_2\text{O} + \text{SiO}_2 + 64\text{kJmol}^{-1}\text{CO}_2 (1.4)
\]
Wollastonite

\[
\text{CaSiO}_3 + \text{CO}_2 + 2\text{H}_2\text{O} \quad \leftrightarrow \quad \text{CaCO}_3 + \text{SiO}_2 + 90\text{kJmol}^{-1}\text{CO}_2
\] (1.5)

Being these reactions all exothermic, they can theoretically yield energy, the heat released can be used in the other steps of the processing chain. However, the reactions are slow mostly due to the slow cation release into water (dissolution of the silicates). To speed it up a mineral pre-treatment is required as well as the addition of enhancing chemical to the make-up solution. Mechanical pre-treatment consists of particle size reduction down to 10-37 \(\mu\text{m}\) and has the benefit to increase the total surface area and therefore to enhance the surface-reaction controlled dissolution process and to increases the structural disorder of the mineral making it more reactive (Kleiv and Thornhill, 2006). However, the large amount of energy consumed makes the mechanical pre-treatment a particular critical part of the entire mineral carbonation process.

Thermal pre-treatment are also applied in particular in case of serpentine to reduce its high hydration and to weaken the crystalline bonds to facilitate the release of the metals during dissolution.

Regarding the addition of chemical enhancers to the solution, whatever agent is used to extract the cations from the silicates, it must be easily recoverable at the end of the process. But because of its inevitable losses, it must not be expensive. Suitable agents that have been investigated are: HCl (Lackner et al., 1995), sulfuric acid (Maroto-Valer et al., 2005), and organic compounds such as EDTA, oxalate, and citrate (Park et al., 2003; Krevor, 2009).

Aqueous mineral carbonation has received more attention than direct mineral carbonation from the scientific community and industries and for it two process options are available, namely: Single-step process and
multi-step process. In the case of direct mineral carbonation, to our knowledge no studies have been dedicated to envisage a scale up of the process and most of the works have concerned investigations of the kinetics of the alkaline industrial residues.

1.3.2 The process

As mentioned in the previous section, two aqueous mineral carbonation process configurations are available, namely: Single-step process and multi-step process. They are separately discussed in the next two sections. The third section deals with one of the most critical and debated problems of the aqueous reaction: The formation of a passivating surface layer on the silicate particle during a single-step carbonation process.

Single-step aqueous mineral carbonation

The single-step process aims at dissolving the silicates and precipitating the carbonates in the same reactor. Given the different optimal operating conditions which favor dissolution and precipitation, i.e., high temperature and low pH, and high temperature and high pH, respectively, the combination of the two processes is quite challenging. The most comprehensive experimental work on single-step aqueous mineral carbonation process was performed by Albany Research Center (O’Connor et al., 2005) and the results are published on several technical reports and summarized in Gerdemann et al. (2007). They systematically investigated the effect of process variables on the performance of the process are (i.e., energy penalty and extent of reaction): Temperature, partial pressure of CO₂, particle size, solution chemistry, methods of rock comminution, and mineral pretreatment options, and type of the reactor.
1.3 Mineral carbonation

Table 1.1: Optimal operating conditions for aqueous mineral carbonation (Gerdemann et al., 2007). Symbols indicate: *, High temperature pretreatment.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>T, °C</th>
<th>P_{CO_2}, bar</th>
<th>Carrier solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>185</td>
<td>150</td>
<td>0.64 M NaHCO_3, 1 M NaCl</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>100</td>
<td>40</td>
<td>distilled water</td>
</tr>
<tr>
<td>Serpentine*</td>
<td>155</td>
<td>115</td>
<td>0.64 M NaHCO_3, 1 M NaCl</td>
</tr>
</tbody>
</table>

O’Connor et al. (2005) selected the optimal operating conditions for the three ground silicates as listed in Table 1.1.

The best-process today is with olivine and under the conditions given in Table 1.1. At these conditions the extent of the reaction is 61% and the processing streams necessary to sequester 100 kg CO_2/hr, based on a preliminary mass balance, amount to a feed stream of 300 kg of olivine/hr, yielding a product stream of 400 kg/hr. This assumes a mineral recovery of 90 wt.% and an average magnesium oxide content in olivine of 50 wt.%.

The process utilizes a slurry of water mixed with olivine which is reacted with carbon dioxide in a stirred batch autoclave at constant temperature and CO_2 partial pressure. With reference to Figure 1.6, first olivine is crushed and milled in three stages to a particle size of D_{80} = 37 μm. Together with the separation of impurities, about 80 kWh/ton of olivine are consumed during this operation. A water solution with the composition given in Table 1.1 is added to the reactant flow, thus a producing slurry with 15-30 wt.% of solids. The slurry and CO_2 are heated up and fed to the autoclave. A constant CO_2 pressure is maintained during the reaction. After withdrawal, the slurry can be separated into carbonation products, i.e., magnesite (MgCO_3) and free silica (SiO_2), and unreacted...
olivine by means of classification techniques. As shown by chemical analysis of classified solid material and backscatter electron (BSE) imaging, the carbonation products mainly have particles size of less than 25µm and appear as separate particles (O’Connor et al., 2001).

**Multi-step aqueous mineral carbonation**

The multi-step process consists in dissolving the silicates and precipitating the carbonates in the separated reactors optimizing in this way the occurring reactions.
Park and Fan (2004) studied multi-step mineral carbonation process known as pH-swing process. They dissolved grained serpentine in a fluidized bed at 70°C adding a mixture of organic substances such as orthophosphoric acid, oxalic acid, and EDTA and internal grinding. The produced solution rich in magnesium and iron ions was reacted in a first step with NH₄OH at pH 8.6 producing iron oxide and in a second step with NH₄OH under a CO₂ atmosphere of 1 bar at pH 9.5 obtaining an producing Mg-carbonate such as nesquehonite. The highest reaction extent of 65% in 1 hr was obtained by using 0.9 vol.% oxalic acid, 0.9 wt.% orthophosphoric acid, and 0.1 wt.% EDTA.

Kakizawa et al. (2001) proposed a two-step mineral carbonation process using wollastonite in a slurry with 5 wt.% suspension. In the first step, calcium is extracted from the silicate at 60°C using a solution added with acetic acid. In the second step at 80°C, CO₂ is added to the system and the leached ions precipitate as calcium carbonate. 48% of Ca²⁺ was extracted after 250 min and 20% of it precipitated in 30 min at 60°C and 30 bar of CO₂.

**Formation of a passivating layer**

During the aqueous mineral carbonation reaction the system becomes supersaturated with respect to several Si- and Fe-phases whose precipitation onto the silicate surface might occur and hinder further dissolution of the mineral by forming a passivating layer. Several studies have been dedicated to understand the formation of this layer and its composition as well as to find operations to mitigate its effect. Some of these studies are reported below.

O’Connor et al. (2001) studied mineral carbonation at 185°C and 115 atm of CO₂ using olivine in distilled water and they analyzed the product
solids by means of X-ray diffraction. At these conditions, they collected residual solids after 24 hour made by unreacted forsterite, fine magnesite particles (<10 µm), and silica particles separated from magnesite. However, longer time of carbonation determined the formation of a silica-rich layer coating the unreacted particles. Using serpentine at the same operating conditions, the residual material was characterized by grains coated with Si⁴⁺ uniformly, suggesting that as the Mg²⁺ was removed zone enriched in silica were produced, isolated magnesite crystals with rounded edges, silica crystals with angular edges indicating different time of precipitation during the process, and Fe-phases, mostly of magnetite.

Bearat et al. (2006) studied the carbonation of San Carlos olivine (Mg₀.₉₁₅Fe₀.₀₈₅SiO₄). By performing experiments at operating conditions proposed by O’Connor et al. (2005), i.e., 185°C, 135 bar, 0.64 M NaHCO₃ and 1 M NaCl, at 1500 rpm. They formed a solid product consisting of separated crystals of magnesite, amorphous silica, and unreacted olivine as well as of intergrown clusters. This results indicated that magnesite could directly precipitate from solution simultaneously with silica. The residual olivine showed both a silica-rich layer cracked and exfoliated and etch-pits where congruent dissolution occurred. They also investigated systematically the effect of the suspension composition. The extent of the carbonation reaction increased with initial mass of olivine used, demonstrating the importance of particle/particle abrasion in exposing fresh olivine reaction surfaces and enhancing carbonation. Moreover, the introduction of abrasive (e.g., quartz) and larger particles (larger size fraction) led to a marked increase in carbonation since they disrupted the passivating silica-rich layer as it formed.

Park et al. (2003) in a study on the the effect of chemical surface activation on serpentine (Mg₃Si₂O₅(OH)₄) dissolution kinetics observed the precipitation of silica and/or iron-oxide crystals onto the serpen-
tine surface after 2 hrs of dissolution. They proposed that the formation of this layer changed the reaction kinetics from surface controlled to mass-transfer controlled. They studied the effect of various catalysts/chemicals such as HCl, acetic acid, sodium acetate, ascorbic acid, KHP, CaCl$_2$, oxalic acid, orthophosphoric acid, and EDTA. They observed that in the case of solution with no effective chelating agents, both the solution and the residual material colored in red/brown due to the formation of iron precipitates by the Fe(III) ions in solution and on the serpentine surface. While in presence of strong chelants (0.9 vol.% oxalic acid, 0.9 wt.% orthophosphoric acid, and 0.1 wt.% EDTA) Fe(III) ions formed aqueous complexes with ligands without precipitating on the reactive serpentine surface.

Park and Fan (2004) investigated mineral carbonation process using a fluidized bed reactor. They dissolved ground serpentine (<75 µm), at 70°C in acidic solvents (i.e., (a) a mixture of 1 vol.% orthophosphoric acid, 0.9 wt.% of oxalic acid and 0.1 wt.% EDTA, (b) 1.4 M ammonium bisulfate), fluidizing them with internal grinding media. After the dissolution step, the solution was separated from the residual solid and added with NH$_4$OH up to pH 8.6 in a way that isolated crystals of iron oxide and magnesium carbonate could precipitate. The unreacted solid was processed to remove the SiO$_2$ layer. With the final aim to enhance dissolution reaction, they applied several methods for removing the SiO$_2$ layer from reactive serpentine layer such as internal grinding (using 20 vol.% of either 2 mm glass beads or 5 mm zirconia beads), ultrasound, acoustic, and microwave. They found out that by applying an internal grinding the silica layer could be removed throughout bombardments between the larger and harder grinding media and fine serpentine. Among the applied methods, the fluidization with 2 mm glass beads and the ultrasonic method were found to be the most efficient.
Contrarily, to all above results, in a recent study by Daval et al. (2009a) on the carbonation of wollastonite at 90°C and 250 bar, the formation of a silica-rich layer on the silicate particles was not observed to have a negative effect on the kinetics by itself. Daval et al. (2009a) observed that such a layer is indeed porous and ions can pass through towards the solution. However, calcite crystals occurred as a uniform surface coating covering the silica layer (Daval et al., 2009b), and also within pores and cracks, thereby blocking the connectivity of the originally open nanoscale porosity. Calcite crystals ultimately might have been responsible for controlling transport of solutes through the silica layers. Therefore, authors concluded that when the layer contains only silica it is not passivating, but as soon as calcite crystals from within the pores the it becomes partially passivating.

The discrepancy raised between the last two studies reported and the earlier ones might be explained by arguing a possible different physical properties of the silica-rich layer on the olivine and serpentine particles from the one on wollastonite or by pointing out the different scale of the applied measurements. Similar measurements at the nanoscale performed in Daval et al. (2009a,b) could have shown also in the other studies characteristics of the silica-rich layer similar to the ones on the wollastonite particles.

1.4 Objective of the thesis

General research on the mineral carbonation focuses on the enhancement of the carbonation reaction kinetics and on the reduction of the energy consumption of the entire process. Although several studies have been carried out still these issues have not been addressed and in particular
the understanding of the elementary processes that would allow a more oriented process design is still missing.

In the case of aqueous mineral carbonation, the main open issues in this regard concern the comprehension of the effect of the process variables on the thermodynamics and the kinetics of:

- the dissolution reaction of silicates, e.g. the effect of solution composition (pH, ionic strength, salts), particle size, suspension density;
- the precipitation reaction of carbonates, e.g. the effect of temperature, partial pressure of CO$_2$, solution composition (pH, ionic strength, water activity, salts), seeds;
- the CO$_2$ solubility, e.g. the effect of temperature, partial pressure of CO$_2$, solution composition.

When single-step configuration is applied, i.e. when dissolution and precipitation must occur in the same reactor vessel, the elementary processes listed above must be simultaneously optimized.

In the case of direct carbonation, the main open issues concern the selection of the appropriate material. As a matter of the fact, despite the exothermic nature of the carbonation reaction, the kinetics is hindered by the material composition and reactivity. Silicates carbonate directly very slowly while some alkaline industrial materials might be very fast. However, upon selection of the appropriate material the kinetics study must be undertook to understand similarly to aqueous mineral carbonation how process variables influence the process performance. Therefore, the effect of temperature, partial pressure of CO$_2$, humidity, and particle size on the thermodynamics and the kinetics of direct carbonation reaction must be characterized.
Up to now, the issues listed above have been only partially addressed and it is the aim of this thesis to contribute to then by a fundamental study based on an experimental and a modeling work. We approached the study of aqueous mineral carbonation and direct mineral carbonation by examining systems with low complexity such as Olivine-salts-CO$_2$-H$_2$O for dissolution and MgCl$_2$-Na$_2$CO$_3$-CO$_2$-H$_2$O for precipitation, and fly-ash-CO$_2$ for direct carbonation, respectively.

The thesis is structured in two parts. In the first part, the study of the elementary processes of aqueous mineral carbonation such as dissolution and precipitation are presented and discussed. In particular, Chapter 2 and Chapter 3 report the experimental and the modeling results of two studies on the dissolution of olivine in presence of CO$_2$, inorganic salts, and organic salts at high temperature. Chapter 4 and Chapter 5 are dedicated to Mg-carbonate precipitation in particular to the thermodynamics and the kinetics of precipitation at high temperature and at high CO$_2$ pressure under various solution composition. The second part made by Chapter 6 and Chapter 7 focuses instead on direct mineral carbonation reporting and discussing the results of fly-ash carbonation at high temperature and under several CO$_2$ atmosphere composition. Finally, in Chapter 8 the conclusions about the entire thesis’s work are given.
Chapter 2

Dissolution - Study of the effect of CO$_2$ and inorganic salts

This chapter reports the results of an experimental study on the dissolution kinetics of olivine (Mg$_{1.82}$Fe$_{0.18}$SiO$_4$) at operating conditions relevant to the mineral carbonation process. In particular, we investigated the effects of CO$_2$ fugacity ($f_{CO_2}$) and of salinity on the kinetics of olivine dissolution, which is assumed to be the rate-limiting step of the overall carbonation process. Dissolution experiments were carried out at 120°C in a stirred flow-through reactor. Different pH values (between 3 and 8) and solution compositions were investigated by varying $f_{CO_2}$ and by dosing LiOH (for pH control), NaCl, and NaNO$_3$. The

$^1$Most of this chapter has been published as Prigiobbe et al. (2009a)
specific dissolution rate values, $r$, were estimated from the experimental data using a population balance equation (PBE) model coupled with a mass balance equation. The logarithms of the obtained $r$ values were regressed with a linear model as a function of pH and compared to the model reported earlier (Hänchen et al., 2007) for experiments with neither CO$_2$ nor salts. Our results confirm that, at a given temperature, olivine dissolution kinetics depends on pH only, and that $f_{CO_2}$ and the concentrations of NaCl and NaNO$_3$ affect it through their effect on pH.

### 2.1 Introduction

As already mentioned in *Chapter 1* aqueous mineral carbonation of olivine involves CO$_2$ dissolution in water, the dissolution of the silicate minerals, and the precipitation of Mg-carbonates. In particular, the dissolution of the silicate minerals is considered to be the rate-limiting step of the entire aqueous mineral carbonation process. In the case of the dissolution of forsterite, the magnesium end-member of olivine, the chemical reaction in a CO$_2$-free solution is:

$$\text{Mg}_2\text{SiO}_4(s) + 4\text{H}_2\text{O} \rightleftharpoons 2\text{Mg}^{2+} + \text{H}_4\text{SiO}_4(aq) + 4\text{OH}^-.$$  \hspace{1cm} (2.1)

This reaction has been extensively studied at ambient pressure and temperature and its kinetics has been found to depend primarily on pH. Two different mechanisms for olivine dissolution have been postulated at 25°C, corresponding to a pH-dependence for pH < 8, and to no pH-dependence for higher values (Wogelius and Walther, 1991; Pokrovsky and Schott, 2000; Rosso and Rimstidt, 2000). The first mechanism is governed by the adsorption of one H$^+$ ion onto two olivine cells leading to a preferential release of magnesium over silicon and to the formation
of a thin Mg-depleted, and Si-rich (altered) layer. At higher pH values, the dissolution is controlled by the formation of Mg(OH)$_2^+$ complexes and exhibits a preferential release of silicon into solution, thus creating a Si-depleted and hence Mg-rich surface layer. Our group studied (Hänchen et al., 2006) olivine dissolution at temperatures between 90 and 150°C and at pH values between 2 and 12.5 (tuned using HCl and LiOH), and observed the same behavior, and hence they proposed the same mechanism. In particular, the specific dissolution rate, $r$, depends on pH in the pH range from 2 to 8.5, and it is given by the following equation (that corresponds to a linear dependence of the logarithm of $r$ on pH at a given temperature):

$$r = a_{H^+}^nA e^{-\frac{E_a}{RT}},$$

(2.2)

where $r$ is the specific dissolution rate (mol cm$^{-2}$ s$^{-1}$), $T$ is the temperature (K), $R$ is the gas constant ($8.3145 \times 10^{-3}$ kJ K$^{-1}$mol$^{-1}$), $a_{H^+}$ is the hydrogen ion activity (-), and $A$ is a preexponential factor (mol cm$^{-2}$s$^{-1}$). In the above mentioned study (Hänchen et al., 2006) the parameters $A$, $E_a$ (activation energy), and $n$ (reaction order for H$^+$) were estimated by fitting all the experiments to Eq. 2.2, thus resulting in the following values: $A = 0.0854$ mol cm$^{-2}$ s$^{-1}$, $E_a = 52.9$ kJ mol$^{-1}$, and $n = 0.46$. Moreover, to assess the influence of CO$_2$ on olivine dissolution, in the same work a few experiments were also carried out at 120°C under a CO$_2$ partial pressure (from 15 to 180 bar) and in a pH range between 3 and 6 (adjusted by LiOH addition) (Hänchen et al., 2006). The measured dissolution rates were the same as, or slightly higher than, those without CO$_2$ up to a pH value of 5, and markedly lower beyond this value.

Although earlier studies have reported and justified such dissolution inhi-
2. Dissolution - Study of the effect of CO\textsubscript{2} and inorganic salts

Dissolution (Wogelius and Walther, 1991; Pokrovsky and Schott, 2000), others have questioned such a conclusion (Golubev et al., 2005). There is, however, agreement about the importance of the formation of Mg-carbonate complexes on the olivine surface in determining the dissolution behavior. It is worth noting that the pH effect on silicate dissolution can in principle be exploited to control the mineral carbonation process, namely by dissolving silicates at low pH and by precipitating carbonates at high pH, i.e. through a so called pH-swing (or multi-stage) mineral carbonation process (Park et al., 2003).

Inorganic salts such as NaCl, NaHCO\textsubscript{3}, and KHCO\textsubscript{3} have been used in different works to enhance the carbonation of silicates (Geerlings et al., 2002; O’Connor et al., 2002; McKelvy et al., 2005). However, in a thorough study of forsterite CO\textsubscript{2}-free dissolution at 25°C in a pH range from 1 to 4, it has been shown that the dissolution rate was not affected by the presence of the inorganic salts KNO\textsubscript{3}, Mg(NO\textsubscript{3})\textsubscript{2}, Na\textsubscript{2}SO\textsubscript{4}, and MgSO\textsubscript{4} at an ionic strength of up to 12 M (Olsen, 2007). Nevertheless, specific studies regarding the dissolution kinetics of Mg-silicates at high CO\textsubscript{2} fugacity, salinity, and temperature, the operating conditions typically reported for the mineral carbonation process (O’Connor et al., 2002), are still missing. Hence, the effects of CO\textsubscript{2} and salinity on olivine dissolution kinetics are not clear enough, both qualitatively and quantitatively, at the conditions of interest for mineral carbonation. Thus, with this work we aimed at achieving a deeper understanding of these effects on olivine dissolution kinetics in order to be able to optimize the mineral carbonation process. Olivine dissolution was studied at 120°C in a H\textsubscript{2}O-CO\textsubscript{2}-LiOH-NaCl/NaNO\textsubscript{3} system, for different values of CO\textsubscript{2} fugacity (in the range 0.4 to 123 bar), of pH (2 to 8), and of salinity (salt concentration up to 2.5 m). For each experiment, the values of \( r \) were estimated by fitting the experimental data (olivine concentration...
vs. time) with a population balance equation (PBE) model coupled with a mass balance equation (Hänchen et al., 2007). Finally, the obtained values of \( r \) were regressed using the model reported in Eq. 2.2.

## 2.2 Materials and methods

Natural San Carlos gem-quality olivine crystals having an average size of \( \sim 0.5 \) cm were handpicked, crushed, and sieved into different size fractions. The size fraction between 90 and 180 \( \mu \)m was cleaned ultrasonically using ethanol to remove adhering fines and dried overnight at 60\(^\circ\)C. The specific surface was measured by nitrogen adsorption using the BET method and the resulting value of 797±55 \( \text{cm}^2 \text{ g}^{-1} \). The average composition as measured by electron microprobe analysis was found to be Mg\(_{1.82}\) Fe\(_{0.18}\)SiO\(_4\) (\( M_{\text{mol}} = 146.4 \) g mol\(^{-1} \)).

The dissolution experiments were performed in a stirred 300-ml titanium (grade 2), high-pressure, high-temperature, flow-through reactor fed by an HPLC pump (see Fig. 2.1). Agitation was supplied by a blade stirrer suspended from the top of the reactor and driven by a magnetic coupling. In the experiments under a CO\(_2\) atmosphere, a stirrer entraining the gas into the solution was employed to facilitate gas-liquid equilibrium. To ensure that mass transport limitations did not influence the dissolution rate, the effect of the stirring rate was studied at a high dissolution rate, i.e. at the lowest pH value, and the stirrer rate for all experiments was set at a value above which no influence of the stirring rate could be detected under those conditions.

The dissolution kinetics was studied in a LiOH-CO\(_2\) aqueous system. Selected experiments were also carried out in NaCl/NaNO\(_3\)-LiOH-CO\(_2\) aqueous solutions. Small amounts of LiOH were added to the solution
in order to achieve pH values higher than 4 in the presence of CO\(_2\). This hydroxide was chosen since Li\(^+\) concentrations of the solution could be accurately monitored online, as described below. All runs were performed at a temperature of 120\(^\circ\)C, with a liquid volume between 160 and 180 ml and a remaining volume of 130 ml containing the gas atmosphere. Carbon dioxide 99.995 vol.\%-purity (PanGas, Werk Dagmersellen, Switzerland), fed to the reactor from a high-pressure buffer tank and via a front-pressure regulator, was used to pressurize the solution at specific values, ranging from 2 to 100 bar. The gas was fed to the solution through the stirrer to facilitate the achievement of gas-liquid equilibrium. The stirrer was operated at 700 rpm to avoid mixing limitations and particle sedimentation.

For the entire duration of each experiment, the feed solution was purged with N\(_2\) 99.999 vol.\%-purity (PanGas, Werk Dagmersellen, Switzerland), fed directly from a gas cylinder. Such a solution, consisting of ultrapure water only or of ultrapure water with electrolytes, i.e. LiOH, NaCl, and
2.2 Materials and methods

NaNO$_3$, was introduced into the reactor at a constant flow rate of either 2 or 5 ml min$^{-1}$, after being pre-heated up to 90°C with a heat exchanger, in order to minimize the temperature drop at the entrance of the reactor. A second HPLC pump was used to withdraw liquid at exactly the same flow rate as the inlet pump, in order to maintain a constant liquid level in the reactor. Before passing through the second pump, the outlet stream was cooled down to ambient temperature by a copper-tubular heat exchanger, then its flow rate was measured with a flow meter and finally it was depressurized to ambient pressure by using a hydraulic disconnection. For each experiment, the reactor was initially filled with a known amount of olivine, closed, and flushed with CO$_2$ to purge O$_2$ from it. Then a known amount of solution was pumped into the vessel and heated up to 120°C. Once the system stabilized, the reactor was pressurized and kept at these conditions for the entire run. The Mg$^{2+}$ and Li$^+$ concentrations in the outlet solution were measured online by means of an ion chromatograph (CS12A column, Dionex). Solution samples were taken with a fraction collector at regular intervals and their silicon concentration was measured with a spectrophotometer using the Molybdate Blue method (Grasshoff and Anderson, 1999; ICRAM, 2001). The standards for the Mg$^{2+}$ and Si$^{4+}$ measurements were prepared with the feed solution to take into account the effects of salinity on the analysis. The geochemical software package EQ3/6 v8.0 (Wolery and Jarek, 2003) was used to model the composition of the solution and pH, assuming that the time scale for achieving equilibrium was smaller than the residence time (30-90 min). A database employing Pitzer equations to estimate the activity coefficients of the aqueous species at high ionic strength was used. Based on the measured temperature and pressure, the CO$_2$ fugacity was calculated by using a noniterative procedure developed by Spycher et al. (2003), based on the Redlich-Kwong equation.
of state for the CO$_2$-H$_2$O mixture. The value of $f_{CO_2}$ together with the temperature and Mg$^{2+}$ and Si$^{4+}$ concentrations, was used to calculate the actual pH value using EQ3/6.

2.3 Mathematical model

The dissolution of olivine was modeled by a 1D population balance equation (PBE) model (Randolph and Larson, 1988), assuming constant particle shape. This equation together with a flow-through reactor model allows the description of the temporal evolution of olivine particles (Hänchen et al., 2007).

The governing equations are given by:

$$\frac{\partial f}{\partial t} - D \frac{\partial f}{\partial L} = 0,$$

(2.3)

$$V \frac{dc}{dt} = -\frac{dm}{dt} - Qc,$$

(2.4)

where $f$ is the particle size distribution, (m$^{-1}$); $D$ is the dissolution rate, (m s$^{-1}$); $m$ is the moles of olivine (moles); $V$ is the volume of the suspension in the reactor, (m$^3$); $Q$ is the flow rate through the reactor, (m$^3$ s$^{-1}$); $c$ is the concentration of olivine in solution, (moles m$^{-3}$), and $L$ is the characteristic particle length, (m). The general initial conditions for eqn. 2.3 and 2.4 when nucleation does not occur are:

$$f_i(L,0) = f_0(L),$$

(2.5)

$$c(0) = c_0,$$

(2.6)

where $f_0(L)$ is the initial size distribution of olivine particles and $c_0$ is the initial concentration of olivine in solution. By solving eq. 2.3 with
2.3 Mathematical model

the method of characteristics yields the following solution:

\[ f(L, t) = f_0(L + Dt), \quad L \geq 0, \quad t \geq 0. \tag{2.7} \]

To solve eq. 2.4 in order to describe the evolution over time of olivine concentration in solution the first term in the right-hand side of eq. 2.4 must be related either to the particle size distribution or to the particle volume distribution. With this aim, we first defined the moment of a distribution:

\[ \mu_n = \int_0^\infty L^n f \, dL, \tag{2.8} \]

and by assuming convex particles whose particle shape is given by size-independent and time-invariant shape factors \( k_a \) and \( k_v \), we defined:

\[ a = k_a L^2, \]
\[ v = k_v L^3, \]

where \( a \) and \( v \) are the surface area and volume of a single particle. Since mostly the particle volume distribution is measured, it is better to give the PBE in 2.3 in terms of the volume particle distribution, \( \phi \). \( f \) and \( \phi \) are related by the following relationship:

\[ f(L, t) \, dL = \phi(v, t) \, dv, \tag{2.9} \]

hence, eq. 2.8 expressed in terms of particle volume becomes:

\[ \mu_n = \int_0^\infty \left( \frac{v}{k_v} \right)^{n/3} \phi \, dv. \tag{2.10} \]

Combination of the first term in the right-hand side of eq. 2.4 together
with eqn. 2.7, 2.8, and 2.10 yields:

\[
\frac{dm}{dt} = -3\rho k^{1/3}_{v} D \int_{(k^{1/3}_{v} D t)^{3}}^{\infty} \phi_0 (v^{1/3} - k^{1/3}_{v} D t)^2 dv,
\]

(2.11)

with \( \rho \) the molar density of olivine, (mol cm\(^{-3}\)) and \( \phi_0 \) the initial particle volume distribution. Eq. 3.3 can be recast into a simpler form:

\[
\frac{dm}{dt} = -3k_{v}\rho D \mu_2,
\]

(2.12)

where \( \mu_2 \) is the second moment of the particle size distribution. Combination of eq. 2.4 and eq. 3.3 yields:

\[
V \frac{dc}{dt} = 3k_{v}\rho D \mu_2 - Qc.
\]

(2.13)

Once the initial olivine particle size distribution, the initial olivine concentration in solution, and \( k_{v} \) are known, eq. 2.13 can be regressed over the experimental concentrations of Mg\(^{2+} \) (\( c_{\text{Mg}} \)) and Si\(^{4+} \) (\( c_{\text{Si}} \)), expressed as olivine equivalents (\( c \)), that in a perfect stoichiometric dissolution process is given by

\[
c = c_{\text{Si}} = \frac{c_{\text{Mg}}}{1.82},
\]

(2.14)

to estimate the dissolution rate, \( D \).

The conversion of \( D \) into specific dissolution rate, \( r \) (mol cm\(^{-2} \) s\(^{-1} \)) which is generally used in geochemistry to express the rate of mineral dissolution, is in the following. The specific dissolution rate \( r \) is defined through the following expression:

\[
\frac{dm}{dt} = -r A = -r \alpha k_{a} \mu_2,
\]

(2.15)
2.3 Mathematical model

where $\alpha$ is a factor given by

$$\alpha = \frac{A_{BET,0}}{k_a\mu_{2,0}}, \quad (2.16)$$

with $A_{BET}$ the particle surface measured with the BET method and $\mu_{2,0}$ the second moment of the initial particle size distribution.

Comparing eq. 2.12 and eq. 2.15, and using the definition given in eq. 2.16, the relationship between $D$ and $r$ is given by:

$$3\rho k_v D = \alpha k_a r = \frac{A_{BET,0}}{\mu_{2,0}} r, \quad (2.17)$$

and the conversion from $D$ to $r$ simplifies in

$$r = \frac{D}{\gamma}, \quad (2.18)$$

where $\gamma$ is a parameter function of measurable prosperities grouping all the constants of eq 2.17:

$$\gamma = \frac{A_{BET,0}}{3\rho k_v \mu_{2,0}} = \frac{a_{BET} M_{mol} m_0}{3\rho \int_0^\infty \phi_0(v)v^{2/3}dv}, \quad (2.19)$$

with $a_{BET}$ the BET specific surface area, (cm$^2$ g$^{-1}$); $M_{mol}$ the molar mass of olivine, (g mol$^{-1}$), and $m_0$ the total initial mass of particle population, (mol); $\phi_0$ the initial volume distribution. The value of $\gamma$ used in this work was equal to $3.72 \times 10^{-4}$ m$^3$ mol$^{-1}$. 

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2.4 Preliminary results on the effect of CO$_2$

For sake of completeness of this chapter, herein we report the results obtained in a preliminary survey to study the effect of CO$_2$ at 90 and 120$^\circ$C. Specific data regarding olivine dissolution experiments carried out are reported in Table 2.1. In particular, for each experiment, the applied operating conditions, i.e. CO$_2$ partial pressure ($P_{CO_2}$), LiOH ($Li^+$) concentrations, flow rate ($Q$), aqueous concentration of olivine equivalent ($O_{eq}$), initial olivine mass ($m_0$), duration of the experiment, Mg-Si ion concentration ratio (Mg/Si) are listed, together with the resulting specific dissolution rate ($r$), and the calculated pH.

In all experiments carried out under a CO$_2$ atmosphere, ion concentrations were well below the solubility limit of MgCO$_3$ with saturation indices below -2, thus precluding the possibility of MgCO$_3$ precipitation. For two experiments, the overall concentrations were so low that the Si concentration was below the determination limit, and therefore, no Mg/Si ratio could be calculated. In the first set of experiments with low Mg-concentrations and no additional alkalinity (Fig. 2.2), the dissolution rate increases moderately with CO$_2$ pressure as the pH decreases correspondingly. In the second set, at both 15 and 100 bar of CO$_2$ pressure, the dissolution rate decreases as the alkalinity, and consequently the pH, was increased by the addition of LiOH or by higher Mg-concentrations. It can be readily observed (Fig. 2.3) that in the presence of CO$_2$ and at low pH, dissolution rates exhibited a very similar behaviour as a function of pH as in the experiments without CO$_2$. However at pH >5 the rate significantly deviates from its behaviour relative to pH and decreases much more strongly with increasing pH than for CO$_2$-free solutions. Moreover, the dissolution rate at pH $\leq$ 5 in the presence of CO$_2$ is app-

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$^2$Most of this section has been published as Häntchen et al. (2006)
2.4 Preliminary results on the effect of CO$_2$

approximately twice as large as under a nitrogen atmosphere. It should be noted that the three experiments at 90°C and the two experiments at 150°C carried out under a CO$_2$ atmosphere also show higher dissolution rates than the values obtained using the correlation for the experiments under a nitrogen atmosphere.
Table 2.1: Operating conditions and experimental results of experiments under CO$_2$ atmosphere.

<table>
<thead>
<tr>
<th>T, $^\circ$C</th>
<th>$P_{\text{CO}_2}$, bar</th>
<th>Li$^+$, mM</th>
<th>pH</th>
<th>$r$, $\text{mol/cm}^2\text{s} \times 10^{10}$</th>
<th>$Q_{\text{eq}}$, $\mu$M</th>
<th>$Q$, ml/min</th>
<th>$m_0$, mg</th>
<th>Duration, hr</th>
<th>Mg/Si, (-)</th>
<th>Exp. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 180</td>
<td>0</td>
<td>3.18</td>
<td>1.50</td>
<td>53.01</td>
<td>2</td>
<td>15.5</td>
<td>4.5</td>
<td>1.72</td>
<td>R53</td>
<td></td>
</tr>
<tr>
<td>90 140</td>
<td>0</td>
<td>3.25</td>
<td>1.40</td>
<td>84.42</td>
<td>2</td>
<td>31.2</td>
<td>7.9</td>
<td>2.05</td>
<td>R52</td>
<td></td>
</tr>
<tr>
<td>90 100</td>
<td>0</td>
<td>3.27</td>
<td>1.60</td>
<td>94.99</td>
<td>2</td>
<td>40.0</td>
<td>7.7</td>
<td>1.39</td>
<td>R51</td>
<td></td>
</tr>
<tr>
<td>120 140</td>
<td>0</td>
<td>3.34</td>
<td>7.10</td>
<td>61.88</td>
<td>2</td>
<td>6.6</td>
<td>3.1</td>
<td>2.01</td>
<td>R55</td>
<td></td>
</tr>
<tr>
<td>120 180</td>
<td>0</td>
<td>3.29</td>
<td>8.50</td>
<td>55.06</td>
<td>2</td>
<td>6.1</td>
<td>6.6</td>
<td>1.61</td>
<td>R56</td>
<td></td>
</tr>
<tr>
<td>120 100</td>
<td>0</td>
<td>3.39</td>
<td>5.50</td>
<td>48.63</td>
<td>2</td>
<td>6.4</td>
<td>6.3</td>
<td>1.76</td>
<td>R54</td>
<td></td>
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<tr>
<td>120 100</td>
<td>0</td>
<td>3.66</td>
<td>3.90</td>
<td>303.33</td>
<td>5</td>
<td>100.2</td>
<td>3.5</td>
<td>1.84</td>
<td>R62</td>
<td></td>
</tr>
<tr>
<td>120 15</td>
<td>0</td>
<td>3.84</td>
<td>2.90</td>
<td>41.92</td>
<td>5</td>
<td>27.7</td>
<td>5.7</td>
<td>1.97</td>
<td>R64</td>
<td></td>
</tr>
<tr>
<td>120 100</td>
<td>40</td>
<td>4.20</td>
<td>2.20</td>
<td>40.24</td>
<td>2</td>
<td>13.3</td>
<td>7.4</td>
<td>1.84</td>
<td>R60</td>
<td></td>
</tr>
<tr>
<td>120 15</td>
<td>53</td>
<td>5.03</td>
<td>0.6</td>
<td>36.83</td>
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<td>R66</td>
<td></td>
</tr>
<tr>
<td>120 15</td>
<td>260</td>
<td>5.69</td>
<td>0.2</td>
<td>45.02</td>
<td>5</td>
<td>187.0</td>
<td>11.7</td>
<td>1.90</td>
<td>R68</td>
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<tr>
<td>120 15</td>
<td>591</td>
<td>6.03</td>
<td>0.015</td>
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<td>5</td>
<td>8.2</td>
<td>6</td>
<td>n.a.</td>
<td>R61</td>
<td></td>
</tr>
<tr>
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<td>0.011</td>
<td>2.15</td>
<td>4</td>
<td>215.4</td>
<td>3</td>
<td>n.a.</td>
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<td></td>
</tr>
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<td>11.5</td>
<td>28.84</td>
<td>2</td>
<td>3.5</td>
<td>7</td>
<td>1.66</td>
<td>R57</td>
<td></td>
</tr>
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<td>150 140</td>
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<td>3.39</td>
<td>10.0</td>
<td>42.13</td>
<td>2</td>
<td>4.7</td>
<td>6.3</td>
<td>1.90</td>
<td>R59</td>
<td></td>
</tr>
</tbody>
</table>

The drop in the dissolution rates at pH $>$5 was explained by a mechanism suggested by Pokrovsky and Schott (2000). Their proposed mechanism for the dissolution at alkaline conditions involved the formation of $\text{MgOH}_2^+$ surface groups, whose concentration determined the dissolution rate, and whose formation and detachment was independent of pH, thus explaining the independence of the dissolution rate of pH. In the presence of CO$_3^{2-}$ ions, whose concentration increases with increasing pH, these groups could react and form $\text{MgCO}_3^-$ surface groups, thereby inhibiting the dissolution process. The same inhibition mechanism was already proposed by Wogelius and Walther (1991).

Olivine dissolution results by Pokrovsky and Schott (2000) at low pH and low CO$_2$ pressure (i.e. at low CO$_3^{2-}$ ion concentration, $m_{\text{CO}_3^{2-}} < 10^{-7}$), show dissolution rates that do not differ from those from the correlation found for CO$_2$-free solutions. Dissolution was stoichiometric for these
2.4 Preliminary results on the effect of CO$_2$

Figure 2.2: Dissolution rate of olivine, $r$ (mol cm$^{-2}$ s$^{-1}$), vs. $P_{CO_2}$ at 120$^\circ$C: ▲ experiments with low Mg-concentrations and no additional alkalinity, △ experiments with addition of LiOH or increased Mg-concentration.
2. Dissolution - Study of the effect of CO$_2$ and inorganic salts

Figure 2.3: Dissolution rate of olivine, $r$ (mol cm$^{-2}$ s$^{-1}$), vs. pH at 120$^\circ$C: dashed line is our correlation without CO$_2$, ⋆ experiments without CO$_2$, ▲ experiments with CO$_2$ and no additional alkalinity, △ experiments with CO$_2$ and with LiOH.
2.4 Preliminary results on the effect of CO$_2$

cases. Results of Wogelius and Walther (1991) at elevated pH and low CO$_2$ pressure, having a CO$_3^{2-}$ ion concentration higher than 10$^{-4}$ m, show a decrease of the dissolution rate in the presence of CO$_2$. Experiments under similar conditions by Pokrovsky and Schott (2000) and Golubev et al. (2005) show no decrease with respect to the correlations found by the same authors in CO$_2$-free solutions. In all three studies, dissolution became increasingly non-stoichiometric with increasing pH, exhibiting an excess of silica.

Therefore, we concluded that at low pH (pH $\leq$ 5) and low CO$_3^{2-}$ concentration ($m_{CO_3^{2-}} < 10^{-7}$), our results agreed with literature results in that the presence of CO$_2$ does not negatively affect the dissolution rate, but rather favours it with dissolution rates two times larger than those without CO$_2$ at the same pH. At higher pH (pH $>$ 5) and higher CO$_3^{2-}$ concentration ($m_{CO_3^{2-}} > 10^{-7}$), comparisons with earlier results are difficult since, as mentioned, there is no agreement with respect to the effect of CO$_2$ and most reported experiments only exhibited non-stoichiometric dissolution.

The negative deviation of the dissolution rate from its trend in CO$_2$-free solutions in our results occurs already at a pH between 5 and 6 indicates that at high CO$_2$ pressure and therefore increased CO$_3^{2-}$ ion concentration (compared to low pressure experiments) this inhibition effect can already become significant under conditions where the surface of the olivine is depleted in magnesium and the dissolution mechanism is not relying on the formation of $>$MgOH$_2^+$ surface groups.
2.5 Further results on the effect of CO\textsubscript{2} and salts

Given the observation made in previous section, a more extensive experimental campaign was undertook to investigate the effect of CO\textsubscript{2} on olivine dissolution and understand if CO\textsubscript{2} inhibited olivine dissolution at pH $>5$. Together with these investigations also the study of the effect of inorganic salts such as NaCl and NaNO\textsubscript{3} was done.

All experiments were performed at 120$^{\circ}$C and for each of them the applied operating conditions, i.e. CO\textsubscript{2} fugacity ($f_{\text{CO}_2}$), LiOH (Li$^+$) and salt (either NaCl or NaNO\textsubscript{3}) concentrations, flow rate ($Q$), suspension volume ($V$), initial olivine mass ($m_0$), and duration of the experiment are listed in Table 2.2, together with the resulting specific dissolution rate ($r$), and the calculated pH. Two sets of experiments are shown:

- Experiments 27 to 37 (reported also in Hänchen et al. (2006)), carried out with neither CO\textsubscript{2} nor salt, in which the pH was adjusted by adding HCl or LiOH;

- Experiments 54 to 135, performed under a CO\textsubscript{2} atmosphere with or without salt addition.
2.5 Further results on the effect of CO$_2$ and salts

Table 2.2: Olivine dissolution at 120°C. Operating conditions and experimental results. Symbols indicate type of salt, * NaCl and ** NaNO$_3$.

<table>
<thead>
<tr>
<th>pH</th>
<th>$f_{CO_2}$, bar</th>
<th>Li$^+$, m</th>
<th>Salt, m</th>
<th>$Q$, ml/min</th>
<th>V, ml</th>
<th>$m_0$, mg</th>
<th>Duration, hr</th>
<th>$r$, mol/cm$^2$s x $10^{10}$</th>
<th>Exp. No.</th>
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<td>10.3</td>
<td>28</td>
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<td>-</td>
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<td>59</td>
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<td>27</td>
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<td>0</td>
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<td>68</td>
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<td>36</td>
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As an example, in Figure 2.4 Exp. No. 92 (at pH = 3.44, corresponding to fast dissolution) is analyzed in more detail. In particular, the measured $Mg^{2+}$ and $Si^{4+}$ concentrations, expressed in olivine equivalents according to Eq. 2.14, are plotted over time, together with their arithmetic average. These experimental data are compared with the simulation results, obtained by solving Eqn 2.3 and 2.4, numerically. The specific dissolution rate $r$, reported in the figure legend, was obtained by least-squared minimization of the residuals between the experimental data and the model results. In this case, the agreement is rather satisfactory, as in all the other experiments.

In Figure 2.4, the $Mg^{2+}$ and $Si^{4+}$ concentrations vary in time according to the dissolution dynamics, but the $Mg^{2+}$ to $Si^{4+}$ concentration ratio is always stoichiometric. This was not always the case, as illustrated in Figure 2.5, where the time evolution of the ratio of the two concentrations...
2.5 Further results on the effect of CO$_2$ and salts

Figure 2.4: Ion concentration over time during a fast dissolution experiment, Exp. No. 92. Symbols: (+) Mg$^{2+}$ concentration, (○) Si$^{4+}$ concentration, (*) arithmetic average, and (–) model.

is plotted in the case of the Exps. No. 36, 60, and 119. The behavior observed in this figure is indeed general, thus indicating that after an initial transient phase, the Mg$^{2+}$ to Si$^{4+}$ concentration ratio stabilized to its stoichiometric value corresponding to 1.82. For modeling and regression purposes and to reduce the variability, the arithmetic average of the two concentrations expressed in olivine equivalents was used (Eq. 2.14).

For all the experiments reported in Table 2.2, the logarithm of the value of $r$, estimated using the method described in section 2.3, is plotted as a function of the calculated pH value in Figure 2.6. In this figure, we plot also the values obtained in eight experiments without CO$_2$, where HCl was used to acidify the solution, that were reported and analyzed in our previous work (Hänchen et al., 2007). Experiments carried out with and without CO$_2$, with and without salt addition, can be distinguished by
2. Dissolution - Study of the effect of CO$_2$ and inorganic salts

The main conclusion that can be drawn by analyzing these results is that the change in the dissolution rate could be accounted for by the change in solution pH only. Varying the CO$_2$ fugacity, or the LiOH or HCl concentration, or the salinity, produced a change in the pH value, which in turn led to a change in $r$, but there was no evidence of a direct and independent effect of these parameters on the dissolution rate. Therefore, all experimental data in Figure 2.2 were regressed using a single equation, namely the following linearized form of Eq. A.26:

$$\log r = -npH + B \quad (2.20)$$

with $r$ in mol cm$^{-2}$ s$^{-1}$, pH = -log$a_{H^+}$, $n = 0.52 \pm 0.047$ and $B = 7.59 \pm 0.24$, defined as the logarithm of $A e^{-\frac{E_0}{RT}}$, based on a 95% confi-


2.6 Conclusion

The conclusion of this comprehensive experimental work is that the specific dissolution rate of olivine at a given temperature in the pH range between 2 and 8 depends on pH only. The effects of CO₂ fugacity, LiOH, HCl, salt concentrations, and combinations thereof are important inasmuch as they affect the pH, but not directly and independently. There is no inhibition effect of the presence of CO₂ on olivine dissolution at
Figure 2.6: Logarithm of $r$ values plotted over pH for each run at 120$^\circ$C and linear model described in Eq. A.26. Namely, (○) experiments without CO$_2$; (△) experiments with CO$_2$, with or without LiOH; (▽) experiments with CO$_2$ and NaCl; (♦) experiments with CO$_2$ and NaNO$_3$; (—) Eq. 2.20 with $n = 0.52$ and $B = 7.59$ (this work); (---) Eq. 2.20 with $n = 0.46$ and $B = 8.05$ (Hänchen et al., 2007).
pH higher than 5 as previously reported, which is important because these are the conditions where carbonate precipitation is favoured. Our investigation was carried out at 120°C, but we would argue that general conclusions are general and could be applied to any temperature in the range between 25°C and 150°C, where several studies by our group and others have shown that the dissolution mechanism is the same. We believe that this is an important finding towards the design and optimization of an effective mineral carbonation process.
2. Dissolution - Study of the effect of CO\textsubscript{2} and inorganic salts

hindering
Chapter 3

Dissolution - Study of the effect of oxalate and citrate

Aqueous mineral carbonation reaction is kinetically controlled by the dissolution of the silicate whose rates increase with temperature, proton concentration, and in presence of organic ligands, e.g., oxalate and citrate. In order to accelerate dissolution, we investigated the effect of oxalate and citrate on San Carlos olivine ($\text{Mg}_{1.82}\text{Fe}_{0.18}\text{SiO}_4$) dissolution. To this purpose, flow-through dissolution experiments were performed at 90 and 120°C, at CO$_2$ fugacity between 4 and 81 bar, and using $10^{-3}$ and $10^{-1}$ m of oxalate and of citrate. The pH was varied between 2 and 7 by adding HCl, LiOH, and CO$_2$ fugacity. Dissolution reaction of this silicate has been extensively investigated at high temperature and at high CO$_2$ partial pressure and it is described by a surface-reaction controlled
mechanism at condition far from the equilibrium. At 90 and 120°C, specific dissolution rate \( (r) \) increased with salt concentration. The highest enhancement was of one order of magnitude and it was observed in the pH region where the dominant species are oxalate and citrate, i.e., pH >5. The dissolution process was modeled by population balance equation (PBE) coupled with a mass balance and a surface-reaction controlled kinetics based on adsorption mechanism of two ions on one surface site described by Langmuir adsorption isotherm.

3.1 Introduction

At low temperature, far from the equilibrium, olivine (Mg\(_2\)SiO\(_4\)) dissolution is surface-reaction controlled through a proton-promoted mechanism (Pokrovsky and Schott, 2000). Earlier studies (Grandstaff, 1986; Wogelius and Walther, 1991; Olsen and Rimstidt, 2008) on the effect of weak organic acids highlighted the dissolution enhancing effect of these compounds although focusing on a range of operating conditions different from the ones relevant to mineral carbonation. Hence, their potential enhancement effect on olivine dissolution at high temperature and at high CO\(_2\) partial pressure has not been explored, yet. To bridge this gap and with the final aim to accelerate mineral carbonation, we undertook an experimental campaign to characterize olivine dissolution kinetics at high temperature, at high CO\(_2\) partial pressure, and in the presence of oxalate and citrate. We performed experiments at 90°C and 120°C and at a CO\(_2\) fugacity \( (f_{CO_2}) \) between 4 and 81 bar using Na\(_3\)C\(_6\)H\(_5\)O\(_7\)-2H\(_2\)O (trisodium citrate dihydrate salt) and Na\(_2\)C\(_2\)O\(_4\) (disodium oxalate salt). The applied maximum temperature was chosen on the basis of the thermal stability of oxalic acid and of citric acid. At low ionic strength the thermal stability limit of citric and oxalic acids is around 125°C.
3.2 Background

3.2.1 Olivine crystal structure

Olivine crystallizes in the orthorhombic system (space group Pbnnm). The key structure unit of olivine is a serrated chain of octahedra lying parallel to the c-axis joined together by silicon-centered tetrahedra (Birle et al., 1968; Awad et al., 2000). A schematic polyhedral diagram of olivine is shown in Figure 3.1. It consists of independent Si tetrahedra linked by divalent octahedral cations. The divalent cations are in sixfold coordination with their nearest oxygen neighbors. These cations occupy two different sites, namely, M(1) and M(2) sites, in the structure. M(1) occupies a distorted octahedron connecting two Si tetrahedral edges, whereas M(2) is in a less-distorted octahedron, which connects one tetrahedron edge and three tetrahedral apexes. In the olivine
structure, three different positions for the oxygen atoms are recognized and in the Si tetrahedron they are bonded as reported below:

- One O(1) atom bonded to one Si atom, to two M(1) atoms, and to one M(2) atom;
- One O(2) atom bonded to one Si atom, to two M(1) atoms, and to one M(2) atom;
- Two O(3) atoms, each bonded to one Si atom, to one M(1) atom, and to two M(2) atoms.

Each octahedron containing M(1) atom has two of each type of oxygen atoms. Each octahedron containing M(2) atom has:

- One O(1) atom;
- One O(2) atom;
- Four O(3) atoms.

### 3.2.2 Olivine dissolution in aqueous solution

In an aqueous solution in presence of chemical additives, dissolution can be schematically described as a phenomenon governed by four elementary processes (Furrer and Stumm, 1986; Stumm, 1992): 1) The attachment of the reactants to the surface; 2) reaction at the surface; 3) the rate controlling detachment of the species from the surface into the solution; 4) the transport of the detached species into the bulk solution, and 5) protonation subsequent to detachment restoring the incipient surface configuration. In the case of an enhancement effect of the additives
the third step is highly sped up and otherwise in the case of inhibited dissolution.

At low temperature, far from the equilibrium, and in water, olivine dissolution kinetics is surface-reaction controlled governed by a proton-promoted mechanism consisting of an ion-exchange reaction followed by an adsorption reaction (Pokrovsky and Schott, 2000; Zakaznova-Herzog et al., 2008) resulting in an overall dissolution reaction given by:

\[
\text{Mg}_2\text{SiO}_4(s) + 4\text{H}^+ \leftrightarrow \text{H}_4\text{SiO}_4 + 2\text{Mg}^{2+}.
\] (3.1)

When organic substances are added to the solution, simultaneously to the proton adsorption reaction a ligand-exchange reaction occurs (Wogelius and Walther, 1991; Liu et al., 2006). Therefore olivine dissolution reaction becomes proton- and ligand-promoted resulting in an overall dissolution reaction faster than reaction 3.1 and given by:

\[
\text{Mg}_2\text{SiO}_4(s) + 2\text{L}^{2-} + 4\text{H}^+ \leftrightarrow 2\text{MgL} + \text{H}_4\text{SiO}_4,
\] (3.2)

where L indicates the ligand.

In previous works (Hänchen et al., 2006, 2007; Prigiobbe et al., 2009a), we observed that at high temperature, at high CO₂ partial pressure, and in the presence of inorganic salts olivine dissolution far from the equilibrium still depended only on the pH.

### 3.2.3 Effect of protons

In a ligand-free solution, surface reaction at the olivine/water interface is proton-promoted. It involves surface reactions combined with diffusion
of protons into the olivine crystal structure and the subsequent protonation of the oxygen atoms associated with one or both of the octahedral sites. Protons readily diffuse throughout the first one-two unit cell of olivine, i.e., 5 to 20 Å into the structure (Awad et al., 2000; Pokrovsky and Schott, 2000; Zakaznova-Herzog et al., 2008). With preferential adsorption onto O(1) which corresponds to the oxygen with the highest electron density (i.e., O(1) 21.660 evu (electrostatic valency units), O(2) 21.655 evu, and O(3) 21.642 evu). Because Mg(1) is associated with two O(1) sites and Mg(2) with only one, Mg(1) will preferentially react with protons (via oxygen atom coordination). Protonation promotes dissolution because protons create highly polarized interatomic bonds in the immediate of magnesium atom facilitating the detachment of the silicon group as $H_4SiO_4$. Similarly, at high pH, the adsorption of $OH^-$ leads to hydroxylation of the mineral surface by reacting with magnesium atoms destabilizing the magnesium bonds and facilitating its detachment as Mg(OH)$_2$.

### 3.2.4 Effect of organic salts

In presence of either organic salts, surface reaction at the olivine/water interface becomes both proton- and ligand-promoted. Organic substances might either enhance or inhibit mineral dissolution. Organic acids can enhance the dissolution of silicates by reducing the solution pH, by complexing the crystalline surfaces, and by lowering the apparent solubility of the dissolving mineral forming complexes with the released ions in solution. At the same time, they can inhibit the dissolution by forming complexes on the crystalline surface that hinders the release of ions.

To illustrate the proton- and ligand-promoted reaction mechanisms, a
two-dimensional diagram of olivine surface is presented in Figure 3.1.f. Upon protonation of the O(1) atom in the Mg(1)–O(1)–Mg(2) surface site, the bond between Mg(2) and O(1) lengthens and breaks leaving the O(1) atom with its affixed proton attached to the adjacent silica group and Mg(1). As these Mg(2)–O(1) bonds break, water molecules or organic ligands over-coordinates Mg(1) and weaken the bond between the silicon and the magnesium allowing the release of the silicon as $H_4SiO_4$ to solution (Liu et al., 2006). The rate of silica release is proportional to the strength of the interaction of the ligand with the Mg(1) atom.

Organic salts can enhance the dissolution of silicates by reducing solution pH, by complexing their crystalline surfaces, and by lowering the apparent solubility of the dissolving mineral forming complexes with the released ions in solution. Being dissolution of olivine far from the equilibrium controlled by surface-reaction, in the enhanced case the first two phenomena dominate. However, organic substances might inhibit the dissolution by forming complexes on the crystalline surface that hinder the release of ions. In this case, the third step of the dissolution (desorption) is severely slowed down.

Upon dissociation of the organic salts, the produced organic ligands can form inner-sphere complexes (defined as surface complexes where there is covalent bond between the oxygen atoms in the molecule of the adsorbed organic-species and the surface metal ion) with the metal ion belonging to a superficial functional group shifting the electron density towards the metal ion at the surface and weakening the metal-oxygen lattice bonds in the lattice of the surface (ligand-promoted mechanism). On the other hand, the organic ligands can form outer-sphere complexes (defined as surface complexes between hydrated mineral surface and the adsorbed organic-species therefore a hydrogen bond forms between the protonated oxygens atom at the mineral surface and the oxygen atoms
in the organic molecule) with the protonated oxygens of superficial functional group. These complexes can inhibit dissolution by either strengthening the metal-oxygen bond impairing the proton effect or protecting sterically the central-metal cations from the formation of inner-sphere complexes that catalyze the reaction. Additionally, organic ligands can form surface complexes that bridge two or more cations at the surface lattice (called polynuclear complexes) and retard dissolution.

Bidentate ligands weaken more effectively the metal-oxygen bond facilitating the metal release because they form mononuclear complexes that are strong surface chelates (ring structure of the ligand bound to the metal center at the surface). Among them, ligand forming surface 5-ring chelate such as oxalate, citrate, malonate, and salicylate are more efficient than 6-ring or 7-ring chelate such as phthalate and succinate, while monodentate complexes showed little or no effect and can inhibit dissolution by displacing ligands that catalyze the reaction (Furrer and Stumm, 1986; Stumm, 1992).

Few studies have been carried out on the effect of organic substance on olivine dissolution. Grandstaff (1986) investigated the effect of $10^{-3}$ M oxalate and EDTA at $25^\circ$C and observed an increase of one order of magnitude on the dissolution rate between pH 3.5 and 4.5. Wogelius and Walther (1991) studied the effect of $10^{-3}$ m ascorbic acid and 0.05 m potassium acid phthalate at $25^\circ$C and measured the highest enhancement of 6 times with respect to a ligand-free solution at pH 4. Olsen and Rimstidt (2008) investigated the effect of 0-0.35 m sodium oxalate on olivine dissolution at $25^\circ$C. The highest increase of the dissolution rate was of 6 times with respect to a ligand-free solution where oxalate ion was the dominant species, i.e. pH $>4.2$. In an earlier work (Hänchen et al., 2006), we examined the effect of $10^{-4}$ and $10^{-3}$ M of citric acid on forsterite dissolution at $90^\circ$C and the results suggested that organic
ligands also enhance dissolution at high temperatures.

Investigations of the effect of organic acids on the mineral carbonation reaction were carried out by Park et al. (2003) and Krevor (2009). Park et al. (2003) studied the carbonation kinetics of serpentine using a fluidized bed reactor at 70°C in an organic solvent solution. They found a solution containing a mixture of three different organic compounds, namely, 1 vol.% of orthophosphoric acid, 0.9 wt.% of oxalic acid and 0.1 wt.% of EDTA enhanced the magnesium release while preventing the precipitation of Fe$^{3+}$ onto the mineral. Krevor (2009) studied the effect of trisodium citrate salts at 120°C and at 20 bar of CO$_2$ during the dissolution of serpentine. He observed faster dissolution in 7 hours in presence of 0.5 M of trisodium citrate salt. About 80% of the initial mass of the mineral was dissolved; whereas, at the same operating conditions but without salt only 10% of the material dissolved, indicating the enhancement effect of trisodium citrate on serpentine dissolution.

### 3.2.5 General rate laws

The dissolution rate is, according to transition state theory, function of the concentration of the precursor of the activated complex whose desorption controls the overall dissolution reaction kinetics (Lasaga, 1981). In presence of $n$ parallel mechanisms responsible for the formation of activated complexes, the specific dissolution rate is:

$$ r = \sum_{i=1}^{n} \alpha_i C_i^{m_i}, \tag{3.3} $$

where $\alpha_i$ is the rate coefficient of the $i$th-reaction mechanism associated to the $i$th-species, (s$^{-1}$); $C_i$ is the mineral surface concentration of the activated complex upon adsorption of the $i$th species, (mol m$^{-2}$); $m_i$ is
the order of the reaction. As it is not possible to know the composition of
activated complex, $C_i$ in practice reduces to the concentration of the ad-
sorbed species on the surface that lead to the formation of the activated
complex. Assuming an adsorption mechanism described by Langmuir
isotherm, $C_i$, is given by:

$$C_i = \frac{\Theta_i K_{app,i} a_i}{1 + K_{app,i} a_i}, \quad (3.4)$$

where $\Theta_i$ is maximum surface coverage due to the $i$th-species, (mol m$^{-2}$); $a_i$ is the $i$th-species activity in solution, (-); and $K_{app,i}$ is the apparent
equilibrium constant for the adsorption, defined as (Stumm, 1987):

$$K_{app,i} = K_{int,i} e^{\frac{\Delta z_j F \Psi_j}{RT}}, \quad (3.5)$$

with $K_{int,i}$ the intrinsic surface adsorption equilibrium constant; $\Delta z_j$
the net change in charge on electrostatic plane $j$ subsequent to the ad-
sorption of the species $i$, (-); $F$ the faraday constant, (C mol$^{-1}$); $\Psi_j$ the
electrical potential at the layer $j$ relative to the bulk solution, (V); $T$
the temperature, (K); and $R$ the gas constant, (J K$^{-1}$mol$^{-1}$).

Combination of eqn. 3.3 and 3.4 gives:

$$r = \sum_{i=1}^{n} \alpha_i \left( \frac{\Theta_i K_{app,i} a_i}{1 + K_i a_i} \right)^{m_i} = \sum_{i=1}^{n} r_i. \quad (3.6)$$

In a dilute solution, $C_i$ is described by Freundlich isotherm:

$$C_i = K_i a_i^{e_i}, \quad (3.7)$$

where $e_i$ is the order of the reaction. Substituting $C_i$ from eq. 3.7 into
eq. 3.3, we obtain:

\[ r = \sum_{i=1}^{n} \alpha_i (K_i a_i^{e_i})^{m_i}, \]  

(3.8)

which can be simplified into the commonly used form of the specific dissolution rate:

\[ r = \sum_{i=1}^{n} k_i a_i^{n_i} = \sum_{i=1}^{n} r_i. \]  

(3.9)

In dissolution process of particles with heterogeneous surface, such as dissolution of mineral and heterogeneous catalysts, the specific dissolution rate of the \(i\)th mechanism is described by a more complex equation given by Langmuir-Hinshelwood isotherm (Masel, 1996):

\[ r_i = \frac{k_i \prod K_j a_j}{1 + \sum K_j a_j}. \]  

(3.10)

with \(a_j\) indicating the activity of the \(j\)th-species, (-). or more commonly given by (Lasaga, 1981):

\[ r_i = k_0 A e^{-E_a/RT} a_{H^+}^{n_{H^+}} \prod a_j^{e_j} g(I) f(\Delta G), \]  

(3.11)

where \(A\) is the preexponential coefficient, (mol cm\(^{-2}\)), \(E_a\) is the apparent activation energy of the overall reaction, \(g(I)\) is a function of the ionic strength, and \(f(\Delta G)\) is a function of the Gibbs free energy of the reaction. Table 3.1 lists some of the works on mineral dissolution where the reaction rate has been describe either by one of the equation given above or by a combination of them.
3. Dissolution - Study of the effect of oxalate and citrate

Figure 3.1: The atomic scale structure of olivine looking along the $a$-axis. a. Complete lattice structure of olivine; b. SiO$_4$ tetrahedral unit; c. M(1)-O octahedral unit of Mg(1); d. M(2)-O octahedral unit of Mg(2). A projection of the unit cell is shown by the black rectangle (Chatterjee et al., 2009); f. Schematic diagram indicating the activated complex on olivine surface in the enhanced dissolution mechanism (modified after Pokrovsky and Schott (2000); Olsen and Rimstidt (2008); Liu et al. (2006)). L indicates the organic ligand.
3.3 Material and methods

The dissolution kinetics of natural San Carlos gem-quality olivine grains (Mg$_{1.82}$Fe$_{0.18}$SiO$_2$), with a particle size between 90 and 180 µm and a specific surface of $797 \pm 55$ cm$^2$ g$^{-1}$, was studied at 90 and 120°C using a flow-through reactor described in section 2.2. For the entire duration of the experiment, the feed solution was purged with N$_2$ 99.999 vol.%-purity (PanGas, Werk Dagmersellen, Switzerland), fed directly from a gas cylinder. A solution, consisting of ultrapure water with electrolytes, i.e. HCl, LiOH, C$_6$H$_5$Na$_3$O$_7$-2H$_2$O (sodium citrate tribasic dihydrate salt, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) and C$_2$Na$_2$O$_4$ (oxalic acid sodium salt, 99.0 wt.%-purity, Fluka Chemie AG., Neu-Ulm, Switzerland), was fed to the reactor at a constant flow rate of about 5 ml min$^{-1}$ after being pre-heated up to 90°C with a heat exchanger to minimize temperature drop at the reactor entrance. These organic substances were chosen because they are particularly efficient in promoting the dissolution reaction by forming bidentate mononuclear chelates with magnesium atom on the olivine surface and by acting as catalysts they might be recyclable within the process (Pazouki and Panda, 1998; Singh and Singh, 2008).

The system was pressurized with CO$_2$ 99.995 vol.%-purity (PanGas, Werk Dagmersellen, Switzerland) and maintained at the same pressure through continuous flux from a buffer tank regulated via front-pressure regulator. In order to minimize redox reaction involving the iron released during dissolution, the system was purged with CO$_2$ a number of times to reach the composition of the fed CO$_2$ in the vessel. To estimate dissolution kinetics the concentration of the released magnesium was measured online by means of ion chromatograph (IC with CS12A column, Dionex).
3. Dissolution - Study of the effect of oxalate and citrate

### Table 3.1: Studies of mineral dissolution in presence of additives and at atmospheric condition of CO₂.

- $k_1$ and $k_2$ are rate constants; $K$ is the adsorption constant; $\alpha$ is the activity of the subscripted species, (-); $c$ is the solution concentration of the subscripted species, (m); $C$ is the surface concentration of the subscripted species, (mol m$^{-2}$); subscript $l$ indicates ligand. Note: *, $\alpha$ indicates a product of model parameters.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Mineral</th>
<th>Additives in order of reaction promotion</th>
<th>Concentration of additives</th>
<th>T, (°C)</th>
<th>pH</th>
<th>Dissolution rate law, $r$ (mol/cm$^{-2}$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furrer and Stumm (1986)</td>
<td>$\delta$-Al$_2$O$_3$, BeO</td>
<td>Salicylate, oxalate, malonate, phthalate, succinate, benzoate.</td>
<td>$2 \times 10^{-4}$-0.025 M</td>
<td>25</td>
<td>2.5-6</td>
<td>$\delta$-Al$_2$O$_3$: $k_1C_H^3 + k_2C_l$; BeO: $k_1C_H^2 + k_2C_l$</td>
</tr>
<tr>
<td>Grandstaff (1986)</td>
<td>(Mg,Fe)$_2$SiO$_4$ (Fo82)</td>
<td>EDTA, phthalate</td>
<td>0.001-100 mM</td>
<td>26</td>
<td>4.5</td>
<td>$k_1a_H + k_2a_l^{0.5}$</td>
</tr>
<tr>
<td>Zinder et al. (1986)</td>
<td>Goethite</td>
<td>Oxalate</td>
<td>0.25-1 mM</td>
<td>25</td>
<td>3-6</td>
<td>$3.3 \times 10^{13}C_H^3 + 1.1 \cdot 10^0C_lC_H$</td>
</tr>
<tr>
<td>Christopher and Fogler (1998)*</td>
<td>CaCO$_3$</td>
<td>pH$\geq8$ EDTA, DTPA, CDTA pH$&lt;8$ CDTA, EDTA, DTPA</td>
<td>$10^{-3}$-0.25 M</td>
<td>25</td>
<td>4-12</td>
<td>$k_1a_H + k_2a_H^2O + \sum \frac{a_l}{1+KC_l}$</td>
</tr>
<tr>
<td>Olsen and Rimstidt (2008)</td>
<td>(Mg,Fe)$_2$SiO$_4$ (Fo92)</td>
<td>Oxalate</td>
<td>0-0.35 m</td>
<td>25</td>
<td>0.5-7</td>
<td>$10^4(k_1a_H^{0.46} + k_2c_l^{0.4}a_H^{0.47})$</td>
</tr>
<tr>
<td>Wogelius and Walther (1992)</td>
<td>(Mg,Fe)$_2$SiO$_4$ (Fo91)</td>
<td>KHP</td>
<td>19 mM</td>
<td>25</td>
<td>1-4</td>
<td>$0.8 \cdot 10^{-12}a_H^{0.45} + 9.1 \cdot 10^{-12}a_H^{0.54} + 5.3 \cdot 10^{-15} + 2.3 \cdot 10^{-17}a_H^{-0.31}$</td>
</tr>
<tr>
<td>Authors</td>
<td>Mineral</td>
<td>Additives in order of reaction promotion</td>
<td>Concentration of additives</td>
<td>T, (°C)</td>
<td>pH</td>
<td>Dissolution rate law, $r$ (mol/cm$^{-2}$s)</td>
</tr>
<tr>
<td>-------------------------</td>
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<td>------------------------------------------</td>
</tr>
<tr>
<td>Blake and Walter (1999)</td>
<td>Feldspars</td>
<td>Citrate, oxalate</td>
<td>2-20 mM</td>
<td>70, 80</td>
<td>6</td>
<td>Labradorite: $10^{-13.45}C_l^{0.6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Albite: $10^{-14.05}C_l^{0.8}$</td>
</tr>
<tr>
<td>Kline and Fogler (1981)</td>
<td>Kaolinite, sodium montmorillonite, illite, pyrophyllite, muscovite, talc, and biotite</td>
<td>no OS but HF</td>
<td>0-5 M</td>
<td>20-50</td>
<td>1.5-5.7</td>
<td>$\frac{a_{HF}}{1+K_{HF}}$</td>
</tr>
<tr>
<td>Cama and Ganor (2006)</td>
<td>Kaoline</td>
<td>Oxalate</td>
<td>2 $10^{-3}$-7 mM</td>
<td>25,50,70</td>
<td>2.5-3.5</td>
<td>$3 \cdot 10^{17} e^{-E_a/RT} \cdot \left(6.1 \times 10^{-3} \frac{64(a_{ox}+a_{Hox})^{0.48}}{1+64(a_{ox}+a_{Hox})^{0.48}}\right)^2$</td>
</tr>
<tr>
<td>Golubev et al. (2006a)</td>
<td>Na-Montmorillonite, citrate, oxalate, smectite</td>
<td>EDTA, 3,4-DHBA</td>
<td>10$^{-2}$-30 mM</td>
<td>25</td>
<td>1-12</td>
<td>$k_1 \left(1 - \frac{K_{Cl}}{1+K_{Cl}}\right) + \frac{K_{Cl}}{1+K_{Cl}}$</td>
</tr>
<tr>
<td>Liu et al. (2006)</td>
<td>(Mg,Fe)$_2$SiO$_4$ (Fo92)</td>
<td>Oxalate</td>
<td>0.02 m</td>
<td>25</td>
<td>0-7</td>
<td>$k_1 a_{H} a_{O}^{m_1} + k_2 a_{H} a_{O}^{m_2} + k_1 a_{H} a_{L}^{m_2}$</td>
</tr>
<tr>
<td>Golubev and Pokrovsky (2006b)</td>
<td>Diopside</td>
<td>EDTA, citrate, oxalate, acetate, gluconate, and 2,4-DHBA</td>
<td>0.01-0.1 M</td>
<td>25</td>
<td>5.3-11</td>
<td>$k_1 \left(1 - \frac{K_{Cl}}{1+K_{Cl}}\right) + \frac{K_{Cl}}{1+K_{Cl}}$</td>
</tr>
</tbody>
</table>
3. Dissolution - Study of the effect of oxalate and citrate

In an early phase of the experimental campaign samples of the outlet solution were taken with a fraction collector at regular intervals and analyzed with the inductively coupled plasma-atomic emission spectrometry (ICP-AES, Vista-mpx) to measure magnesium, iron, and silicon concentration. Concentration of magnesium obtained from ICP-AES and from IC were compared to test the validity of the IC measurements (see Figure 3.3), given the higher accuracy of the ICP-AES determination. Moreover, concentration ratio of magnesium over iron, and of magnesium over silicon from ICP-AES measurements were calculated to verify the stoichiometric dissolution process of olivine (see Figure 3.3). The calibration standards for ICP-AES for Mg, Fe, and Si atoms were prepared with the feed solution to take into account the background effect of the solution. The calibration line was built on five measurement points in the range centered on the Mg concentrations determined by IC (-10% of the minimum value and +10% of the maximum value). The wavelengths of the central peak of each element of interest were: 279.078, 383.829 nm for Mg, 250.690, 251.611, 288.158 nm for Si, and 234.35, 238.204, 239.563, 259.940, 261.187 nm for Fe. At these wavelengths, the peaks of the three elements overlapped neither with each other nor with other minor elements present in solution. Three repetitions for each sample were executed and then averaged.

3.4 Mathematical model

The dissolution of olivine was modeled by a 1D population balance equation (PBE) model coupled with a mass balance equation described in section 2.3.
3.5 Results

Olivine dissolution experiments, carried out at 90°C and 120°C, are reported in Table 3.2. In particular, for each experiment, the operating conditions applied, namely the CO₂ fugacity, \( f_{CO_2} \), the concentration of LiOH, HCl, and citrate and oxalate (molality), the flow rate \( Q \), the volume of the suspension \( V \), initial olivine mass \( m_0 \), and the duration of the experiment are listed, together with the resulting specific dissolution rate \( r \), and the calculated pH.

Experiments at 90°C were carried out between pH 2 and 7, whereas those at 120°C were performed between pH 4 and 7, because at low pH and high temperature oxalic acid decomposition to formic acid and CO₂ accelerates (Crossey, 1991).

In Figure 3.2 the logarithm of the specific dissolution rate, estimated as described in section 3.4, is shown as function of pH, the data at 90°C (filled circles) and at 120°C (hollow circles) under high CO₂ pressure and with 0.1 m of oxalate are plotted and compared with literature data at 25°C, atmospheric CO₂, and with \( \sim 0.1 \) m of oxalic acid (Olsen and Rimstidt, 2008). The lines indicate the specific dissolution rate, mol cm\(^{-2}\) s\(^{-1}\), in absence of oxalate and they correspond to the following equations given at each temperature:

- At 25°C, \( \log r = -0.46 \) pH - 11.03 (Olsen and Rimstidt, 2008),
- At 90°C, \( \log r = -0.46 \) pH - 8.66 (Hänchen et al., 2006),
- At 120°C, \( \log r = -0.52 \) pH - 7.59 (Prigiobbe et al., 2009a).

This section is structured in four parts. First, preliminary results are presented in order to verify stoichiometric dissolution, as assumed by
3. Dissolution - Study of the effect of oxalate and citrate

the mathematical model described in section 3.4. In the second part, the results of the experiments, namely, the calculated specific dissolution rates at the investigated temperatures are discussed and compared with literature data. In the third part, SEM images of untreated and reacted olivine are shown. Finally, in the fourth part, section 3.6, a dissolution mechanism is proposed and through surface complexation modeling a mechanistic dissolution rate equation is derived.
3.5 Results

Figure 3.2: Logarithm of $r$ vs. pH at 25, 90, and 120°C in presence of CO$_2$. Symbols indicate: *, linear model for an ligand-free solution at 120°C in presence of CO$_2$ (Prigiobbe et al., 2009a); **, linear model for a ligand-free solution at 90°C (Hänchen et al., 2006); +, literature data (Olsen and Rimstidt, 2008); ++, linear model in a ligand-free solution at atmospheric CO$_2$ (Olsen and Rimstidt, 2008).

3.5.1 Stoichiometry

To verify the applicability of the dissolution model given by eq. 3.3 that is based on the assumption that the dissolution process is fully stoichiometric, we measured the concentration of three atoms Mg, Fe, and Si in the outlet solution of the experiments 167 and 168 (Figure 3.3). These two experiments were chosen because they were performed with the largest applied concentration of organic substances, they were in a pH range where the organic substances has the strongest effect and of interest for mineral carbonation process because the precipitation of magnesite is there favored (Hänchen et al., 2008).
3. Dissolution - Study of the effect of oxalate and citrate

Table 3.2: Operating conditions and results of the olivine dissolution experiments at 90°C and 120°C.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>T, °C</th>
<th>pH</th>
<th>fCO₂, bar</th>
<th>HCl†, mL/min</th>
<th>NaOH/Na₂C₂O₄, mol</th>
<th>Q₀, ml/min</th>
<th>m₀, mg</th>
<th>Dura-, Dura, mol/cm².s</th>
<th>r, mol/cm².s</th>
<th>x 10¹⁰</th>
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<tbody>
<tr>
<td>90</td>
<td></td>
<td>2.0</td>
<td>0.135†</td>
<td>0.1</td>
<td>5.1</td>
<td>189</td>
<td>43.0</td>
<td>5.50</td>
<td>3.11</td>
<td>195</td>
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<td>1.00</td>
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<td>0.1</td>
<td>4.9</td>
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<td>0.082†</td>
<td>0.1</td>
<td>5.0</td>
<td>193</td>
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<td>2.30</td>
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<tr>
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<td>3.5</td>
<td>0.082†</td>
<td>0.1</td>
<td>5.0</td>
<td>193</td>
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<td>6.00</td>
<td>2.71</td>
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<td>0.1</td>
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<td>0.88</td>
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</table>
At low and high temperature, proton-promoted dissolution of olivine initially is a non-stoichiometric process with a preferential release of magnesium in the acid pH region and of silicon in the neutral-alkaline pH region (Pokrovsky and Schott, 2000; Hänchen et al., 2006). Contrarily, we observed that in presence of oxalate at 90 and 120°C and citrate at 20°C, dissolution was fully congruent for the entire duration of the experiment (Figure 3.3). Similar observation was made by Stumm (1992), in the case of kaolinite, and by Grandstaff (1986) and Wogelius and Walther (1991), in the case of olivine. This congruent dissolution process in presence of organic substances confirms that surface organic complexes containing Mg/Fe and Si atoms participate in the formation of the activated complex of the dissolution reaction and suggests that by enhancing the detachment of the Mg/Fe-metal the system can reach the stoichiometric dissolution much faster than in the case of a ligand-free solution.

In Figure 3.3, the comparison of Mg concentrations measured using both IC and ICP-AES are shown. ICP-AES was expected to be more accurate because of the complete decomposition of the organo-metallic complexes during the analysis (Ammann, 2007). By comparing these measurements with the ones from IC, it is possible to see that the formation of the aqueous Mg-complexes did not determine an underestimation of the total magnesium released during dissolution.

Given the reproducibility of these two analytical methods and the observation of a fully stoichiometric dissolution process, we decided to base our calculation of the specific dissolution rate by fitting eq. 3.3 on the olivine equivalent calculated from Mg$^{2+}$ concentrations determined with IC.
3. Dissolution - Study of the effect of oxalate and citrate

Figure 3.3: Concentrations of Mg$^{2+}$, Fe$^{2+}$, and Si$^{4+}$ ions (mM) for experiment 167 at 120$^\circ$C with 0.1 m of oxalate (a, b) and 168 with 0.1 m of citrate (c, d). The lines in parts (a) and (c) have slope equal to the stoichiometric ratio between the displayed ions, namely, Si:Mg = 0.55 and Fe:Mg = 0.1. Lines in parts (b) and (d) indicate the fitting with the model (eq. ), solid line for the IC measurements and dashed line for the ICP-AES measurements.

3.5.2 SEM images

Scanning electron microscope (SEM) images for unreacted olivine and reacted olivine from experiments performed between pH 4.5-5 are reported in Figure 3.4. The comparison of the two photomicrographs in parts a and b of Figure 3.4 highlights that the olivine surface before reaction is intact, though not perfectly smooth, but after being attacked by protons and organic ligands concave holes were created. This surface morphology change is even more evident by comparing parts a, c, d, and e of Figure 3.4 corresponding to images taken from experiments with increasing concentration of oxalate. In this pictures, the size of such holes increases with sodium oxalate concentration. The mechanism
behind this morphology change is the adsorption of oxalate ions onto the olivine surface and the formation of a Mg-ligand complex at the surface. As said above, the formation of this surface complexes weaken the bonds within the crystal bonds at the olivine surface permitting Mg atom to leave the crystal as a Mg-ligand complex. In crystals containing screw dislocation, the result of this leaching phenomenon is the formation of concave parts on a surface (Christopher and Fogler, 1998). Similarly, in presence of 0.1 m of sodium citrate, olivine surface roughness increases but at a smaller extent (Figure 3.4.f), supporting the observation in section A.6.1 about the weaker effect of sodium citrate than sodium oxalate on olivine dissolution kinetics.

### 3.5.3 Mechanism of dissolution

At 90 and 120° C dissolution was enhanced by the presence of both citrate and oxalate, with an effect increasing with organic substance concentration. We ascribed the catalytic effect to the oxalate and citrate ions, namely $\text{C}_2\text{O}_4^{2-}$ and $\text{C}_6\text{H}_6\text{O}_2\text{O}_7^{2-}$, respectively, since they are the dominant species in the pH region where olivine enhanced dissolution was observed and because bidentate ligands are expected to have an higher catalytic effect (see section 3.2.4).

As mentioned in section 3.2.4, dissolution mechanisms consists of simultaneous adsorption onto the olivine surface of a proton and of an oxalate ion. In particular, the proton is adsorbed on the oxygen atom bonded to the silicon atom and the magnesium atom at the olivine crystalline surface (Pokrovsky and Schott, 2000) and the oxalate on the magnesium atom bonded to the protonated oxygen leading to the formation of inner-sphere complexes (Olsen and Rimstidt, 2008; Liu et al., 2006).
3.6 Modeling

3.6.1 Solution speciation model

Solution speciation was modeled at the thermodynamic equilibrium using EQ3/6 v8.0 software package with the cmp database employing the B-dot model to estimate the activity coefficients of the aqueous species (Wolery and Jarek, 2003). The activity coefficient model B-dot is valid for solution with ionic strength up to 3 m (Helgeson, 1969), therefore it was applicable to all our experiments because their ionic strength ranged between $4 \cdot 10^{-3}$ to 1.3 m.

The cmp database was modified by adding the reactions of dissociation of citric acid ($C_6H_8O_7$) and of oxalic acid ($C_2H_2O_4$), and of formation of the magnesium-oxalate complexes ($MgC_2O_4$) in solution (see Table 3.3).

Table 3.3: Logarithm of the equilibrium constants of dissociation of citric acid (1-3) (Benezeth et al., 1997) and oxalic acid (4-5) (Kettler et al., 1998), and complexation of magnesium in solution (6) (Prapaipong et al., 1999).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>0°C</th>
<th>25°C</th>
<th>60°C</th>
<th>100°C</th>
<th>150°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>C$_6$H$_7$O$_6$ ↔ C$_6$H$_5$O$_4$ + H$^+$</td>
<td>-4.841</td>
<td>-4.759</td>
<td>-4.765</td>
<td>-4.871</td>
</tr>
<tr>
<td>3.</td>
<td>C$_6$H$_5$O$_4$ ↔ C$_6$H$_5$O$_3$ + H$^+$</td>
<td>-6.394</td>
<td>-6.397</td>
<td>-6.526</td>
<td>-6.759</td>
</tr>
<tr>
<td>4.</td>
<td>C$_2$H$_2$O$_4$ ↔ C$_2$H$_2$O$_3$ + H$^+$</td>
<td>-1.443</td>
<td>-1.401</td>
<td>-1.481</td>
<td>-1.664</td>
</tr>
<tr>
<td>5.</td>
<td>C$_2$O$_4$ ↔ C$_2$O$_3$ + H$^+$</td>
<td>-4.199</td>
<td>-4.264</td>
<td>-4.466</td>
<td>-4.780</td>
</tr>
<tr>
<td>6.</td>
<td>Mg$^{2+}$ + C$_2$O$_4$ ↔ MgC$_2$O$_4$</td>
<td>-2.948</td>
<td>-3.187</td>
<td>-3.4598</td>
<td>-3.712</td>
</tr>
</tbody>
</table>

Based on the average values of the measured temperature and pressure during each run, $f_{CO_2}$ was calculated by using a noniterative procedure developed by Spycher et al. (2003) which is based on the Redlich-Kwong equation of state for the CO$_2$-H$_2$O mixture. The calculated $f_{CO_2}$ together with the average values of temperature, Mg$^{2+}$, Fe$^{2+}$, and Si$^{4+}$
concentrations, and the known amounts of HCl, LiOH, sodium oxalate, and sodium citrate were used to calculate pH and solution composition for each experiment. Simulation results of 0.1 m sodium oxalate solution at the operating conditions applied during the experiments are reported in Figure 3.5. In these speciation diagrams, it is evident the effect of the non-ideality of the solution on the oxalate ion activity.

From solubility calculation, all investigated systems resulted to be undersaturated with respect to olivine and magnesite with supersaturation ratio below 0.02 and 0.18, respectively, confirming the far from the equilibrium condition of the dissolution and precipitation processes. However, all investigated systems resulted to be supersaturated at least with respect to two iron-bearing phases such as hematite and goethite, although none of these species precipitated during the experiments.

### 3.6.2 Surface complexation model

A surface complexation model was developed to describe olivine dissolution kinetics in solution containing oxalate ions (or more in general containing bidentate ligands) and in condition far from the equilibrium. The model for enhanced dissolution combines the proton-promoted reactions formulated by Pokrovsky and Schott (2000) and the ligand-promoted reactions and the mechanism of the formation of the activated complex proposed by Liu et al. (2006) and Olsen and Rimstidt (2008). Four overall mechanisms were identified at the olivine-solution interface: Proton exchange, proton adsorption leading to polymerization, ligand exchange, and rate-controlling desorption.

The scheme in Figure 3.1.f shows olivine surface upon an ion exchange precursor reaction. In this surface configuration, two atoms O(1) and Mg(1) belonging to the surface groups Mg$_2$SiO$_4$(s) (named site S$_o$) react
with protons (H\(^+\)) and oxalate ions (X\(^{2-}\)) forming the activated surface complex that leads to dissolution.

Being the overall present study performed between pH 2 and 7, the surface complexation model is developed considering the olivine surface composition at pH <pH\(_{pzc}\) (pH of zero charge point). Above this pH, dissolution rate is expected to be independent from pH (Pokrovsky and Schott, 2000). pH\(_{pzc}\) for olivine is around 9 at 25°C (Pokrovsky and Schott, 2000) and, at 120°C, it is expected to be smaller but still higher than 7 since in previous studies (Hänchen et al., 2006; Prigiobbe et al., 2009a) we measured olivine dissolution rate decreasing with pH up to pH 8.

Initially, a precursor ion-exchange reaction takes place at the olivine surface group Mg\(_2\)SiO\(_4\) (named site S\(_o\)). This reaction is responsible for the rapid release of Mg\(^{2+}\) in solution leading to the silica-enriched surface layer, i.e. the formation of the surface group H\(_4\)SiO\(_4\) (named site S):

\[
S_o + 4H^+ \leftrightarrow S + 2Mg^{2+}.
\] (3.12)

The H\(_4\)SiO\(_4\)\(_s\) surface group polymerizes bringing together two isolated silica tetrahedra at the surface and forming silica dimers connected with each other by an oxygen atom (Si-O(1)-Si) which is linked to a magnesium ion Mg(1) deeper in the structure. On the bridging oxygen O(1), a H\(^+\) ion is adsorbed (protonation reaction) leading to the decomposition of the silica dimers and the release of the silicon group as H\(_4\)SiO\(_4\)(aq).

The overall stoichiometry of the polymerization and protonation reactions is given by:

\[
S + nH^+ \leftrightarrow S_H,
\] (3.13)

with \(n\) equal to 0.5 (Pokrovsky and Schott, 2000).

Sites S and S\(_H\) forms inner-sphere complexes on the olivine surface ad-
sorbing a ligand such as water molecules and oxalate ions ($X^{2-}$) (Olsen and Rimstidt, 2008; Liu et al., 2006):

\[ S_H + X^{2-} \leftrightarrow S_{HX}. \]  

(3.14)

Since the enhancement effect of oxalate ions occurs when a surface site contains both a proton and a ligand ion and is much higher when oxalate is adsorbed instead of water, in our model we considered only the effect of the formation of $S_{HX}$ sites where $X^{2-}$ is a ligand. Upon reaction 3.14, the formed bonds between the organic oxygens of the ligand and the Mg(1) atom destabilize the one between O(1) and Mg(1) at the olivine surface by bond polarization. Consequently, the silicon detaches as silicic acid ($H_4SiO_4$) and magnesium as magnesium oxalate complex ($MgX$):

\[ S_H \leftrightarrow H_4SiO_4 + nH^+, \]  

(3.15)

\[ S_{HX} \leftrightarrow H_4SiO_4 + nH^+ + MgX. \]  

(3.16)

In a ligand-free solution, the dissolution reaction is only proton-promoted and the desorption of $S_H$ through reaction 3.15 controls the entire kinetics.

Reactions 3.13 and 3.14 defines the surface complexation model for enhanced olivine dissolution.

The mass action equations of reactions 3.12, 3.13, and 3.14 are respec-
3. Dissolution - Study of the effect of oxalate and citrate

tively listed below:

\[ K_{EX} = \frac{\{S\}a_{Mg}^2}{a_H^4\{So\}}, \quad (3.17) \]
\[ K_H = \frac{\{SH\}}{a_H^n\{S\}}, \quad (3.18) \]
\[ K_{HX} = \frac{\{SHX\}}{a_X\{SH\}}, \quad (3.19) \]

where \( K_{EX}, K_H, \) and \( K_{HX} \) are the apparent equilibrium constants of the corresponding surface reactions formulated assuming the electrostatic term for surface reactions equal to zero; \( a_i \) indicates the activity of the specified species, (-), and \( \{j\} \) the concentration of the \( j \)th surface site, (mol cm\(^{-2}\)).

### 3.6.3 Kinetic model

In this section, we report the kinetics model developed to describe the catalytic effect of sodium oxalate on olivine dissolution based on the surface complexation reactions given in section 3.6.2.

We considered dissolution due to two parallel reactions whose dissolution rates are proportional to the concentration of the adsorbed protons and oxalate ions, consequently they are proportional to the concentration of the surface complexes \( \{SH\} \) and \( \{SHX\} \). The resulting specific dissolution rate of olivine, \( r \) (mol cm\(^{-2}\) s\(^{-1}\)), is then given by the sum of the specific dissolution rates due to protonation, \( r_H \), and oxalate ion
3.6 Modeling

adsorption, \( r_X \):

\[
\begin{align*}
    r_H &= b_H \{S_H\}, \\
    r_X &= b_X \{S_HX\}, \\
    r &= r_H + r_X,
\end{align*}
\]

(3.20)

(3.21)

(3.22)

where \( b_H \) and \( b_X \) are the kinetic constants, \((s^{-1})\).

Combining eq. A.19 with the equation for the balance of the sites:

\[
\{S_o\} + \{S\} + \{S_H\} + \{S_{HX}\} = C,
\]

(3.23)

where \( C \) is the total concentration of sites on olivine surface containing magnesium equal to \(2.2 \times 10^{-5}\) mol m\(^{-2}\) (Wogelius and Walther, 1991; Pokrovsky and Schott, 2000) and \( \{S_H\} + \{S_{HX}\} \) the sum of protonated sites, and with eqn 3.17 through A.11, \( r \) becomes:

\[
r = \frac{b_H K_H a^n_H C}{1 + K_H a^n_H + \frac{a^2_{Ma}}{K_{EX} a^n_H} \left(1 + \frac{b_X K_X a_X}{1 + K_X a_X}\right)}.
\]

(3.24)

Defining:

\[
r_H = b_H K_H a^n_H C,
\]

(3.25)

\[
\beta = \frac{b_X}{b_H},
\]

(3.26)

and eliminating the term \( \frac{a^2_{Ma}}{K_{EX} a^n_H} \) because negligible at low magnesium activity and at low pH, eq. A.22 rewrites as:

\[
r = \frac{r_H}{1 + K_H a^n_H} \left(1 + \beta K_X a_X\right).
\]

(3.27)
Being $r_H$ the simplified equation of the specific dissolution rate due to only surface protonation, we substituted it with the Arrhenius equation already adopted in our earlier works (Hänchen et al., 2006, 2007; Prigiobbe et al., 2009a):

$$r_H = a^n_H A e^{-E_a/RT},$$

with $E_a = 52.9 \text{ kJ mol}^{-1}$, $n$ the order of the protonation reaction, (-), and $A$ the preexponential factor, (mol cm$^{-2}$s$^{-1}$). In this work, at 90°C we used $n$ and $A$ equal to 0.46 and 0.089 mol cm$^{-2}$ s$^{-1}$, respectively (Hänchen et al., 2006), and at 120°C $n$ and $A$ equal to 0.52 and 0.264 mol cm$^{-2}$ s$^{-1}$, respectively (Prigiobbe et al., 2009a).

The model parameters are therefore $\beta$, $K_X$, and $K_H$. By choosing the apparent equilibrium constant of proton adsorption $K_H$ in a way that the logarithm of $r$ in absence of oxalate becomes pH independent at pH lower than 2 and decreases linearly with pH otherwise (Pokrovsky and Schott, 2000; Hänchen et al., 2006), $K_H$ results to be equal or smaller than 0.2. Hence, the model parameters reduced to $\beta$ and $K_X$. These parameter values were estimated by a nonlinear least-squares minimization algorithm applied to eq. A.26 and the experimental data as explained in section 3.7.1.

### 3.7 Discussion

#### 3.7.1 Parameter estimation

Specific dissolution rate for experiments performed at 25 (Olsen and Rimstidt, 2008), 90, and 120°C with 0.1 m sodium oxalate were fitted with eq. A.26 on the log$r$-pH plane. The model parameters $\beta$ and $K_X$
were estimated using the optimization *matlab* routine *lsqcurvefit* and their optimal values are reported in Table A.2. The high $R^2$ between 0.95 and 0.97 and the close correspondence between the best-fit functions and the experimental data for a broad pH range confirm the validity of eq. A.26 (Figure A.4). Moreover, by comparing our best-fit function for the data at 25°C from literature (Olsen and Rimstidt, 2008) (see part a in Figure 3.7) which are given by:

$$r = 10^{-11.3} a_H^{0.46} + 10^{-9.44} a_H^{0.47} a_X^{0.40},$$  

(3.28)

$$r = \frac{10^{-13.3} a_H^{0.46}}{1 + 0.2 a_H^{0.46}} \left( \frac{1 + 10670 a_X}{1 + 970 a_X} \right),$$  

(3.29)

we can observe a close correspondence of the two models. As a matter of the fact, the two rate equations despite their different mathematical form have a similar dependence on the oxalate ion activity (part b Figure 3.7). However, a comparison of the $r$ values at pH 5 (indicated by dotted line in Figure 3.7) highlights a slight underestimation of the experimental specific dissolution rate by eq. 3.28. In our case (eq. 3.29), the rate equation combines two Langmuir adsorption isotherms, one associated with proton adsorption and one with ligand adsorption reaching a saturation state earlier than the model given by eq. 3.28. The advantage of the proposed model is that it is based on surface complexation modeling based on olivine-solution interface mechanisms proposed by earlier mechanistic studies (Pokrovsky and Schott, 2000; Liu et al., 2006). Therefore, we envisage that our model by giving a deeper understanding of the interaction of olivine with ions in solution can help to select better operating conditions and solution compositions for an enhanced olivine dissolution process.
3.7.2 Effect of sodium oxalate and sodium citrate

To investigate the effect of increasing organic salt concentrations, experiments were performed in the pH range between 4.5-5.5 where the organic substances are expected to be more effective because the dominant species in the solution are the bidentate ligands (i.e., C$_2$O$_4^{2-}$ (oxalate) and C$_6$H$_6$O$_7^{2-}$ (citrate)) capable of strong promotional effect by forming mononuclear surface complexes (Stumm, 1992). Six experiments were carried out at 120°C and ~ 80 bar of fCO$_2$, using sodium oxalate and sodium citrate at concentration equal to 0.001, 0.01, and 0.1 m (Figure 3.8). In this pH range, $r$ increased with the organic substance and in all cases it was larger than in a ligand-free system at the same operating conditions, represented by linear function in Figure 3.8. At the minimum dosage of 0.001 m (triangles in Figure 3.8), $r$ did not depend on the type of ligand and it was slightly higher than in an ligand-free solution. The difference becomes larger at 0.01 m (squares in Figure 3.8) and increased at 0.1 m (circles in Figure 3.8) with the highest effect in presence of oxalate (white circle, corresponding to exp. 215 in Table 3.2) where $r$ was 11 times higher than in a solution without organic salts. Comparing the experiments performed with 0.1 m of sodium oxalate (exp. 215) and with 0.1 m of sodium citrate (black circle, corresponding to exp. 168 in Table 3.2), we obtained the highest enhancement effect on dissolution with oxalate. One should consider that exp. 168 was performed at pH 4.77 and exp. 215 at pH 5.46 with comparable organic ion concentra-
tions, namely $10^{-2.5}$ and $10^{-2}$ m for citrate ion ($C_6H_6O_7^{2-}$) and oxalate ion ($C_2O_4^{2-}$), respectively. Therefore, in the first case the proton effect was higher. Despite that, $r$ was larger in exp. 215 where oxalate was used. This result leads to the conclusion that oxalate was more effective in over-coordinating the Mg surface atom than citrate.

Given the higher catalytic effect of sodium oxalate salt, we investigated its effect at concentration equal to 0.1 m at other pH values and at lower temperature due to the stability limit of oxalate around 125$^\circ$C (Kettler et al., 1998).

### 3.7.3 Temperature effect

Dissolution reaction was studied at 90$^\circ$C and 120$^\circ$C and compared with literature data by Olsen and Rimstidt (2008) at 25$^\circ$C, in presence of about 0.1 m sodium oxalate, and at atmospheric CO$_2$. Temperature could affect the dissolution reaction kinetics in two ways: By changing the equilibrium constants of acid dissociation and ion adsorption and by varying the reaction rate constants. We observed the dissolution rate increasing with temperature and that oxalate catalyzed better the reaction than citrate both at 90 (exp. 172 and 175 in Table 3.2) and at 120$^\circ$C (exp. 162, 166, 168, and 170 in Table 3.2).

A comparison of the specific dissolution rate models at 25, 90, and 120$^\circ$C in a ligand-free solution and in presence of oxalate is displayed in Figure 3.9. In this figure, the dot-pairs are placed on the graph in correspondence of the values of $r$ in the two different systems at pH 5. The distance within the dot-pairs changes with temperature and reaches its maximum at 90$^\circ$C corresponding to 1.05 order of magnitude of enhancement effect due to oxalate ions. The trend of the dot-pair distance trend is due to a combination of effects:
3. Dissolution - Study of the effect of oxalate and citrate

- The increase of second dissociation constant of oxalic acid with temperature (see Table 3.3) determining larger oxalate ion concentrations at pH 5, this effect would enhance dissolution;

- The decrease of the adsorption constant of oxalate ions ($K_X$) with temperature due to the exothermic nature of the adsorption process (see Table A.2), this effect would reduce dissolution;

- The increase of the kinetic constant with temperature, this effect would enhance dissolution;

- The approach of the thermal stability limit of oxalic acid with increasing temperature which is around 125°C (Kettler et al., 1998).

The overlapping of these effects led therefore to the highest enhancement at 90°C. However, the change in the organic substance might change this behavior given a different chemical and physical properties as well as different interaction with the olivine surface.

3.8 Conclusion

This work evidences the role of organic acids in enhancing the dissolution kinetics of olivine at operating conditions relevant for mineral carbonation for CO$_2$ storage. We proposed a surface complexation model of independent adsorption of two ions on one surface site described by Langmuir adsorption isotherm which combines two olivine-solution interface mechanisms developed in earlier works in a ligand-free solution (Pokrovsky and Schott, 2000) and in presence of oxalate (Liu et al., 2006; Olsen and Rimstidt, 2008). The model is in good agreement with the observed effect of oxalate and citrate on the experimental data of olivine
dissolution at 90 and 120°C and with literature data at 25°C (Olsen and Rimstidt, 2008). Oxalate promoted olivine dissolution at higher extent than citrate in a pH region suitable for magnesite precipitation (Hänchen et al., 2008). Previous studies (Gautier et al., 2009) highlight that oxalate favors magnesite precipitation without decreasing its solubility (Jordan et al., 2007) due to its ability to facilitate dehydration of Mg$^{2+}$ ions which is responsible for the slow kinetics of magnesite precipitation.

These results open the possibility to combine efficiently in a single-step process olivine dissolution and magnesite precipitation during mineral carbonation by using organic substances.
3. Dissolution - Study of the effect of oxalate and citrate

Figure 3.4: SEM images showing the surface of unreacted forsterite (a) used in this study and after exp. 96 at pH 5.09 (Prigiobbe et al., 2009a) (b), exp. 165 (c), 164 (d), and 167 (e) with 0.001, 0.01, and 0.1 m of Na$_2$C$_2$O$_4$, and after exp. 168 (f) with 0.1 m of Na$_3$C$_6$H$_5$O$_7$. Note the formation of etch pits in all reacted samples in comparison to the initial unreacted surface.
Figure 3.5: Speciation of oxalic acid and ionic strength vs. pH. Symbols indicate: – ion concentration in the upper part and ionic strength in the lower, (m), –·– ion activity, (-). The discontinuity in the lines is due to $f_{CO_2}$ change: from 76 to 19 bar at 90°C and from 81 to 4 bar at 120°C. Simulations at 25°C are at $10^{-3.5}$ bar of CO$_2$. 
Figure 3.6: Upper parts: Logarithm of the specific dissolution rate vs. pH and the best-fit of the functions given in eq. A.26. Lower parts: Speciation of oxalic acid with nominal concentration of 0.1 m. The discontinuity in the lines is due to $f_{CO_2}$ change: from 76 to 19 bar at 90°C and from 81 to 4 bar at 120°C. Simulations at 25°C are at $10^{-3.5}$ bar of CO$_2$. 
3.8 Conclusion

Figure 3.7: Part a: Logarithm of the specific dissolution rate \( (\text{mol cm}^{-2} \text{s}^{-1}) \) vs. pH at 25°C at \( 10^{-3.5} \) bar of CO\(_2\) and the best-fit function by Olsen and Rimstidt (2008) (dashed line, eq. 3.28) and in this work (solid line, eq. 3.29). Part b: Logarithm of the specific dissolution rate vs. oxalate ion activity, \( a_x \) (-).
3. Dissolution - Study of the effect of oxalate and citrate

Figure 3.8: Logarithm of the specific dissolution rate (mol cm$^{-2}$ s$^{-1}$) vs. pH. Best-fit functions at various concentration of sodium oxalate and experimental data with oxalate and citrate.

Figure 3.9: Logarithm of the specific dissolution rate (mol cm$^{-2}$ s$^{-1}$) vs. pH at 25°C and at $10^{-3.5}$ bar of CO$_2$ and at 90 and 120°C at high CO$_2$ fugacity. Best-fit functions estimated in presence of 0.1 m of sodium oxalate and linear models for a ligand-free solution. Dot-pairs mean to highlight the enhancement effect of oxalate at pH 5.
Chapter 4

Thermodynamics and precipitation mechanism of Mg-carbonate

The precipitation of different forms of Mg-carbonate has been studied at temperatures between 25 and 120°C and at a partial pressure of CO₂ between 1 and 100 bar. These conditions are relevant for mineral carbonation applications. Precipitation was triggered by the supersaturation created by mixing Na₂CO₃ solutions in equilibrium with a CO₂ atmosphere with MgCl₂ solutions. Experiments were monitored using attenuated total reflection Fourier transform infrared (ATR-FTIR) and Raman spectroscopy as well as a focused beam reflectance measurement (FBRM) probe and a turbidimeter. Solubility and supersaturation were

³Most of this chapter has been published as Hänchen et al. (2008)
calculated using the software package EQ3/6. Solids were identified using X-ray diffraction (XRD) analysis and scanning electron microscope (SEM) images. At 25°C and $P_{\text{CO}_2} = 1$ bar, only the hydrated carbonate nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) precipitates, as it has previously been observed. Solutions undersaturated with respect to nesquehonite did not form any precipitates in experiments lasting 16 h. Induction times increased with decreasing supersaturation with respect to nesquehonite. At 120°C and $P_{\text{CO}_2} = 3$ bar, hydromagnesite ($\text{(MgCO}_3)_4 \cdot \text{Mg(OH)}_2 \cdot 4\text{H}_2\text{O}$) was formed which transformed within five to fifteen hours into magnesite ($\text{MgCO}_3$). Solutions undersaturated with respect to brucite ($\text{Mg(OH)}_2$) did not form any precipitates in experiments lasting 19 h. At 120°C and $P_{\text{CO}_2} = 100$ bar, direct formation of magnesite and, at elevated levels of supersaturation, the simultaneous precipitation of magnesite and hydromagnesite has been observed. In the latter case, hydromagnesite transformed within a few hours into magnesite. Solutions undersaturated with respect to hydromagnesite did not form any precipitates in experiments lasting 20 h.

4.1 Introduction

Being natural minerals, the properties and the formation of Mg-carbonates have been studied for a very long time already. Nevertheless, open questions still remain both in regard to the formation of Mg-carbonates in natural systems as well as to their production in the laboratory and in industrial processes. The complexity of the Mg-carbonate system, with numerous different forms of hydrated or basic carbonates, is certainly one reason for the lack of a complete understanding of all the issues involved in the formation of Mg-carbonates. Industrial production processes for Mg-carbonate have only received
limited attention due to the low value of the resulting product, which
for most uses can be substituted either by natural material or by
other minerals like Ca-carbonate. Most often, no particular form of
Mg-carbonate is required and, consequently, industrial processes often
produce low purity mixtures of different Mg-carbonate forms.

However, efforts to counter global warming have brought forward a new
use for Mg-carbonate, for it to serve as a means to store anthropogeni-
cally generated carbon dioxide in a solid, stable and permanent form in
order to prevent the latter from accumulating in the atmosphere.

In the work reported in this chapter, besides a brief overview of various
processes to produce Mg-carbonate under laboratory or industrial con-
ditions, we studied the operating conditions required to produce differ-
ent forms of Mg-carbonate using various in situ measurement techniques
such as Raman and Infrared spectroscopy. Detailed experimental results
of the formation of three different forms of Mg-carbonate (nesquehonite
(MgCO$_3$·3H$_2$O), hydromagnesite ((MgCO$_3$)$_4$·Mg(OH)$_2$·4H$_2$O) and
magnesite (MgCO$_3$)) are presented and discuss by interpreting them in
the light of the observed kinetics and of the underlying thermodynamics.

4.2 The Mg-carbonate system

Like with other carbonate systems, in the MgO-CO$_2$-H$_2$O system a
number of hydrated and basic carbonates can be formed, all of which,
however, are metastable compounds. A list of possible forms of Mg-
carbonates is given in Table 4.1. Commonly, all forms containing hy-
droxy groups (i.e. Mg(OH)$_2$) are called basic carbonates since they form
alkaline solutions upon their dissolution. The stable phases in equilibrium
with aqueous solutions containing dissolved Mg-ions and carbon dioxide
are either brucite (Mg(OH)$_2$, magnesium hydroxyde), at very low partial pressures of CO$_2$, or magnesite (MgCO$_3$) as illustrated for the temperature range between 0 and 60° C by Königsberger et al. (1999), who based their calculations on calorimetrically measured thermodynamic properties and solubility data, using a Pitzer model for the activity coefficients.

Using the software package EQ3/6 (Wolery, 1992) and a database employing a Debye-Hückel model for the activity coefficient determination, it is possible to calculate thermodynamic properties over a wide range of temperature and pressure. The model includes two aqueous magnesium complexes, MgHCO$_3^+$ (aq) and MgCO$_3^0$ (aq). The standard state used is one molal, i.e., one mol per kg of water. The reference state that of infinite dilution. Phase diagrams based thereon are shown in Figure 4.1; the solubilities of the different compounds are displayed in Figure 4.2. The results extend the model presented by Königsberger et al. (1999) to higher temperature and pressure levels, i.e., more relevant for mineral carbonation. It also shows that magnesite is the most stable Mg-carbonate under all conditions.

In early studies of the MgO-CO$_2$-H$_2$O system, reported values for the Gibbs free energy of magnesite differed noticeably (see Kittrick and Peryea, 1986, for a discussion). When taking the upper end of the reported values, the result was that magnesite was the most stable Mg-carbonate compound only at elevated temperatures. One of the first authors publishing a comprehensive study of the MgO-CO$_2$-H$_2$O system, Langmuir (1965), therefore concluded magnesite to be unstable below 60° C at a partial pressure of CO$_2$ of one bar. Numerous later studies have since disproved this assertion, showing magnesite to be the most stable carbonate at all temperatures and partial pressures of CO$_2$ (e.g., Christ and Hostetler, 1970; Kittrick and Peryea, 1986). The earlier conclusion about a greater stability of the hydrated forms of Mg-carbonate,
4.2 The Mg-carbonate system

Figure 4.1: Phase diagrams for the system MgO-CO$_2$-H$_2$O.

Hydromagnesite, nesquehonite, lansfordite and artinite, at lower temperatures, is now considered to be an artifact due to kinetic inhibitions in the formation of magnesite.
4. Thermodynamics and precipitation mechanism of Mg-carbonate

Despite being the stable carbonate form, the formation of magnesite at ambient temperature is virtually impossible. Most commonly, only the mineral nesquehonite can be precipitated from aqueous solutions at 25°C and moderate partial pressure of CO₂, i.e. close to ambient pressure or below (Dell and Weller, 1959; Davies and Bubela, 1973; Ming and Franklin, 1985; Kloprogge et al., 2003; Zhang et al., 2006). At higher temperatures, i.e., above approximately 40°C, various basic Mg-

Figure 4.2: Solubilities of different magnesium carbonates and magnesium hydroxide (brucite, Mg(OH)₂) in solution with no foreign ions. From top to bottom, nesquehonite, hydromagnesite and magnesite, white surface is brucite.

4.3 Production of different forms of Mg-carbonate

Despite being the stable carbonate form, the formation of magnesite at ambient temperature is virtually impossible. Most commonly, only the mineral nesquehonite can be precipitated from aqueous solutions at 25°C and moderate partial pressure of CO₂, i.e. close to ambient pressure or below (Dell and Weller, 1959; Davies and Bubela, 1973; Ming and Franklin, 1985; Kloprogge et al., 2003; Zhang et al., 2006). At higher temperatures, i.e., above approximately 40°C, various basic Mg-
4.3 Production of different forms of Mg-carbonate

Table 4.1: List of selected minerals in the MgO-CO$_2$-H$_2$O system. In the expression of the activity product $Q$, $a_i$ is the activity of specified species and $a_{solid}$ is the activity of the relevant mineral. Values for $\Delta G_f^0$ are those in the cmp database of the software package EQ3/6 (Wolery, 1992)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Composition</th>
<th>Activity product</th>
<th>$\Delta G_f^0$, kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brucite</td>
<td>Mg(OH)$_2$</td>
<td>$\frac{a_{Mg}a^2OH}{a_{solid}}$</td>
<td>-835.32</td>
</tr>
<tr>
<td>Magnesite</td>
<td>MgCO$_3$</td>
<td>$\frac{a_{Mg}aCO_3}{a_{solid}}$</td>
<td>-1027.83</td>
</tr>
<tr>
<td>Nesquehonite</td>
<td>MgCO$_3$· 3H$_2$O</td>
<td>$\frac{a_{Mg}aCO_3a^3H_2O}{a_{solid}}$</td>
<td>-1723.95</td>
</tr>
<tr>
<td>Lansfordite</td>
<td>MgCO$_3$· 5 H$_2$O</td>
<td>$\frac{a_{Mg}aCO_3a^5H_2O}{a_{solid}}$</td>
<td>-2199.20</td>
</tr>
<tr>
<td>Artinite</td>
<td>MgCO$_3$· Mg(OH)$_2$· 3 H$_2$O</td>
<td>$\frac{a_{Mg}aCO_3a^2OHa^3H_2O}{a_{solid}}$</td>
<td>-2568.62</td>
</tr>
<tr>
<td>Hydromagnesite</td>
<td>(MgCO$_3$)$_4$· Mg(OH)$_2$· 4 H$_2$O</td>
<td>$\frac{a_{Mg}a^4CO_3a^2OHa^4H_2O}{a_{solid}}$</td>
<td>-5864.66</td>
</tr>
</tbody>
</table>

Carbonates are usually formed by precipitation, mostly in the form of hydromagnesite (Dell and Weller, 1959; Davies and Bubela, 1973; Fernandez et al., 2000; Zhang et al., 2006). In fact, the transformation from nesquehonite to hydromagnesite has been widely reported at temperatures between 50 and 100$^\circ$C, both for a suspension of particles and for the dry compound, if at least some residual water vapour is present in the latter case (Dell and Weller, 1959; Davies and Bubela, 1973).

The minimum reported temperature for the production of the anhydrous form, magnesite, is about 60 to 100$^\circ$C, its formation also requiring the presence of an elevated CO$_2$ pressure (Baron and Favre, 1958; Baron, 1958; Deelman, 2001; Giammar et al., 2005). Reportedly, the formation of magnesite is most often either preceded by the formation of hydromagnesite or observed only in suspensions of solid hydromagnesite, i.e., with the anhydrous carbonate being the result of a transformation from hy-
4. Thermodynamics and precipitation mechanism of Mg-carbonate dromagnesite to magnesite (Sayles and Fyfe, 1973; Stevula et al., 1978). This transition can be very slow, hence, below 150°C and at moderate pressures its duration is often in the order of days. In addition to higher temperatures, also high salinity, high CO$_2$ pressure and low magnesium concentrations (for closed systems) are known to accelerate the (trans)formation (Sayles and Fyfe, 1973). Zhang (2000) reported transformation times between 2 h at 200°C in a solution saturated with NaCl, and over 100 days at 110°C and lower salinity in a closed system. Magnesite formation without an apparent initial or intermediate hydromagnesite presence has been reported under high CO$_2$ pressure, for experiments coupling the dissolution of Mg-silicates with carbonate precipitation. Using a microreactor equipped with synchrotron X-ray diffraction and Raman spectroscopy, magnesite formation was detected at $P_{CO_2} = 150$ bar and temperatures between 150 to 180°C (Wolf et al., 2004b). Production of magnesite had already been reported earlier under similar conditions (O’Connor et al., 2002).

4.3.1 Mechanisms of Mg-carbonate formation

Mg-carbonate precipitation is strongly kinetically controlled, as the sequence of formation of the different compounds is governed by kinetic constraints. The difficulty in precipitating the anhydrous Mg-carbonate (i.e., magnesite) is often attributed to the highly hydrated character of Mg$^{2+}$ ions in solution (Sayles and Fyfe, 1973; Deelman, 2001). As it was stated, hydrated forms of magnesium carbonate precipitate much more easily than the anhydrous form, and therefore magnesite formation is often either preceded by the precipitation of hydromagnesite or of other forms of hydrated carbonates, or possibly even by the initial formation of brucite. With increasing temperature this transformation and the direct
precipitation of magnesite become fast enough to allow for the formation of magnesite without a discernable appearance of the hydrated phases.

The initial appearance of thermodynamically unstable phases is a common phenomenon and often referred to as the Oswald rule of stages (Mullin, 1993, p. 200). In the case of magnesium carbonates, the initial formation of highly hydrated compounds, such as nesquehonite, being replaced by less hydrated forms such as hydromagnesite, can be partially explained by the fact that water molecules, being dipoles having strong electrostatic interaction with all ions, form a barrier around the Mg-cations and are easily incorporated into the carbonate structure.

The Mg-cation has a highly ionic character because it belongs to the second group of the periodic table. In particular, magnesium possesses strongly bonded layers of water dipoles, Bol et al. (1970) distinguished six water molecules in primary hydration and twelve water molecules in secondary hydration, and only the secondary hydration numbers can be influenced by changing the state variables of the system (e.g., the concentration or the temperature) (Burgess, 1978).

This high hydration energy is due to the high ratio between the electrical charge and the ion surface area of Mg$^{2+}$. Therefore the reduction of water activity as in strongly saline environments could favour the dehydration by reducing the thickness of the secondary hydration layer (Christ and Hostetler, 1970).

Since CO$_3^{2-}$ ions have a larger ion radius and are not completely surrounded by water, they are adsorbed on the crystal surface easier and, therefore, a low Mg$^{2+}$ to CO$_3^{2-}$ ion ratio, $r_i = [\text{Mg}^{2+}]/[\text{CO}_3^{2-}]$, might help to keep the water molecules away from the crystal surface.

The hydrated compounds precipitated first can transform following two possible mechanisms: shrinkage (that is, dehydration) and dissolution-
precipitation solvent mediated transformation. Two examples are brought herein: nesquehonite-hydromagnesite transition studied by Davies and Bubela (1973), Lanas and Alvarez (2004), and Zhang et al. (2006), and hydromagnesite-magnesite transition studied by Zhang (2000).

4.4 Experimental

4.4.1 Experimental methods

Two different experimental set-ups were used in this study, namely a stirred 300 ml titanium high pressure reactor for high temperature experiments (Figure 4.3), and a 500 ml glass reactor for experiments at ambient pressure. A stirring rate of 300 rpm was used in all experiments. They have been described more in detail previously (Hänchen et al., 2006; Schöll et al., 2007). Precipitation of magnesium carbonate from the \( \text{H}_2\text{O}-\text{CO}_2-\text{Na}_2\text{CO}_3-\text{MgCl}_2 \) system was investigated in experiments of three different types, i.e., under different operating conditions:

- \( T = 25^\circ\text{C} \) and \( P_{\text{CO}_2} = 1 \text{ bar} \) (Type 1);
- \( T = 120^\circ\text{C} \) and \( P_{\text{CO}_2} = 3 \text{ bar} \) (Type 2);
- \( T = 120^\circ\text{C} \) and \( P_{\text{CO}_2} = 100 \text{ bar} \) (Type 3).

In all cases an aqueous solution of \( \text{Na}_2\text{CO}_3 \) was prepared, heated up to the desired temperature and the gas phase flushed with \( \text{CO}_2 \). For the low temperature experiments a \( \text{CO}_2 \) atmosphere in the reactor was maintained by feeding a small stream of \( \text{CO}_2 \) through a dip tube into the reactor throughout the entire experiment. For the high temperature
4.4 Experimental

Experiments the reactor was heated up, pressurized with CO₂ and then kept at a constant pressure by feeding CO₂ via a front pressure regulator.

Supersaturation with respect to Mg-carbonate was achieved by adding a solution of MgCl₂, after making sure that dissolution and speciation of CO₂ stabilized. This addition defines the start of the induction period, whose end is defined by the onset of precipitation, i.e., the time of first detection of solid particles. At the end of the precipitation experiment, the produced solids were collected, filtered, washed with de-ionised water and dried in an oven at 60°C for about 12 hrs, and then characterized using SEM/EDX (Bruker axs, model D8 Advance) and X-ray diffraction (Zeiss, model LEO 1530). Simple bulk chemical analysis of the solid produced was used with a few samples only. It agreed well with the species identification achieved based on the very distinct crystal shape and the experimental XRD data.

Figure 4.3: Scheme of the experimental set-up used for the high-temperature experiments.
4. Thermodynamics and precipitation mechanism of Mg-carbonate

4.4.2 Monitoring

The solutions of both the experiments at ambient pressure and at 100 bar (type 1 and type 3) were monitored using Raman spectroscopy (Mettler-Toledo, model RA 400). Infrared spectroscopy (Attenuated Total Reflectance Fourier Transformed Infrared spectroscopy, ATR-FTIR, Mettler Toledo, ReactIR 4000, K6Conduit) was used alternatively during part of the experiments at ambient pressure (type 1). With IR and Raman spectroscopy, it is possible to detect and measure the concentration of dissolved molecular species in solution, e.g. HCO$_3^-$ and CO$_3^{2-}$ ions, but not of mono-atomic species such as Mg$^{2+}$ ions, since IR and Raman spectroscopy measure properties associated to the bonds between atoms in the molecule. Raman spectroscopy, in addition, allows also to detect and identify suspended solid compounds in solution, a task which cannot be achieved using IR spectroscopy only. The online monitoring has been used among other tasks for verifying the achievement of a state of equilibrium before the addition of the MgCl$_2$ solution. The onset of precipitation was measured with different tools during the experiments. During the experiments of type 1 a Focussed Beam Reflectance Measurement instrument (FBRM, Lasentec, model 600L) for measuring in situ the chord length distribution (CLD) was used. During the experiments of type 2 a turbidity meter (Mettler Toledo, model FSC402) was used to monitor the turbidity variations. During the experiments of type 3 Raman spectroscopy was used. Commonly, FBRM is used for detecting the onset of precipitation, in our case we have tested the sensitivity of both the turbidity meter and Raman spectroscopy during the ambient pressure experiments. We observed that the induction times obtained from all three techniques differed only very slightly.
Figure 4.4: Raman spectrum of the experimental solution; band position of selected species with the associated Raman shift values: magnesite, 1099 cm\(^{-1}\); nesquehonite, 1100 cm\(^{-1}\); hydromagnesite, 1119 cm\(^{-1}\). The peak position of mainly aqueous species is affected by temperature: (a) Experiment type 1 (1 bar, 25 °C): HCO\(^3\)\(^−\), 1017 cm\(^{-1}\); CO\(^3\)\(^−\), 1065 cm\(^{-1}\); CO\(_2\)(aq), 1364 cm\(^{-1}\). (b) Experiment type 3 (100 bar, 120 °C): HCO\(^3\)\(^−\), 1003 cm\(^{-1}\); CO\(^3\)\(^−\), 1032 cm\(^{-1}\); CO\(_2\)(aq), 1351 cm\(^{-1}\).
Figures 4.4 and 4.5 illustrate two precipitation experiments of type 1 and 3. Figure 4.4(a) shows a Raman spectrum of the experimental solution exhibiting the \( \text{CO}_3^{2-} \), \( \text{HCO}_3^- \), \( \text{CO}_2(\text{aq}) \) and nesquehonite absorption bands. Figure 4.4(b) shows a Raman spectrum of the experimental solution with the \( \text{HCO}_3^- \), hydromagnesite and magnesite absorption bands. The position of the peaks for the different compounds matches those of the characteristic Raman bands reported in the literature (Edwards et al., 2005). The peak position differs only slightly between suspensions and dry solids, which were additionally identified using XRD. An algorithm for peak deconvolution of overlapped Raman peaks was applied. The peaks were described using Gaussian functions; the resulting separated peaks were then integrated over time. In Figure 4.5(a) and Figure 4.5(b) the evolution of the integrated peaks of these species during the precipitation experiments is shown; also plotted is the number of particles as measured by FBRM. Concentrations are related to the integrated peak area for \( \text{CO}_3^{2-} \), \( \text{HCO}_3^- \), and \( \text{CO}_2(\text{aq}) \) and the precipitated solid nesquehonite (\( \text{MgCO}_3 \cdot 3\text{H}_2\text{O} \)), hydromagnesite (\( (\text{MgCO}_3)_4 \cdot \text{Mg(OH)}_2 \cdot 4\text{H}_2\text{O} \)), and magnesite (\( \text{MgCO}_3 \)).

As the peak areas of the species \( \text{CO}_3^{2-} \), \( \text{HCO}_3^- \), and \( \text{CO}_2(\text{aq}) \) reach a plateau, thus indicating the achievement of equilibrium, a solution of \( \text{MgCl}_2 \) is added (start of the induction period for Mg-carbonate precipitation). The end of the induction period can easily be detected both from the peak area curve of precipitated solids and from the curve indicating the number of particles that start growing rapidly as the precipitation starts. At the same time, the \( \text{CO}_3^{2-} \), \( \text{HCO}_3^- \), and \( \text{CO}_2(\text{aq}) \) curves start to decrease due to a reduction of the solution measurement volume seen by the Raman probe caused by the increased solid concentration in the suspension.
4.5 Experimental results

Experiments were carried out over a range of sodium and chloride concentrations. Due to our experimental protocol, the initial magnesium and chloride concentrations are related, i.e. $[\text{Cl}^-] = 2 [\text{Mg}^{2+}]$. The solubility of Na-carbonates and MgCl$_2$ limit the maximum sodium and chloride concentration achievable experimentally, although by varying the ratio between the MgCl$_2$ and the Na-carbonate solutions, these limits can be shifted to a certain extent. The range of possible experiments can best be illustrated by plotting the initial Mg concentration obtainable in our system over the range of Cl and Na concentrations together with the solubility of various Mg-compounds.

The supersaturation ratio, $S$, for all compounds is calculated using the activity product, $Q$, as defined in Table 4.1:

$$S = \left( \frac{Q}{K_{sp}} \right)^{\frac{1}{n}} \quad (4.1)$$

where $K_{sp}$ is the corresponding equilibrium constant or solubility product and $n$ is the total number of aqueous species formed upon dissolution of the compound, including water, e.g., $n = 5$ for nesquehonite and $n = 2$ for magnesite.

4.5.1 Low temperature experiments

For the experiments at 25°C and $P_{\text{CO}_2} = 1$ bar the solubilities of artinite, nesquehonite, hydromagnesite and magnesite (from top to bottom) are shown in Figure 4.6 together with the range of possible initial Mg-concentrations. It can be seen that over the plotted range of Na and Cl concentration all solutions are undersaturated with respect to artinite.
4. Thermodynamics and precipitation mechanism of Mg-carbonate

(as well as with respect to brucite, not shown here) and always super-saturated with respect to hydromagnesite and magnesite. Except for high sodium and chloride (i.e. MgCl$_2$) concentrations, the solutions are also supersaturated with respect to nesquehonite.

The solution compositions of the precipitation experiments carried out are shown in Figure 4.7 where contour lines indicate conditions of constant supersaturation ratio of the initial solution with respect to nesquehonite. The main property varying along these iso-supersaturation lines is the ratio between Mg$^{2+}$ and CO$_3^{2-}$ ion concentrations, $r_i$, as indicated by a second set of contour lines. Operating conditions along with supersaturation ratio and Mg$^{2+}$ to CO$_3^{2-}$ ratio are listed in Table 4.2.

Table 4.2: Experimental conditions and results: 25°C, $P_{CO_2} = 1$ bar

<table>
<thead>
<tr>
<th>$c_{Na}$, mol/kg</th>
<th>$c_{Cl}$, mol/kg</th>
<th>$S_{nes}$, (-)</th>
<th>$S_{lan}$, (-)</th>
<th>$S_{Mag}$, (-)</th>
<th>$S_{HM}$, (-)</th>
<th>$r_i ([Mg^{2+}]/[CO_3^{2-}]),$ (-)</th>
<th>$t_{ind}^a$, min</th>
<th>$t_{exp}$, min</th>
<th>Exp. No</th>
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<td>1.14</td>
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<tr>
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<td>1.14</td>
<td>1.72</td>
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<td>25.4</td>
<td>600</td>
<td>1120</td>
<td>10</td>
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</table>

$^a$N.A. means that no precipitation was observed.

All solids from the low temperature experiments exhibit the typical mor-
4.5 Experimental results

Phology of nesquehonite crystals (well-formed needles) as shown in Figure 4.8(a). Such identification is confirmed by the very good match between the nesquehonite pattern obtained from a database and our X-ray measurements (see Figure 4.8(b)).

The experiments can be grouped into three sets. Two sets at approximately constant ion ratio, i.e. $r_i \simeq 5$ and $r_i \simeq 25$, and one set at constant supersaturation ratio, i.e. $S_{Nes} \simeq 1.11$.

Plotting the induction time over the supersaturation ratio $S$ with respect to nesquehonite for set one, at $r_i \simeq 5$, and including one experiment at $r_i \simeq 6.5$, one can clearly see that the induction time increases as $S_{Nes}$ approaches one whereas almost instantaneous precipitation occurs as the supersaturation is increased to $S_{Nes} = 1.15$ (Figure 4.9(a)). A very similar behavior is observed at $r_i \simeq 25$ (Figure 4.9(b)). The uncertainty in the measured induction time can be inferred from the different times measured when repeating experiments at $S_{Nes} = 1.12$ and $S_{Nes} = 1.14$.

Induction times for the third set, at constant $S_{Nes}$, only exhibit a weak trend and, given the limitations of the thermodynamic model used, therefore, do not allow for conclusions to be made about the influence of the Mg$^{2+}$ and CO$_3^{2-}$ ratio on precipitation kinetics. Similarly, differences between set one and two, i.e., high and low Mg$^{2+}$ and CO$_3^{2-}$ ratio, are too small to draw any conclusions in that respect.

However, it is quite evident that at ambient temperature supersaturation with respect to nesquehonite is governing precipitation kinetics. Therefore, the most likely reaction path is the direct nucleation and growth of nesquehonite. In fact, nesquehonite was identified using Raman spectroscopy as the only solid Mg-compound detected over the course of the whole experiment. Moreover, experiments conducted at MgCl$_2$ concentrations corresponding to undersaturation with respect to nesquehonite
(not shown in Fig. 4.7) and lasting more than 16 hours did not yield any Mg-carbonate precipitation.

The formation of nesquehonite at low temperature is well known from literature (see Section 4.3). Although any solution precipitating nesquehonite is also supersaturated with respect to magnesite as well as hydromagnesite, their nucleation kinetics as well as the kinetics of transformation from nesquehonite into hydromagnesite or magnesite are too slow to allow for their formation at ambient temperature.

### 4.5.2 Transformation of nesquehonite

As described in Section 4.3, the transformation of nesquehonite into hydromagnesite has been observed at temperatures above 50°C. We have studied this transformation for temperatures ranging from 50 to 72°C. Online in-situ Raman spectroscopy as described in Section 4.4.2 was used to monitor the disappearance of nesquehonite and the formation of hydromagnesite. The Raman spectra thus obtained are shown for one experiment in Figure 4.10. Experiments were carried out at atmospheric CO₂ concentration.

Up to 60°C, the transformation is preceded by an induction period with no discernable change in the Raman signal, followed by the simultaneous disappearance of nesquehonite and the appearance of hydromagnesite during a time period that depends on the operating conditions and is reported in Table 4.3. Above 60°C, the induction time is close to zero. As reported in Table 4.3, increasing the temperature accelerates the transformation. It should be noted that the nesquehonite crystals used as seeds had been previously formed in different experiments.
4.5 Experimental results

Table 4.3: Transition experiments from nesquehonite into hydromagnesite at atmospheric CO\textsubscript{2} concentration for several different temperatures.

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>$t_{\text{trans}}$, min</th>
<th>$t_{\text{ind}}$, min</th>
<th>Exp. No. (Source material)</th>
<th>Exp. No.</th>
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<td>108</td>
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<td>4</td>
<td>34</td>
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4.5.3 High temperature, low pressure experiments

For the experiments at 120° C and $P_{\text{CO}_2} = 3$ bar the solubilities of nesquehonite, brucite, artinite, hydromagnesite and magnesite (from top to bottom) are shown in Figure 4.11 together with the range of Mg-concentrations attainable using our experimental procedure. The sharp increase of the solubilities of hydromagnesite and magnesite at ratios of $c(\text{Cl})$ to $c(\text{Na}) \geq 1$ is due to a significant decrease in the pH as the balance between chloride and metal cations is shifted towards a surplus of the former. The change in pH shifts the balance between CO\textsubscript{3}\textsuperscript{2–} and HCO\textsubscript{3}\textsuperscript{−} ions in the direction of the latter, thereby leading to increasing magnesite and hydromagnesite solubility as expressed via the Mg-concentration in Figure 4.11. The solubility of the other carbonates is much less affected by the phenomenon since their high solubility brings with it high magnesium concentrations, which largely compensate the increased chloride concentrations. It can be seen that except for high sodium and chloride concentrations the solutions are, over the plotted range of Na and Cl concentration, undersaturated with respect to nesquehonite and always
supersaturated with respect to artilnite, hydromagnesite and magnesite. Except for low chloride concentrations, the solutions are also supersaturated with respect to brucite.

Table 4.4: Experimental conditions and results: $120^\circ$C, $P_{CO_2} = 3$ bar

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>$P_{CO_2}$, $P_{tot}$, $c_{Na}$, $c_{Cl}$, $S_{Bru}$, $S_{Nes}$, $S_{HM}$, $S_{Mag}$, $r_i([Mg^{2+}]/[CO_3^{2-}])$, $t_{ind}$, $t_{exp}$</th>
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</tr>
</thead>
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<td></td>
</tr>
<tr>
<td>2.7 4.7</td>
<td>0.2 0.4 1.45 0.75 5.25 285.5 322 0 (^b) 50 38</td>
<td></td>
</tr>
<tr>
<td>3.1 5.1</td>
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<td></td>
</tr>
<tr>
<td>3 5 0.4</td>
<td>0.08 1.36 0.75 5.15 84 2.8 0 (^b) 140 40</td>
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</tr>
<tr>
<td>2 4 0.5</td>
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<tr>
<td>3.1 5.1</td>
<td>0.66 0.38 2.41 1.05 9.1 199 5.6 0 (^b) 980 42</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)N.A. means that no precipitation was observed.

\(^b\)Precipitation occurred before addition of MgCl\(_2\) was fully completed, i.e., before targeted supersaturation was achieved.

Solution compositions of the precipitation experiments are shown in Figure 4.12 as red symbols, where contour lines indicate conditions of constant supersaturation ratio of the initial solution with respect to brucite (lower left corner) and nesquehonite (upper right corner). One experiment was carried out at a lower CO\(_2\) pressure and could therefore not be represented on the graph. The operating conditions for all experiments at $120^\circ$C and $P_{CO_2} \approx 3$ bar along with supersaturation and Mg\(^{2+}\) to CO\(_3^{2-}\) ion ratio are listed in Table 4.4. All but one experiment were carried out at a Mg\(^{2+}\) to CO\(_3^{2-}\) ratio between three to six. As it can be seen, most experiments were carried out under conditions of supersaturation with respect to brucite, with some of them also being supersaturated with respect to nesquehonite (incl. the experiment at a lower pressure,
4.5 Experimental results

not indicated on Figure 4.7).

In the experimental set-up used for the experiments at 120°C the MgCl$_2$ solution was added via an HPLC pump. The addition time was two minutes. Observed induction times at 120°C were considerably shorter than at ambient temperature; indeed, except for two experiments, precipitation started before the addition of the MgCl$_2$ solution was completed. In one experiment where the solution was highly undersaturated with respect to brucite no precipitation was observed over the entire experimental duration of nineteen hours. For the experiment close to supersaturation with respect to brucite, precipitation started about one minute after the addition of the MgCl$_2$ solution was complete. In all other experiments, precipitation started before the addition of the MgCl$_2$ had finished, making it impossible to measure an induction time. The evolution of the supersaturation during the MgCl$_2$ solution addition is illustrated in Figure 4.13 where the solubilities of several Mg-carbonates expressed as Mg-concentration, at constant sodium concentration, are plotted over MgCl$_2$, i.e. chloride concentration. Plotted as well is the Mg-concentration in solution as generated by the addition of MgCl$_2$. It can clearly be seen that with the increasing addition of MgCl$_2$ solution, supersaturation, first with respect to magnesite, and then subsequently with respect to hydromagnesite, brucite and in the second example also with respect to nesquehonite is created.

The duration of the experiments varied between a few hours and more than fifteen hours. The solids collected in the four experiments lasting up to about five hours exhibit the crystal morphology of an agglomerate of very thin platelets (Figure 4.14(a)), typical of hydromagnesite, as confirmed by XRD (Figure 4.14(b)). For the experiment lasting five hours, the longest of this set, it can be seen that the major peak of magnesite at 32.7° is already present in the XRD spectra. Solids collected from
experiments running for more than 15 hours, on the contrary presented the structure of massive hexagonal prisms (Figure 4.15(a)) typical of magnesite. The formation of highly crystalline magnesite was confirmed by XRD (Figure 4.15(b)), with the X-ray diffraction pattern exhibiting a perfect match to the characteristic peaks.

These results suggest that at 120°C and $P_{\text{CO}_2} = 3$ bar supersaturation with respect to brucite determines initial precipitation kinetics. We observed in fact no precipitation in solutions undersaturated with respect to brucite, fast but not instantaneous precipitation at solutions close to the solubility of brucite and very fast precipitation as the Mg-concentration was increased above the solubility of brucite during the addition of MgCl$_2$ solution. However, no brucite was collected in our experiments, hence we conjecture that brucite might only act as a precursor for the nucleation of hydromagnesite or might transform into hydromagnesite during the experiment (in at most one hour, the duration of our shortest experiment).

Compared to low temperature experiments, the formation kinetics of hydromagnesite is greatly increased at 120°C thus allowing for its formation within less than one hour. Similarly, the kinetics of magnesite formation becomes fast enough to transform hydromagnesite to magnesite in a time-span of hours. As mentioned in Section 4.3, this transformation might happen via two different reaction mechanisms, which are not necessarily alternative to each other: dehydratation of hydromagnesite (favored at high concentration of magnesium and high ionic strength), and hydromagnesite dissolution followed by magnesite precipitation (favored at low concentration of magnesium).
4.5.4 High temperature, high pressure experiments

To illustrate the experiments at 120°C and $P_{CO_2}$ of 100 bar, the solubilities of magnesite (bottom) and hydromagnesite are shown in Figure 4.16 together with the range of possible initial Mg-concentrations (uppermost surface). It can be seen that over the plotted range of sodium and chloride concentrations, except for very low Na and Cl values, the initial solutions applied during the experiments are supersaturated with respect to hydromagnesite and magnesite. They are, however, undersaturated with respect to brucite, artinite, nesquehonite, whose solubility is not shown here for the sake of simplicity.

More in detail, solution compositions of the precipitation experiments are shown in Figure 4.17. In this graph, contour lines indicate conditions of constant supersaturation of the initial solution with respect to hydromagnesite (0.7 to 2.7) and to magnesite (10 to 40). Detailed operating conditions along with supersaturation ratio and $Mg^{2+} : CO_3^{2-}$ ratio are reported in Table 4.5. The solution composition and the suspension were monitored using online Raman spectroscopy. The supersaturation ratio values given for each experiment in Figure 4.17 and in Table 4.5 are different, since the simulated $P_{CO_2}$ was equal to 100 bar whereas its measured values were slightly higher.

Three different types of outcomes have been observed. In solutions which are only very slightly supersaturated with respect to hydromagnesite (h3), no precipitation occurred during the whole experiment, of duration 20 hours. At slightly higher supersaturation (h11), precipitation of a solid compound, identified in situ with Raman spectroscopy as magnesite, occurs after a short induction time. Increasing the supersaturation even further reduces the induction time to almost zero, i.e. instantaneous precipitation (h5, h10). At even higher supersaturation levels (h8, h13,
h19), the simultaneous precipitation of two different solids was observed. They were identified as hydromagnesite and magnesite from the comparison of the measured Raman spectra with the characteristic Raman bands (see Section 4.4.2). Hydromagnesite disappears again after about two hours and only magnesite remains in the solution, see Fig. 4.5(b) and 4.18. The final product in all experiments was magnesite, as confirmed by the very good match between the magnesite pattern obtained from a database and the X-ray measurements, as well as by the particle shape seen in SEM micrographs (as illustrated for a low pressure experiment in Fig. 4.15).

Table 4.5: Experimental conditions and results: $120^\circ$C, $P_{CO_2} = 100$ bar, Na-system

<table>
<thead>
<tr>
<th>$T$, $^\circ$C</th>
<th>$f_{CO_2}$, bar</th>
<th>$P_{tot}$, bar</th>
<th>$c_{Na}$, mol/l</th>
<th>$c_{CI}$, mol/l</th>
<th>$S_{HM}$, (-)</th>
<th>$S_{Mag}$, (-)</th>
<th>$r_i([[Mg^{2+}]/[CO_3^{2-}])$, (-)</th>
<th>Exp. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>119</td>
<td>83</td>
<td>106</td>
<td>0.6</td>
<td>0.02</td>
<td>1.1</td>
<td>11.5</td>
<td>6.9</td>
<td>ht3</td>
</tr>
<tr>
<td>119</td>
<td>82</td>
<td>104</td>
<td>0.5</td>
<td>0.1</td>
<td>1.6</td>
<td>21</td>
<td>94</td>
<td>ht11</td>
</tr>
<tr>
<td>119</td>
<td>81</td>
<td>102</td>
<td>1.0</td>
<td>0.1</td>
<td>2</td>
<td>32</td>
<td>8</td>
<td>ht10</td>
</tr>
<tr>
<td>120</td>
<td>85</td>
<td>108</td>
<td>0.6</td>
<td>0.24</td>
<td>2.2</td>
<td>33</td>
<td>100</td>
<td>ht5</td>
</tr>
<tr>
<td>123</td>
<td>84</td>
<td>106</td>
<td>0.7</td>
<td>0.4</td>
<td>2.8</td>
<td>48</td>
<td>129</td>
<td>ht8</td>
</tr>
<tr>
<td>119</td>
<td>83</td>
<td>106</td>
<td>1.0</td>
<td>0.7</td>
<td>3.4</td>
<td>65</td>
<td>105</td>
<td>ht19</td>
</tr>
<tr>
<td>119</td>
<td>82</td>
<td>103</td>
<td>1.0</td>
<td>0.7</td>
<td>3.4</td>
<td>66</td>
<td>102</td>
<td>ht13</td>
</tr>
</tbody>
</table>

These results indicate that under the experimental conditions of $100^\circ$C and $P_{CO_2} = 100$ bar solutions have to be supersaturated with respect to hydromagnesite to allow for unseeded precipitation of magnesium carbonates within 20 h. This is in agreement with Giammar et al. (2005), which at $90^\circ$C and $P_{CO_2} \simeq 90$ bar reported significant precipitation only in experiments supersaturated with respect to hydromagnesite. At the same time, the formation of hydromagnesite in measurable quantities is
only observed at elevated values of supersaturation and is only a temporary phenomenon since in all cases magnesite is the final product.
Figure 4.5: Monitoring of a precipitation experiment with Raman spectroscopy and FBRM. Evolution of concentration (i.e., integrated peak area of the Raman signal) of $\text{CO}_3^{2-}$, $\text{HCO}_3^-$, $\text{CO}_2(\text{aq})$ and $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, as well as of the number of particles measured with FBRM (experiment type 1), and integrated peak area of the Raman signal for magnesite and hydromagnesite (experiment type 3).
Figure 4.6: Solubility, expressed as Mg-concentration, of artinite, nesquenite, hydromagnesite and magnesite (from top to bottom) over a range of Na- and Cl-concentration at 25°C and $P_{\text{CO}_2} = 1$ bar. White wireframe surface shows Mg-concentration of solutions obtainable by mixing Na$_2$CO$_3$ solutions with MgCl$_2$ solutions, i.e. possible initial conditions using our experimental protocol.
Figure 4.7: Contour line representing supersaturation ratio, $S$, with respect to nesquehonite (0.94 - 1.21) and Mg$^{2+}$ to CO$_3^{2-}$ ratio, $r_i$, (5 - 25) over the experimental range of Na- and Cl-concentrations at the possible initial conditions using our experimental protocol, i.e. projected on the wireframe surface in Fig. 4.6. Dashed lines represent pH contour lines (7.4 - 7.6). Symbols indicate solution composition of the precipitation experiments in Table 4.2.
4.5 Experimental results

Figure 4.8: SEM image and X-ray diffraction pattern for the precipitated solids in the Na-system at 25°C, $P_{CO_2} = 1$ bar. Red stars indicate position and height of a reference XRD spectra. Except for a few peaks significantly higher in the reference data, a very good agreement is found.
Figure 4.9: Induction time for precipitation experiments at 25°C in the Na-
system at approximately constant Mg\(^{2+}\) to CO\(_3^{2-}\) ratio, \(r_i\), plotted over sup-
sersaturation ratio, \(S\), with respect to nesquehonite.

(a) \(r_i \simeq 5\) (Exp. No.: 21, 22, 20 and 19)

(b) \(r_i \simeq 25\) (Exp. No. 10, 15, 23, 16, 34, 11)
4.5 Experimental results

Figure 4.10: Raman spectra of the transformation of nesquehonite to hydromagnesite at $72^\circ$C. Peaks at Raman shifts of 1100 cm$^{-1}$ and at 1119 cm$^{-1}$ represent nesquehonite and hydromagnesite, respectively.
Figure 4.11: Solubility, expressed as Mg-concentration, of nesquehonite, brucite, artinite, hydromagnesite and magnesite (from top to bottom) over a range of Na- and Cl-concentration at 120°C and $P_{\text{CO}_2} = 3$ bar. White wireframe surface shows Mg-concentration of solutions obtainable by mixing Na$_2$CO$_3$ solutions with MgCl$_2$ solutions, i.e. possible initial conditions using our experimental protocol.
Figure 4.12: Contour line representing supersaturation ratio, $S$, with respect to brucite (0.7 - 1.3) and nesquehonite, $S$, (0.91 - 1.03) over the experimental range of Na- and Cl-concentrations at 120 °C and $P_{CO_2} \simeq 3$ bar. Dashed contour lines represent pH (6.85 - 7.5). Symbols indicate solution composition of the precipitation experiments.
4. Thermodynamics and precipitation mechanism of Mg-carbonate

Figure 4.13: Solubility, expressed as Mg-concentration, of nesquehonite, brucite, artinite, hydromagnesite and magnesite (from top to bottom) at constant $c(\text{Na})$ over Cl-concentration. Dotted line: trajectory of Mg-concentration in solution as MgCl$_2$ solution is added assuming no precipitation, red symbol denotes final Mg-concentration after completion of MgCl$_2$ solution addition for individual experiment.
Figure 4.14: Typical SEM image and X-ray diffraction pattern for the precipitated solids at 120°C, $P_{CO_2} = 3$ bar for experiments lasting up to five hours. Red symbols mark the position and height of for a reference hydromagnesite spectra. Both peak position and height show a very good match.
Figure 4.15: SEM image and X-ray diffraction pattern for the precipitated solids at 120°C, $P_{\text{CO}_2} = 3$ bar for experiments lasting more than sixteen hours. Red symbols mark the position of characteristic magnesite peaks, indicating an almost perfectly crystalline magnesite.
Figure 4.16: Solubility, expressed as Mg-concentration, for magnesite and hydromagnesite over a range of Na- and Cl-concentration at 120°C and $P_{\text{CO}_2} = 100$ bar. White wireframe surface shows Mg-concentration of solutions obtainable by mixing Na$_2$CO$_3$ solutions with MgCl$_2$ solutions, i.e. possible initial conditions using our experimental protocol (from bottom to top).
4. Thermodynamics and precipitation mechanism of Mg-carbonate

Figure 4.17: Contour line representing supersaturation ratio, $S$, with respect to hydromagnesite (dashed line, 0.7 - 3.5) and magnesite (15 - 75) over the experimental range of Na- and Cl-concentrations at 120°C and $P_{\text{CO}_2} = 100$ bar. Straight solid lines represent pH contour lines (6 - 6.37). Symbols indicate solution composition of the precipitation experiments.
Figure 4.18: Raman spectra of the transformation of hydromagnesite into magnesite for experiment h19 at 119°C and $P_{tot} = 106$ bar. Peaks at Raman shifts of 1099 cm$^{-1}$ and at 1119 cm$^{-1}$ represent magnesite and hydromagnesite, respectively.
4.6 Conclusions

The magnesium carbonate system exhibits a complex behaviour due to the large number of possible phases and to the strong kinetic inhibitions that are dependent on temperature, partial pressure of CO\textsubscript{2} and possibly other parameters. Depending on the operating conditions, usually only one compound is controlling the formation of a solid phase, with the fastest reaction determining the observed overall rate of precipitation. If for given conditions it is known which phase is rate-controlling, precipitation kinetics depends essentially on the supersaturation with respect to this species, i.e., thermodynamics can be used to predict both the appearance of solid phases and the precipitation kinetics. The formation of the anhydrous form of magnesium carbonate, i.e., magnesite, has been demonstrated at 120\textdegree C and a \( P_{\text{CO}_2} \) of 3 bar. However, it required the formation of hydromagnesite as an intermediate substance and is too slow a process for industrial purposes, in particular mineral carbonation. Moreover, to produce magnesite under these conditions, solutions have to be supersaturated not only with respect to magnesite but also brucite and hydromagnesite, which requires e.g. much higher magnesium concentrations than supersaturation with respect to magnesite would be needed. Compared to experiments at \( T = 120\textdegree C \) and \( P_{\text{CO}_2} = 3 \) bar, formation kinetics of magnesite is greatly enhanced at 100 bar thus allowing for its immediate formation. Precipitation was only observed in solutions supersaturated with respect to hydromagnesite (but undersaturated with respect to brucite). At sufficient supersaturation, hydromagnesite simultaneously precipitates with magnesite but transforms then into magnesite within a few hours, i.e., faster than at lower pressures. These results show that precipitation and formation of various Mg-carbonates can be understood and described using thermodynamic
models if the kinetic inhibition had been adequately characterized. They provide a useful basis for the design of operating conditions to precipitate Mg-carbonates in the context of mineral carbonation, e.g., using natural MgO-bearing silicates as substrates.
4. Thermodynamics and precipitation mechanism of Mg-carbonate
Chapter 5

Kinetics of magnesite and hydromagnesite precipitation

Precipitation of MgCO$_3$ is hindered by the high dehydration energy to incorporate magnesium ions into the crystal structure, therefore formation of unstable and hydrated Mg-carbonates (e.g., nesquehonite and hydromagnesite) is kinetically favored. Precipitation of MgCO$_3$ is affected by temperature, P$_{CO_2}$, supersaturation, CO$_3^{2-}$ and Mg$^{2+}$ activity ratio, and Mg$^{2+}$ ion concentration. In this work, we investigated the effect of these process variables on magnesite precipitation kinetics under operating conditions suitable for mineral dissolution with the final aim to select optimal operating conditions to use during a single-step process of aqueous mineral carbonation. To this purpose, precipitation mechanisms of magnesite and of hydromagnesite, which forms under certain condi-
5. Kinetics of magnesite and hydromagnesite precipitation

tions, were investigated using the MgCl$_2$-CO$_2$-Na$_2$CO$_3$ aqueous system at 90, 120, and 150$^\circ$C, at 100 bar of P$_{CO_2}$, and varying MgCl$_2$ between 0.012 and 0.36 m and Na$_2$CO$_3$ between 0.08 and 0.52 m. The system was monitored with online Raman spectroscopy and modeled by population balance equation (PBE) coupled with a mass balance equation. The kinetics of nucleation, growth, and dissolution during transformation were estimated by non-linear regression of the Raman spectra using multivariate kinetics modeling. Induction time determined by the Raman spectra measurements decreased with supersaturation and with temperature following classical nucleation theory, but the induction time of magnesite increased with Mg$^{2+}$ indicating an inhibiting effect of this ion on the precipitation of anhydrous Mg-carbonate. According to this theory, homogeneous nucleation rate ($J$) was estimated between $3.6 \cdot 10^7$ and $3.4 \cdot 10^9$ m$^{-3}$ s$^{-1}$ for magnesite in investigated temperature range and between $1 \cdot 10^6$ and $4 \cdot 10^{11}$ m$^{-3}$ s$^{-1}$ for hydromagnesite at 120$^\circ$C. The growth was better described by the birth and spread mechanism and the estimated growth rate ($G$) varied between $1.3 \cdot 10^{-11}$ and $3.3 \cdot 10^{-9}$ m s$^{-1}$ for magnesite in investigated temperature range and between $1.3 \cdot 10^{-7}$ and $4.6 \cdot 10^{-6}$ m s$^{-1}$ for hydromagnesite at 120$^\circ$C.

5.1 Introduction

Magnesium carbonates are studied for various industrial processes aimed at producing paper, construction materials, paints, rubber, plastics, inert vehicle, pharmaceutical, cosmetic. Recently, interest has raised around magnesite precipitation because of its potential use to store CO$_2$ upon dissolution of Mg-bearing mineral such as wollastonite, olivine, and serpentine and industrial alkaline residues. Only few authors, e.g., Sayles and Fyfe (1973), Saldi et al. (2009), and Gautier et al. (2009), have
conducted a systematic study of magnesite precipitation kinetics at high temperature, and it is completely missing the kinetics at high $P_{CO_2}$. In Chapter 4, we investigated Mg-carbonate precipitation mechanisms over a broad range of temperature and $P_{CO_2}$ but without estimating the kinetics. Therefore, magnesite nucleation and growth at operating conditions relevant for ex situ aqueous mineral carbonation are still unknown. To feel this gap, we studied Mg-carbonate precipitation kinetics at 90, 120, and 150°C and at 100 bar of CO$_2$ in unseeded supersaturated MgCl$_2$-Na$_2$CO$_3$ solutions and the experimental and modeling results are reported herein.

This chapter is divided in three main parts:

- In the first part, section 5.2 reports a literature review on precipitation mechanism of Mg-carbonate at high temperature and high $P_{CO_2}$ and points out the main issue in the precipitation of magnesite from supersaturated solutions. Section 5.3 describes the experimental work, i.e., the set-up, the used protocol, and the applied monitoring tools used.

- In the second part, section 5.4 reports and discusses the experimental results together with the observed precipitation mechanism and the measured induction time.

- In the third part, section 5.5 introduces both the use of Raman spectroscopy as online tool for kinetics studies and the calibration-free method based on multivariate kinetics modeling applied to Raman spectroscopy measurements to estimate the precipitation kinetics of magnesite and hydromagnesite. Then, section 5.6 explains the modeling adopted to fit the time-resolved Raman spectra and to describe the precipitation process together with the constitutive equations for nucleation, growth, and phase transition. The
modeling results and the discussion are then reported in section 5.7 together with the observed precipitation mechanism and the estimated kinetics.

Finally, the conclusion and the implication of this study on the mineral carbonation process are given in section 5.8.

5.2 Background

5.2.1 Mechanism of magnesite and hydromagnesite precipitation

The fundamental driving force for crystallization is the difference in chemical potential between supersaturated and saturated solutions. The chemical potential difference is generally expressed as a function of the supersaturation ($S$), defined as the ratio between the solute concentration in the solution $C$ and the equilibrium concentration (solubility) $C_s$ at a given temperature and pressure. For ionic crystal, $C$ is given by the product of the actual activity of the reactive ions and $C_s$ is that product at equilibrium, their ratio is then powered to the inverse of the sum of the ionic stoichiometric coefficients (Mersmann, 2001).

There are four main methods by which supersaturation can be generated, these include decreasing solution temperature (cooling crystallization), evaporating the solvent (evaporative crystallization), adding chemical reactants (reactive crystallization), and changing the solvent composition (antisolvent crystallization). The choice of a crystallization method is based on the solubility of the solute in a given solvent. In crystallization, small changes in process conditions, such as temperature, solution composition, cooling rate, or crystallizer hydrodynamics/mixing, can result
in a significant variation in the level of supersaturation which in turn affect the kinetics and the crystal properties (such as polymorphic or hydrated form, particle size, shape, purity, and defect structure).

In the case of Mg-carbonate, crystallization kinetics strongly depends on temperature, CO$_2$ partial pressure, and solution composition such as pH, ionic strength, Mg$^{2+}$ ion concentration, and the activity ratio of CO$_3^{2-}$ and Mg$^{2+}$ ions. Among the several Mg-carbonate crystals such as lansfordite, brucite, nesquehonite, artinite, hydromagnesite, and magnesite, magnesite is the most stable compound except for T higher than 100°C and CO$_2$ pressure lower than 10$^{-1}$ bar; in this range the most stable phase is brucite. At low temperature and low P$_{CO_2}$ the formation of hydrated Mg-carbonate crystals such as nesquehonite, hydromagnesite, lansfordite, and brucite is kinetically favored; whereas at high temperature and high P$_{CO_2}$ the anhydrous Mg-carbonate, i.e. magnesite, can either precipitate directly or simultaneously with hydromagnesite that then transforms into magnesite (Hänchen et al., 2008).

Generally speaking, magnesite precipitation rate increases with temperature, CO$_2$ pressure, pH, ionic strength, and CO$_3^{2-}$-Mg$^{2+}$ activity ratio (Christ and Hostetler, 1970; Lippmann, 1973; Sayles and Fyfe, 1973; Pokrovsky and Schott, 1999; Hänchen et al., 2008; Saldi et al., 2009), and decreases with Mg$^{2+}$ ion concentration because of the high dehydration energy of the Mg$^{2+}$ due to the presence of six water molecules surrounding the Mg$^{2+}$ ion thus forming an hydration shell that hinders nucleation and growth (Christ and Hostetler, 1970; Lippmann, 1973; Sayles and Fyfe, 1973). High values of CO$_3^{2-}$-Mg$^{2+}$ activity ratio, i.e., of high concentration of CO$_3^{2-}$ ions with respect to Mg$^{2+}$, translates in a faster kinetics because the carbonate ion has a greater water exchange rate than the magnesium ion (Nielsen and Toft, 1984). Moreover, the displacement by CO$_3^{2-}$ ions of water-shell around Mg$^{2+}$ both present
in solution and on the crystal surface enhances the dehydration rates of Mg$^{2+}$. Therefore, the integration rate is assumed to be controlled by the dehydration of the cations (Mg$^{2+}$) rather than of the anions (CO$_3^{2-}$). Lin and Singer (2005) proposed that the complexation of the cation with a ligand enhances the dehydration rate of the remaining water molecules coordinated with the cation leading to faster precipitation of the dehydrated crystal form.

To mitigate the ion hydration effect authors proposed:

- To reduce water activity: By adding inorganic salts (Sayles and Fyfe, 1973), by increasing CO$_2$ pressure (Lippmann, 1973; Sayles and Fyfe, 1973), and by increasing temperature (evaporative precipitation);

- To reduce Mg$^{2+}$ activity: By adding complexing agents such as organic salts (Lin and Singer, 2005; Gautier et al., 2009; Sandengen et al., 2008);

- To increase CO$_3^{2-}$-Mg$^{2+}$ activity ratio: By increasing CO$_2$ pressure (Lippmann, 1973).

Under certain operating conditions such as high supersaturation with respect to hydrated Mg-phases, magnesite precipitation can either follow the Ostwald rule of phases (Ostwald, 1897). The least stable phase (hydrated forms) precipitates first and then transforms into the most stable one (anhydrous form) or both the unstable and the stable phases precipitate simultaneously and the hydrated unstable phase transforms into magnesite (Zhang, 2000; Hänchen et al., 2008). Zhang (2000) studied the transformation kinetics of hydromagnesite into magnesite at 110, 150, and 200°C and at atmospheric CO$_2$ pressure in brine and saturated NaCl solutions. They observed two transformation mechanisms
occurred: In saturated NaCl solutions direct dehydration of hydromagnesite while in brine solvent-mediated transformation. In both systems, high Mg\(^{2+}\) ion concentrations hindered the transformation kinetics, but in brine containing SO\(_4^{2-}\) ions the activity of Mg\(^{2+}\) was reduced by the formation of MgSO\(_4(aq)\) complexes favoring hydromagnesite transformation through dissolution. However, the reduced magnesium activity decreased supersaturation determining a slower magnesite growth and a smaller final amount.

Similarly, at high temperature, i.e., 126°C and at atmospheric CO\(_2\), Sayles and Fyfe (1973) studied nucleation and growth kinetics of magnesite. They observed that both nucleation and growth were inhibited by increased Mg\(^{2+}\) concentration and enhanced by increased ionic strength and CO\(_2\) pressure.

Sandengen et al. (2008) studied magnesite precipitation by performing seeded experiments with hydromagnesite crystals in a solution of 95 wt.% of monoethylene glycol (MEG) and NaCl at 150°C. Due to the presence of MEG and NaCl, the Mg\(^{2+}\) and water activities decreased enhancing precipitation.

Gautier et al. (2009) has recently explored the effect of oxalate (up to a concentration of 0.01 M) at 120°C. Under these conditions, they measured a faster magnesite formation and suggested that the formation of strong Mg-oxalate complexes in solution and at the magnesite-water interface favored an higher water exchange rate from the Mg\(^{2+}\) hydration shell facilitating nucleation and the integration of the ion onto the magnesite crystalline surface.

The effect of water activity and carbonate ions in a unique rate equation for dissolution and precipitation of magnesite was developed by Pokrovsky and Schott (1999). In their experiments, they observed that
magnesite precipitation was favored at pH >5 and accelerated in presence of high CO$_3^{2-}$, while its dissolution was enhanced at low pH and high ionic strength. By surface complexation modeling of magnesite crystals, they derived a specific rate equation (mol cm$^{-2}$ s$^{-1}$) for dissolution and growth given by:

$$r = k \frac{Ka^4_{H_2O}}{a^4_{CO_3^{2-}} + Ka^4_{H_2O}} (1 - SI^4),$$  \hspace{1cm} (5.1)

where $k$ is the dissolution rate constant; $K$ is the adsorption constant of water molecule onto the Mg atoms at the solid-solution interface; $SI$ is the saturation index with respect to magnesite given by log $S_M$, where $S_M$ is the supersaturation given in eq. 5.28. Eq. 5.1 assumes that the same mechanism occurs during dissolution and precipitation and being developed under low CO$_3^{2-}$ concentration, namely $10^{-6}$-$10^{-3}$ M, it might be not valid at higher carbonate concentrations because of mechanism change.

More recently, Saldi et al. (2009) studied the magnesite growth rates by using hydrothermal atomic force spectroscopy (HAFM) between 80 to 120°C and supersaturation with respect to magnesite between 2.5 and 28.5 and by using mixed-flow reactor at 100°C and with $S_M$ between 4.5 and 10. They observed two growth controlling mechanisms: Step generation via spiral growth at screw dislocation and step advancement away from this dislocation. Under operating conditions applied in the mixed-flow reactor the spiral growth mechanism dominated and they described it by a simplified growth model given by:

$$G = Ae^{\frac{-E_a}{RT}} (S_M - 1)^2,$$

where $A$ is the preexponential factor equal to $6.6 \cdot 10^{-6}$ mol cm$^{-2}$s$^{-1}$; $E_a$
the apparent activation energy equal to 60 kJ mol$^{-1}$; $T$ the temperature, K; and $R$ the gas constant, JK$^{-1}$ mol$^{-1}$. According to HAFM measurements at lower temperature, the step advancement growth mechanism was the controlling mechanism having an apparent activation energy as large as 159 kJ mol$^{-1}$. Such high value is mostly associated to the dehydration energy of magnesium ions resulting in an hindered process at low temperature and the formation of hydrated crystals as observed in Hänchen et al. (2008).

Recent studies investigated the effect of bio-molecules (Elhadj et al., 2006), enzymes (Mirjafari et al., 2007), and bacteria (Ramanan et al., 2009) to enhance carbonate precipitation (calcite and magnesite) and mineral carbonation. Their positive effect is due to their ability to reduce the dehydration energy of the cations (e.i., Ca$^{2+}$ and Mg$^{2+}$) by complexing them in solution and at the solid-liquid interface, hence facilitating the removal of the hydration shell around the cations.

5.2.2 Chemical reactions

The stoichiometry of precipitation of magnesite (reaction 5.2) and hydro-magnesite (reaction 5.3), and its transformation into magnesite (reaction 5.4) are given by:

\[
\begin{align*}
\text{Mg}^{2+} + \text{CO}_3^{2-} & \leftrightarrow \text{MgCO}_3(s), \quad (5.2) \\
5\text{Mg}^{2+} + 6\text{H}_2\text{O} + 4\text{CO}_3^{2-} & \leftrightarrow ((\text{MgCO}_3)_4 \cdot \text{Mg(OH)}_2 \cdot 4\text{H}_2\text{O})_{(s)} + 2\text{H}^+ \quad (5.3) \\
(\text{MgCO}_3)_4 \cdot \text{Mg(OH)}_2 \cdot 4\text{H}_2\text{O} + \text{CO}_3^{2-} + 2\text{H}^+ & \leftrightarrow 5\text{MgCO}_3(s) + 6\text{H}_2\text{O}. \quad (5.4)
\end{align*}
\]

The supersaturation ratio with respect to magnesite ($S_M$) and hydro-
5. Kinetics of magnesite and hydromagnesite precipitation

magnesite \((S_H)\) are defined as follows:

\[
S_M = \left( \frac{a_{Mg^{2+}}a_{CO_3^{2-}}}{K_{sp,M}} \right)^{0.5},
\]

\[
S_H = \left( \frac{a_{Mg^{2+}}a_{CO_3^{2-}}a_{H_2O}^6}{K_{sp,H}} \right)^{1/15},
\]

with \(a_{Mg^{2+}}, a_{CO_3^{2-}}, \) and \(a_{H_2O}\) are the activities of the subscripted species, \((-)\) and \(K_{sp,i}\) the solubility product of the \(i\)th mineral.

Reactions 5.2 to 5.4 are in equilibrium with the reactions of \(CO_2\) dissolution (reaction 5.7) and \(CO_2\) speciation (reactions 5.8 to 5.10):

\[
CO_2(g) \leftrightarrow CO_2(aq),
\]

\[
CO_2(aq) + H_2O \leftrightarrow H_2CO_3,
\]

\[
H_2CO_3 \leftrightarrow HCO_3^- + H^+,
\]

\[
HCO_3^- \leftrightarrow CO_3^{2-} + H^+.
\]

During precipitation of hydromagnesite crystals, pH decreases due to the production of \(H^+\) determining a temporal decrease of \(CO_3^{2-}\) ion concentration and slowing down the reaction. If magnesite and hydromagnesite precipitate simultaneously, the precipitation of magnesite is hindered by the precipitation of hydromagnesite, but as soon as hydromagnesite starts to transform into magnesite, \(H^+\) ions are consumed raising the pH and enhancing magnesite growth. In a saturated \(CO_2\)-system, continuous supply of carbonate species is delivered, but depending on the solution composition and reaction kinetics temporal depletion of \(CO_3^{2-}\) might verify. To avoid such effects, pH can be maintained constant at an optimal value by adding a chemical buffer to the system.
5.3 Material and methods

5.3.1 Experimental apparatus and monitoring tools

Mg-carbonate precipitation kinetics was studied in a MgCl$_2$-Na$_2$CO$_3$-CO$_2$ aqueous system using a 300 ml high-pressure high-temperature titanium reactor described in section 2.2. Batch experiments were performed and monitored with online temperature, pressure, and Raman spectroscopy probes. A stirring rate of 300 rpm was used in all experiments to ensure complete mixing. Raman spectroscopy allowed to measure dissolved molecular species in solution and suspended solid compounds. We used a RA 400 Raman spectrometer from Mettler-Toledo (Greifensee, Switzerland) equipped with a 250 mW frequency-stabilized laser diode at 785 nm and a thermoelectrically cooled CCD detector. Measurements were recorded using a 5/8 in. ball-type immersion probe (Inphotonics, Norwood, USA) connected via a fiber optic (thicknesses of collection and excitation fibers were 100 and 200 $\mu$m, respectively) resistant until 200 bar. Raman spectra were collected at a laser intensity of 150 mW in the Raman shift range from -50 to 3600 cm$^{-1}$ with a resolution of 0.5 cm$^{-1}$ and were averaged over 10 scans using an exposure time of 5 s. The recording time was of 2 minutes.

The system was investigated at 90, 120, and 150$^\circ$C and 100 bar of P$_{CO_2}$. Under these conditions CO$_2$ is supercritical being the critical point for a CO$_2$-H$_2$O mixture around 31$^\circ$C and 74 bar (Spycher et al., 2003). However, it is worth saying this process cannot be called supercritical fluid (SCF) crystallization technique because CO$_2$ is used neither as an antisolvent nor as a solvent but as a reactive agent.

The reactor was filled with a solution of 180 ml of ultrapure water and sodium carbonate (Na$_2$CO$_3$, Merck, Germany), heated up to the desired
temperature and flushed with 99.995 vol.%-pure CO$_2$ (PanGas, Werk Dagmersellen, Switzerland). Then, it was pressurized with CO$_2$ and kept at constant pressure by feeding CO$_2$ via a front-pressure regulator and monitored with online Raman spectroscopy.

In the first part of each experiment, Raman spectroscopy was used to verify the achievement of a state of equilibrium of the system through the concentration of carbonate species such as CO$_3^{2-}$, HCO$_3^-$, and CO$_2$ whose peaks are located at the Raman shift of 1032, 1003, and 1351 cm$^{-1}$ (Edwards et al., 2005), respectively. Once the peak heights stabilized, 20 ml solution of magnesium chlorite hexahydrate (MgCl$_2$-6H$_2$O, Acros organics, Germany) was added to the reactor by an HPLC pump at the rate of 10 ml min$^{-1}$. At the end of this addition supersaturation was achieved and this time marked the start of the induction period, $t_d$, defines as the time that elapsed between the creation of supersaturation and the formation of critical nuclei. In the second part of each experiment (i.e., after the addition of the MgCl$_2$ solution), Raman spectroscopy measurements allowed to follow the evolution of the spectra over time between at the Raman shift of 1099 and 1119 cm$^{-1}$ corresponding to the most resolved peaks of magnesite and hydromagnesite, respectively (Edwards et al., 2005). Figure 5.3 shows the time-resolved Raman peak heights of HCO$_3^-$, magnesite, and hydromagnesite during experiment 13. At the time of the addition of the MgCl$_2$ solution to the system the peak height associated to HCO$_3^-$ decreases sharply due to the decrease of bicarbonate ion concentration while the peaks corresponding to magnesite and hydromagnesite start to grow together indicating a simultaneous precipitation process.

The produced crystals at the end of each experiment were always identified by Raman spectroscopy measurements as magnesite. However, to verify that during the early experimental campaign, the produced solids
were collected, filtered, washed with ultrapure water, and dried in an oven at 60°C for about 12 h, and then characterized using SEM/EDX (Bruker axs, model D8 Advance) and XRD (Zeiss, model LEO 1530). Scanning electron microscopy samples were sputtered with approximately 2 nm of platinum in high vacuum before being recorded with a Leo 1530 microscope (Zeiss/LEO, Oberkochen, Germany). Powder X-ray diffraction patterns were recorded after samples were spread uniformly over the sample holder using a AXS D8 Advance diffractometer from Bruker (40 kV, 40 mA, Cu KR; Karlsruhe, Germany). Patterns were recorded at $2\theta=7-60^\circ$ with a step size of 0.04° and a scan speed of 0.4°/min.

Figure 5.1 shows the XRD spectrum of the produced solid during exp. 7 (reported in Table 5.1). From this diagram is evident the perfect crystalline magnesite. Figure 5.2 reports instead the SEM images of the same sample analyzed with X-ray diffraction and shown the typical magnesite cubic-like shape although eroded due to friction during the experiment.

### 5.3.2 Thermodynamic model

Solution speciation and supersaturation ratio values were modeled at the thermodynamic equilibrium using EQ3/6 v8.0 software package with the cmp database employing the B-dot model to estimate the activity coefficients of the aqueous species (Wolery and Jarek, 2003). The activity coefficient model B-dot is valid for solution with ionic strength up to 3 m (Helgeson, 1969), therefore it was applicable to all our experiments because their ionic strength ranged between 0.5 and 1.4 m. Based on the average values of the measured temperature and pressure during each run, CO$_2$ fugacity was calculated by using a noniterative procedure de-
Figure 5.1: X-ray diffraction pattern of the solid product collected at the end of exp. 7 at 120°C. Red symbols mark the position of characteristic magnesite peaks, indicating an almost perfectly crystalline magnesite.

Figure 5.2: SEM image of the solid product collected at the end of exp. 7 at 120°C. The picture shows the cubic-like magnesite crystals.
5.4 Experimental results and discussion

In this section, the experimental results of the precipitation experiments are presented. The runs were performed at 90, 120, and 150°C, at 100 bar of \( P_{CO_2} \), and using several solution composition adjusted by adding \( Na_2CO_3 \) and \( MgCl_2 \). Table 5.1 reports for each experiment the applied operating conditions, i.e., \( T, f_{CO_2}, MgCl_2 \) and \( Na_2CO_3 \) molalities, and the values of supersaturation with respect to magnesite, \( S_M \), hydromagnesite, \( S_H \), and brucite, \( S_B \), pH, ionic strength, activity of water, and \( CO_3^{2-}-Mg^{2+} \) activity ratio calculated at the beginning of the induction
5. Kinetics of magnesite and hydromagnesite precipitation

5.4.1 Precipitation mechanism

The initial concentration of the added salts and the observed precipitation mechanism are shown in Figure 5.4 together with the initial supersaturation and solution composition. Under supersaturated conditions with respect to magnesite, we observed three precipitation mechanisms: 1) No precipitation after 22 hours, 2) direct precipitation of magnesite, 3) simultaneous precipitation of magnesite and hydromagnesite followed by the transformation of hydromagnesite into magnesite.

Figure 5.5 shows the Raman measurements recorded during two different experiments where direct formation of magnesite occurred (part a of the figure) and where hydromagnesite and magnesite precipitated simultaneously and then hydromagnesite transformed into magnesite (part b of the figure).

At 90°C three experiments were performed, and in all of them magnesite precipitated directly (Figures 5.4.a and 5.4.b).

At 120°C, we observed all three precipitation mechanisms (Figures 5.4.c and 5.4.d), no precipitation when the system was supersaturated only with respect to magnesite, \( S_M = 12 \) (exp. 3, Table 5.1), direct precipitation of magnesite when the system was slightly supersaturated with respect to hydromagnesite, \( S_H \) between 1.6 and 2.2 (experiments indicated with circles Figure 5.4.c), and simultaneous precipitation of hydromagnesite and magnesite followed by transformation at higher values of supersaturation, \( S_H > 2.7 \) and \( S_M > 46 \). At this temperature, no effect of pH, \( I \), and \( a_w \) was observed, but concentration of magnesium, supersaturation, and \( \text{CO}_3^2^-\text{Mg}^{2+} \) activity ratio determined the type of
5.4 Experimental results and discussion

Comparing experiments 1 and 5 with experiments 9/28 and 48/49 in Table 5.1, we see that although they have similar values of \( S_H \) and \( S_M \) they present a different solution composition and different precipitation mechanisms. In particular, experiments 5 and 9/28 characterized by different Mg\(^{2+}\) ion concentration and different CO\(_3^{2-}\)-Mg\(^{2+}\) activity ratio resulted in two different precipitation mechanisms highlighting the importance of magnesium concentration and ion activity ratio on precipitation. The fact that Mg\(^{2+}\) concentration in exp. 9/28 was twice larger than in exp. 5, and the CO\(_3^{2-}\)-Mg\(^{2+}\) activity ratio in exp. 9/28 was five times smaller than in exp. 5 seems to be determining the change of the mechanism from exp. 9/28 and 5.

Experiments performed at 150\(^\circ\)C showed also three type of precipitation (Figures 5.4.e and 5.4.f). Similarly to the experiments carried out at 120\(^\circ\)C, no precipitation verified when the supersaturation with respect to hydromagnesite was lower than 1.4 despite of an high value of \( S_M \), namely, larger than 14 (exp. 23 and 24 Table 5.1). While above this value, direct precipitation of magnesite occurred. Similarly to the experiments carried out at 120\(^\circ\)C, simultaneous precipitation was observed in experiments with \( S_H \) and \( S_M \) higher than 2.8 and 45, respectively.

Finally, comparing the set of experiments performed at the three temperatures, we can see that the change in precipitation mechanism was associated with the simultaneous high concentration of Mg\(^{2+}\), low CO\(_3^{2-}\)-Mg\(^{2+}\) activity ratio and high supersaturation. Since experiments performed at the same temperature and similar CO\(_3^{2-}\)-Mg\(^{2+}\) activity ratio and supersaturation values showed different mechanisms, the discriminating process variables determining the change in the precipitation mechanism can be recognized only in Mg\(^{2+}\) ion concentration. Hence, in highly supersaturated solutions containing high concentration of Mg\(^{2+}\) ions but with low CO\(_3^{2-}\)-Mg\(^{2+}\) activity ratio, simultaneous precipitation
5. Kinetics of magnesite and hydromagnesite precipitation

of hydromagnesite and magnesite should be expected.

Previous studies by Christ and Hostetler (1970) and Sayles and Fyfe (1973) associated a combination of high Mg\(^{2+}\) concentration values and low CO\(_3^{2-}\)\(-\)Mg\(^{2+}\) activity ratio with a retarded nucleation and growth of magnesite.

Given our observations and the ones in literature, we could argue that in our experiments when magnesite and hydromagnesite precipitated together an hindered magnesite precipitation process was indeed occurring. Such a process led to the less soluble hydrated Mg-carbonate at the investigated operating conditions that is hydromagnesite.
Table 5.1: Operating conditions applied during the precipitation experiments. (*) indicates the experiments where direct precipitation of magnesite was observed, while in the others simultaneous precipitation of magnesite and hydromagnesite verified; bdl: below time recording resolution; nd: not determined.

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Figure 5.4: Initial concentration of sodium and magnesium ions present in the performed runs reported in Table 5.1. The isolines in parts (a), (c), and (d) represent: Black continuous line $S_M$, black dashed line $S_H$, red continuous line pH. The isolines in parts (b), (d), and (f) represent: Black continuous line $a_w$, black dashed line $I$, red continuous line $\text{CO}_3^{2-} - \text{Mg}^{2+}$ activity ratio. Symbols indicate: Squares no precipitation, circles direct precipitation of magnesite, diamonds simultaneous precipitation of magnesite and hydromagnesite.
5.4 Experimental results and discussion

Figure 5.5: Raman spectra measured during experiments 11 (a) and 13 (b) and plotted over the time period after the addition of MgCl₂ solution. Part (a) shows the direct formation of magnesite, and part (b) the simultaneous precipitation of magnesite and hydromagnesite followed by the transformation of hydromagnesite into magnesite.
5. Kinetics of magnesite and hydromagnesite precipitation

5.4.2 Induction time

The induction time, $t_d$, i.e., the time period between the attainment of the initial supersaturation and the detection of the onset of particle formation, depends on the monitoring instrument and is proportional to the homogeneous primary nucleation rate, $J_{ho}$, i.e.:

$$t_d \propto \frac{1}{J_{ho}} \propto e^{\left(\frac{B \gamma}{RT^3 \ln 2} S\right)}, \quad (5.11)$$

where $\gamma$ is the crystal-liquid interfacial tension, J m$^{-2}$, $T$ the temperature, K, and $B = -16v_c^2/3R^3$ with $v_c$ the critical volume of the crystal and $R$ the gas constant. At low values of $S$ within the metastable zone width, $\gamma$ is very high and nucleation rate is very low consequently the induction time is very long, otherwise nucleation rate increases exponentially with supersaturation and the induction time becomes very short (Kashchiev et al., 1991).

Several methods can be adopted to measure induction time such as conductivity method, pH method, the intensity of transmitted or scattered light method, the measurement of the activity of the precipitated ions method. In this work, we used the scattered light method based on the Raman spectroscopy measurements to measure $t_d$ and the values are represented in Figure 5.6 over $1/\ln^2 S$.

It can be observed that with increasing supersaturation the induction time decreases for all three temperatures becoming shorter than the time resolution of the measurement (2 min). For a sake of illustration, here we represented $t_d$ for the experiment where it was within two minutes with a value as large as 1.1 min, and we identified them in the diagram as experiments with immediate precipitation.

Looking at the graphs in Figure 5.6 at the same supersaturation level
5.4 Experimental results and discussion

$t_d$ decreased with temperature for both magnesite and hydromagnesite following classical nucleation theory (Kashchiev et al., 1991). But at the same temperature, the induction time of magnesite increased with Mg$^{2+}$ ion concentration, indicating an hindering precipitation effect of Mg$^{2+}$ ions.

![Figure 5.6: Logarithm of the induction time (min) vs. $1/\ln^2 S$.](image)

5.4.3 Effect of magnesium concentration and supersaturation

Comparison of time-resolved maxima of the Raman spectra at the magnesite Raman shift upon spectra pre-processing are shown in Figure 5.7 for four experiments at the same operating conditions but increasing supersaturation. Spectra pre-processing consisted of baseline correction.
and normalization to the final produced magnesite mass calculated with EQ3/6. In this way, the effect of the crystal size and shape on the measurements was removed. These experiments (exp. 11, 6, 7, and 1 reported in Table 5.1) were performed at 120°C, at $f_{CO_2}$ between 80-91 bar, and with the 0.06 m of initial magnesium concentration, increasing supersaturation with respect to magnesite, namely from 21 up to 32, and almost constant supersaturation with respect to hydromagnesite, $\simeq 2.2$.

From this figure it is possible to see that as supersaturation with respect to magnesite increases the time between when the supersaturation was established ($t = 0$) and the detection by Raman spectroscopy measurements of the first nuclei (i.e., the induction period) decreases. Moreover, the first part of each time-resolved maxima in Figure 5.7 is characterized by an higher steepness as supersaturation increases indicating a faster growth of the crystals. Finally, all the patterns approximately reach the same horizontal line associated with the mass of magnesite produced at the equilibrium that slightly varies among the spectra.

Figure 5.8 compares the time-resolved maxima of the Raman spectra at the magnesite Raman shift for experiments run at the same supersaturation with respect to magnesite and hydromagnesite, namely 34 and 2.2, respectively, but with increasing initial magnesium concentration, i.e., from 0.06 to 0.36 m. It interesting to notice the almost overlapped early part of the spectra among the experiments that seems to indicate the same kinetics of nucleation and growth for these experiments. However, as will has been highlighted in section 5.4.2, induction time among these experiments increases with Mg$^{2+}$ concentration. The experiments shown in Figure 5.8 clearly reach at equilibrium different horizontal lines given the largely different magnesite mass produced at the equilibrium.
5.4 Experimental results and discussion

Figure 5.7: Time-resolved peak maximum of magnesite measured during experiment 11, 6, 7, and 1 upon normalization and baseline correction.

Figure 5.8: Time-resolved peak maximum of magnesite measured during experiment 1, 5, and 48 upon normalization and baseline correction.
5.5 Calibration-free method based on multivariate kinetics modeling applied to Raman spectroscopy measurements

Calibration-free method based on multivariate kinetics modeling was applied to Raman spectroscopy measurements to estimate the kinetics of magnesite and hydromagnesite precipitation. Before describing the method an introduction to the use of Raman spectroscopy in kinetics study to derive quantitative information on a process is given.

Raman spectroscopy has received significant attention as a potential technique to characterize pharmaceutical dry powder mixtures as well as in suspensions. Raman scattering results from both the solid and liquid phase; hence, properties of both phases have to be considered for the quantitative application of Raman spectroscopy in heterogeneous processes such as crystallization when the final aim is to estimate unknown kinetics parameters throughout calibration methods (Fevotte, 2007b).

Various authors have applied Raman spectroscopy to monitor transformation of suspensions and to estimate their kinetics (Wang et al., 2000; Ono et al., 2004; Caillet et al., 2006; Aaltonen et al., 2006; Cornel et al., 2009b; Haiyan et al., 2009). In all these works, the highest challenge was to establish a linear relationship between the Raman spectroscopy signal and the mass of the suspension because of the influences of process variables such as solid composition, suspension density, solute concentration, particle size and shape, and temperature.

Cornel et al. (2008a) carried out an extensive study on the effect of suspension density, solute concentration, particle size, and temperature on the Raman signal during polymorphic transformation. They observed
that the Raman signal intensity decreased with particle size and sus-
pension density, while temperature had a negligible effect. Therefore,
the authors recommended for a quantitative use of the Raman measure-
ments of a suspension to carry out an appropriate preprocessing of the
spectra such as baseline correction and normalization of the spectra.

Hu et al. (2006) investigated the effect of particle size on the quantifi-
cation of polymorphic mixture. By analyzing the change of the signal
with the size of the sampling volume of the Raman probe, they noted
the nature of the employed sampling optics dictated the magnitude of
the particle size effects on the Raman measurements. Therefore, if the
sampling optics allowed for the sampling volume to be much larger than
the particle size, the Raman intensity would be independent of particle
size; otherwise, the Raman signal intensity decreases with particle size.

The influence of process variables on Raman measurements makes the
calibration of this monitoring tool for kinetics studies time consuming.
However, this can be overcome by using multivariate kinetics model-
ing that allows to estimate the unknown kinetic parameters by fitting
the measured spectra directly coupling spectroscopy measurements and
a mathematical model that describes the course of the concentrations
of the different components in solution and in suspension over time
(Puxty et al., 2006). Multivariate kinetics modeling was applied ex-
tensively to systems monitored with ultraviolet-visible, near-infrared,
and mid-infrared spectroscopy undergoing complex homogeneous chem-
ical reaction (Puxty et al., 2006). Recently, this method has been used
to estimate kinetic parameters governing a solvent-mediated polymorph
transformation of the α form of L-glutamic acid into the more stable β
form (Cornel et al., 2008a) and to estimate the growth of paracetamol
crystals (Cornel and Mazzotti, 2009a).

In this study, we applied multivariate kinetics modeling to estimate pre-
5. Kinetics of magnesite and hydromagnesite precipitation

cipitation kinetics of magnesite and hydromagnesite. In particular, we applied the model to the measured spectra in the range of Raman shift between 1050-1150 cm\(^{-1}\) containing the most resolved magnesite and hydromagnesite peaks. Beforehand the spectra was preprocessed throughout baseline correction and normalization to the final magnesite mass calculated with EQ3/6. In this way, the effect of the crystal size and shape on the measurements was removed.

Following Puxty et al. (2006) and Cornel and Mazzotti (2008b), the principle of nonlinear fitting of multivariate time-resolved Raman data through multivariate kinetic modeling is based on the representation of the time evolution of the concentration of \(n\) analytes in the system by a polynomial function:

\[
c_j = c_j(t),
\]

(5.12)

where \(j\) indicates the \(j\)th analyte and varies between 1 and \(d\), and \(c_j\) is its concentration at the time \(t\). By assuming that the Raman spectrum measured scales linearly with the mass of scattering material per unit volume, the measured Raman signal intensity at a certain Raman shift \(\lambda\) and at a given time \(t\), \(x(t, \lambda)\), can then be expressed as a linear combination of the signals corresponding to each analyte, i.e.:

\[
x(t, \lambda) = c_1(t)a_1(\lambda) + c_2(t)a_2(\lambda) + \ldots + c_n(t)a_n(\lambda) + e(t, \lambda) = (5.13)
\]

\[
= \sum_{j=1}^{d} c_j(t)a_j(\lambda) + e(t, \lambda) \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad }

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5.5 Calibration-free method based on multivariate kinetics modeling applied to Raman spectroscopy measurements

The shift over time is given by:

\[ x_k(t) = \sum_{j=1}^{d} c_j(t)a_{jk} + e(t) \]  \hspace{1cm} (5.15)

where \( k \) varies between 1 and the \( m \). The \( i \)th Raman signal intensity at the \( i \)th time coordinate and at the \( k \)th Raman shift is written as

\[ x_{ik} = \sum_{j=1}^{d} c_{ij}a_{jk} + e_{ik} = \hat{x}_{ik} + e_{ik}, \ (i = 1, \ldots, n), \ (k = 1, \ldots, m) \]  \hspace{1cm} (5.16)

that in matrix notation becomes:

\[ X = CA + E = \hat{X} + E, \]  \hspace{1cm} (5.17)

where \( X \) is the spectral matrix \((n \times m)\) in which the element \( x_{ik} \) represents the \( k \)th measured Raman intensity for the \( i \)th sample taken at time \( t_i \) and \( C \) \((n \times d)\) represents the state matrix, i.e., the concentrations of the \( d \) analytes considered, and the \( j \)th column of \( C \) is the concentration profile in time of the \( j \)th analyte. The \( j \)th row in the matrix \( A \) \((d \times m)\) represents the discretized pure-analyte spectrum for \( j \)th analyte. The matrix \( E \) \((n \times m)\) represents the matrix of experimental errors. The discretization of the Raman shift coordinate as well as the sampling in time are defined by the settings of the Raman spectrometer.

The estimation of the kinetics parameters through this Raman spectra discretization assumed that the time evolution of the concentration of the \( d \) analytes can be described through a mathematical model that gives:

\[ \hat{c}_j = \hat{c}_j(t, p) \]  \hspace{1cm} (5.18)

where \( c_j \) is the concentration of the \( j \)th analyte given as a function of
time and \( p \) model parameters. Considering eq. 5.17 and 5.18, the time-
resolved Raman spectra can be used to estimate the model parameters
by minimizing the sum of the square of the elements of the residual
matrix \( R \) \((n \times m)\) given by

\[
R(p) = X - \hat{C}(p)A
\]  

(5.19)

where \( X \) is the measured spectra; \( p \) the unknown model parameters;
\( A \) the unknown matrix \((d \times m)\) whose elements \( a_{jk}(\lambda) \) are the
intensity at Raman shift \( \lambda \) of the pure analyte spectrum corresponding to the \( j \)th
analyte; \( C(p) \) is the matrix \((n \times d)\) of the modeled analyte concentrations.

Eq. 5.19 can be solved exactly considering:

\[
X = \hat{C}(p)A,
\]

\[
\hat{C}^T(p)X = \hat{C}^T(p)\hat{C}(p)A,
\]

\[
A = \left(\hat{C}^T(p)\hat{C}(p)\right)^{-1} \hat{C}^T(p)X = C^+(p)X.
\]  

(5.20)

Combining eq 5.19 and eq 5.20, the residual matrix \( R \) becomes:

\[
R(p) = X - \hat{C}(p)\hat{C}^+(p)X = (I - \hat{C}(p)\hat{C}^+(p))X.
\]  

(5.21)

For example, once the model parameters \( p \) of an experiment have been
estimated, they can be used to predict the concentration profiles \( (C_p(p)) \)
of other experiments performed at different operating conditions. Similarly,
from eq. 5.20, matrix \( A \) can be calculated and used to reconstruct
the Raman spectra of other experiments \( (X_r) \). Hence:

\[
X_r = \hat{C}_p(p)A - R(p).
\]  

(5.22)
5.6 Mathematical model

5.6.1 Population balance equation modeling

1D population balance equation (PBE) model was used to describe the precipitation of magnesite and hydromagnesite (Randolph and Larson, 1988). In a perfectly mixed batch crystallizer with constant suspension volume and assuming size-independent growth and neither agglomeration nor breakage, the PBEs can be written as (Mersmann, 2001):

\[
\frac{\partial n_i}{\partial t} + G_i(t) \frac{\partial n_i}{\partial L} = 0, \tag{5.23}
\]

where \(t\) is the time, s; \(L\) is the single size dimension that characterized the crystals, m; \(n_i\) is the number density of crystals of the \(i\)th mineral, \(m^{-4}\), i.e., its particle size distribution (PSD), \(i\) will be substituted by either \(M\) or \(H\) to indicate magnesite and hydromagnesite, respectively; \(G_i\) represents the growth rate of the \(i\)th mineral, m s\(^{-1}\). Note that \(G_i\) can be either positive, if the solute concentration is above the solubility of the \(i\)th mineral (e.g., growth of magnesite and hydromagnesite crystals), or negative, in case the opposite is true and dissolution takes place (e.g., solvent-mediated transformation of hydromagnesite into magnesite). Eqs 5.23 are coupled with a mass balance equation of the concentration, \(c\), of magnesium ions in solution given by:

\[
\frac{dc}{dt} = -3k_{v,M}\rho_M G_M \int_0^{\infty} n_M L^2 dL - 3k_{v,H}\rho_H G_H \int_0^{\infty} n_H L^2 dL, \tag{5.24}
\]

where \(k_{v,i}\) and \(\rho_i\) are the volume shape factors and the solid density of the \(i\)th mineral, respectively. According to the observed morphology at high temperature (Hänchen et al., 2008; Zhang et al., 2006), volume shape factors of 1 (cubic-shape) and 0.02 (layer-shape) were assumed for
magnesite and hydromagnesite, respectively. The densities of magnesite and hydromagnesite are equal to 2980 and 2250 kg m\(^{-3}\), respectively (Webmineral, 2009). The general initial and boundary conditions for eq. 5.23 and eq. 5.24 are:

\[
\begin{align*}
n_i(L_0, t) &= \frac{J_i}{G_i}, \\
n_i(L, 0) &= n_{0,i}(L), \\
c(0) &= c_0,
\end{align*}
\]  

(5.25)  
(5.26)  
(5.27)

where \(J_i\) and \(G_i\) are respectively the nucleation (m\(^{-3}\)s\(^{-1}\)) and the growth (m s\(^{-1}\)) rates of the corresponding \(i\)th mineral; \(n_{0,i}(L)\) is the initial PSD of the \(i\)th polymorph (zero and different from zero in the case of unseeded and seeded processes, respectively); \(c_0\) is the initial concentration of Mg\(^{2+}\) ion. Eq 5.25 describes the generation of new particles through primary nucleation, where \(L_0\) should exceed the critical crystal size, \(L_i^*\), equal to the minimum detectable crystal size. In our case, \(n_{0,i}(L)\) equals 0, since we performed unseeded precipitation experiments.

The supersaturation ratio with respect to magnesite (\(S_M\)) and hydromagnesite (\(S_H\)) are defined as follows:

\[
\begin{align*}
S_M &= \left(\frac{a_{Mg^{2+}} a_{CO_3^{2-}}}{K_{sp,M}}\right)^{0.5}, \\
S_H &= \left(\frac{a_{Mg^{2+}} a_{CO_3^{2-}}^{4} a_{H_2O}^{6}}{K_{sp,H}}\right)^{1/15},
\end{align*}
\]  

(5.28)  
(5.29)

with \(a_{Mg^{2+}}, a_{CO_3^{2-}},\) and \(a_{H_2O}\) the activities of the subscripted species, (-) and \(K_{sp,i}\) the solubility product of the \(i\)th mineral.

We solved the PBEs using the method of moments where the partial differential equations (eqs 5.23) can be solved through a system of ordi-
nary differential equations (ODEs) given by the time derivative of the moments of the PSD of the crystals (Raisch and Vollmer, 2006; Hänchen et al., 2007). The general $j$th moment of the PSD of crystals of the $i$th mineral is defined as

$$\mu_{j,i}(t) = \int_0^\infty n_i L^j dL,$$

and the time derivative of the Zeroth moment is

$$\frac{d\mu_{0,i}}{dt} = \begin{cases} G_i n_{t^*,i}(L_{t^*}^i), & \text{if } S_i \leq 1 \\ J_i, & \text{if } S_i > 1 \end{cases}$$

where $G_i$ represents the dissolution rate of the $i$th mineral when $S_i \leq 1$, that in our case corresponds to hydromagnesite and $L_{t^*}^i$ is its critical crystal size. Substituting $i$ with $H$, $L_{t^*}^H$ can be calculated as

$$L_{t^*}^H = \left| \int_{t^*}^t G_H dt \right|,$$

where $t^*$ is the time when dissolution of hydromagnesite starts, given by:

$$t^* = \min\{t(S_H) \leq 1\}.$$ 

At this time the particle size distribution of the hydromagnesite crystals was reconstructed using the technique proposed by Qamar et al. (2008) based on the analytical solution of the Laplace transformation of the PBE.
The time derivatives of moments 1 to 3 are:

\[
\frac{d\mu_{1,i}}{dt} = G_i \mu_{0,i}, \quad (5.34)
\]
\[
\frac{d\mu_{2,i}}{dt} = 2G_i \mu_{1,i}, \quad (5.35)
\]
\[
\frac{d\mu_{3,i}}{dt} = 3G_i \mu_{2,i}. \quad (5.36)
\]

Combination of eq 5.24 and eq 5.30 yields:

\[
\frac{dc}{dt} = -3k_{v,M} \rho_M G_M \mu_{2,M} - 3k_{v,H} \rho_H G_H \mu_{2,H}. \quad (5.37)
\]

Eqs 5.31 through 5.37 constitute a system of coupled ODEs that can be solved numerically once the initial Mg\(^{2+}\) concentration, \(c_0\), is known.

Assuming the speciation reactions of the ions in solution much faster than the precipitation process, we solved the ODEs system simultaneously with a geochemical model based on both the chemical equilibria given in section 5.2.2 (reactions 5.2 through 5.10) and the reactions corresponding to the formation of the species MgCO\(_3\)\(^{aq}\), MgHCO\(_3^+\), MgCl\(^+\), NaCl\(^{aq}\), NaHCO\(_3\)\(^{aq}\) expected to be at concentration higher than 10\(^{-5}\) m, therefore relevant to the system. B-dot activity coefficient model was used since the ionic strength for the experiments varied between 0.5-1.4 m (Helgeson, 1969). Equilibrium constants of the considered reactions and the parameters of the activity coefficient model were taken from the cmp database of EQ3/6 v.8 (Wolery and Jarek, 2003).

The ODEs system of the momentums and of the mass balance equation was therefore solved simultaneously with the geochemical model. In this way, supersaturation values of magnesite and hydromagnesite as well as the magnesium concentration in solution were calculated at each integration time step of the ODEs system. The ODEs were solved numerically
by the algorithm implemented in the *ode45* MATLAB function and the geochemical model was solved by the nonlinear least-squared minimization method implemented in the *lsqnonlin* MATLAB function.

The solid concentrations profiles of both magnesite and hydromagnesite, (g of solid/kg of solvent), were derived from the third moment of their PSDs and given by:

$$m_i = k_{v,i} \rho_i \mu_{3,i}.$$  \hspace{1cm} (5.38)

The solid concentration profiles of the minerals were used to build the state matrix $\hat{C}$ whose column are formally expressed by eq. 5.18. This matrix was then used to estimate the kinetics parameters (i.e., $p$) of the precipitation model.

### 5.6.2 Constitutive equations

**Nucleation kinetics**

Nucleation mechanism can be identified as primary and secondary. The first mechanism includes both homogeneous nucleation, where nuclei form from solution through formation of clusters, and heterogeneous nucleation where instead the formation of nuclei is facilitated by the presence of foreign particles. The second mechanism occurs when new crystals form from surface nucleation, shear stress, fracture, contact, and brakeage (Mersmann, 2001).

In our system, we assumed primary homogeneous nucleation for both magnesite and hydromagnesite, since no seeds were added to the system, and we considered secondary nucleation of magnesite during transformation of hydromagnesite.

Primary homogeneous nucleation rate is given by classical nucleation
5. Kinetics of magnesite and hydromagnesite precipitation

theory (Kashchiev et al., 1991). It predicts that nucleation rate depends on the difference in the chemical potential of the compound, as a crystal, and the solution. In our work, we adopted a simplified function for the rate of primary homogeneous nucleation given by:

\[ J_{ho} = k_{ho} e^{-K_{ho} S}, \]  

(5.39)

where \( S \) is supersaturation, (-); \( k_{ho} \) is a kinetic parameter given by the product of the probability of the growth of a crystal nucleus to a mature crystal and the solubility of the that crystal; \( K_{ho} \) is a thermodynamic parameter given by:

\[ K_{ho} = \frac{B \gamma^3}{T^3}, \]  

(5.40)

where \( \gamma \) is the crystal-liquid interfacial tension, J m\(^{-2}\), \( T \) the temperature, K, and \( B = -16v_c^2/3R^3 \) with \( v_c \) the critical volume of the crystal and \( R \) the gas constant.

During solvent-mediated transformation, secondary nucleation of the more stable phase might take place (Caillet et al., 2006; Schöll, 2006). This phenomenon is strongly dependent on the surface of the dissolving crystal and the stable phase nucleates on the surface of the metastable particles. In our work, we considered that during hydromagnesite transformation secondary nucleation of magnesite occurred and it was modeled by an empirical form of the secondary nucleation rate equation given by:

\[ J_s = k_s m^n, \]  

(5.41)

where \( k_s \) is the nucleation rate constant, (m\(^{-3}\)s\(^{-1}\)), \( n \) is an empirical exponent, (-), and \( m \) is the solid concentration of hydromagnesite crystals.

An equation similar to eq. 5.41 has been used by Caillet et al. (2007) in the case of transformation of anhydrous form of citric acid into the
monohydrate form and by Cornel and Mazzotti (2008b) and Cornel et al. (2009b) in the case of transformation of the polymorph $\alpha$ of L-glutamic acid into the polymorph $\beta$.

Parameters, $k_{ho}$, $K_{ho}$, $k_s$, and $n$ can be estimated by fitting experimental data.

Induction time, $t_d$, defined as the time period that elapses between when supersaturation is established and when critical nucleus forms is proportional to nucleation rate $J_{ho}$, therefore:

\[
\ln t_d \propto B\gamma^3 \frac{1}{T^3 \ln^2 S}.
\]  

(5.42)

At low values of $S$ within metastable zone width, $\gamma$ is very high and nucleation rate is very low consequently the induction time is very long, otherwise nucleation rate increases exponentially with supersaturation and the induction time becomes very short.

**Growth kinetics**

Crystal growth kinetics can be controlled by transport (a combination of convection and diffusion), by surface integration, and even both processes.

In the case of crystal growth from solution two phenomena happen: (1) The transport of the growth units towards the crystal-solution interface and (2) their incorporation into the crystal at the surface. Therefore, growth kinetics can be either surface integration controlled or diffusion controlled. In particular, in the case of ionic crystal, the growth process can be more complex consisting of the following simultaneous steps: (Mersmann, 1995): (1) Bulk diffusion of solvated ions through the diffusion boundary layer; (2) bulk diffusion of solvated ions through the
adsorption layer; (3) surface diffusion of solvated or unsolvated ions; (4) partial or total desolvation of ions; (5) integration of ions into the lattice; (6) counter-diffusion of released water through the adsorption layer; (7) counter-diffusion of water through the boundary layer.

The controlling mechanism varies with supersaturation, solution composition, and temperature; e.g., transport is limiting at high supersaturation, when the relative velocity between the crystal and the solution is small, and the particle size exceeds 5-10 µm, while surface integration controls the overall kinetics at small supersaturation and high relative velocities.

In the case of transport-controlled kinetics, assuming that convection due to mixing does not limit the process, the growth rate depends on mass diffusion and it is given by (Nielsen and Toft, 1984; Mersmann, 2001):

\[
G_d = k_d \frac{k_a}{3k_v \rho} (P^{1/\xi} - K_{sp}^{1/\xi}),
\]

where \( P \) is the ion activity product of the mineral, (-); \( \xi \) is the sum of the stoichiometric coefficients during reaction, (-), e.g., for magnesite \( P = a_{Mg^{2+}}a_{CO_3^{2-}} \) and \( \xi = 2 \); \( k_a \) and \( k_v \) are the surface and the volume shape factors; \( \rho \) is the crystal density; \( k_d \) is the mass transfer coefficient, (kg m\(^2\) s\(^{-1}\)), given by the Sherwood correlation (Mersmann, 2001):

\[
k_d = \frac{D}{L} \left( 2 + 0.8 \left( \frac{L^4}{\nu^3} \right)^{0.5} Sc^{1/3} \right).
\]

The following definitions are worth doing before the description of the surface-controlled growth mechanism: The edges of the incomplete layers are called steps, the flat terraces between the steps are singular crystal planes, and the kinks on faceted crystals are located at the steps.
In the surface integration controlled kinetics the growth rate is determined by two factors: The density of kinks on the interface, and the barriers, both entropic and enthalpic, for incorporation of a molecule into a kink. The incorporation of ions, in particular, but also of organic molecules from the solution into kinks is mostly related to the hydration shell around the incoming solute atomes/molecules (Vekilov, 2007). The dynamics of the water molecules within the hydration layer surrounding the ion and the water exchange between the solid surface and the bulk water determines the kinetics of incorporation into kinks. Faceted crystals, as in the case of magnesite and hydromagnesite, in contact with solution typically follow the layer growth mode. In this mode, a new layer, typically one lattice spacing high, is deposited on the smooth surface of the previous lattice layer.

Three different models exist to describe the surface controlled growth kinetics (Mersmann, 2001): 1) Burton, Cabrera, Frank (BCF) model that describes the integration of ions in screw dislocation centered surface spiral steps; 2) the Birth and Spread (B + S) model that considers the adsorption of units to the kinks and the formation of nuclei spreading on the surface; and 3) the Poly-Nuclear (PN) model that describes the nucleation and growth of units at the crystal surface. The corresponding equations are given below:

\[
G_{BCF} = k_{BCF}(S - 1) \ln S \tanh \left( \frac{K_{BCF}}{\ln S} \right),
\]

\[
G_{BS} = k_{BS}(S - 1)^{2/3} \ln^{1/6} S \ e\left( -\frac{K_{BS}}{\ln S} \right),
\]

\[
G_{PN} = k_{PN}(S - 1)^{2/3} \ e\left( -\frac{K_{PN}}{\ln S} \right),
\]

where \(k_{BCF}, k_{BS},\) and \(k_{PN},\) m s\(^{-1}\), \(K_{BCF}, K_{BS},\) and \(K_{PN}\) (-) are model parameters depending on the physical and chemical properties of
the system, the crystal-liquid interface tension and temperature. Their values can be estimated by fitting experimental data.

The controlling growth mechanism changes with supersaturation, passing from spiral growth at screw dislocations described by BCF model to step advancement away from dislocations described by B+S model to transport controlled growth. The PN growth mechanism is never the stand-alone controlling mechanism.

**Phase transition**

Precipitation might occur through transition stages following the Ostwalds rule of stages (Ostwald, 1897) and characterized by two different mechanisms: 1) Solvent-mediated (reconstructive) transformation and 2) solid state (displacing) transformation.

Solvent-mediated transformation happens through the dissolution of the metastable phase (e.g., a polymorph and an hydrated crystal) and the renucleation of the stable phase that then grows from solution. The kinetics is controlled by dissolution of the metastable phase and nucleation and growth of the stable one. During transformation, supersaturation with respect to the two phases remains constant and an indication of the controlling mechanism is given by the difference between the initial value of the supersaturation and the one during transformation. If this difference is very low, then the dissolution is very rapid and so is the overall transformation process.

Solid state transformation takes place through the reorganization of the atom bonds within the metastable crystal and in this phase the stable crystal nucleates and grows.

Being the activation energy of the solvent-mediated transformation much
lower than the one of the solid state transformation, the former is favored than the latter, in particular when the process happens in solution. Moreover, solvent-mediated transformation is favored when the phases have a very different crystal structure and the operating temperature is below the melting point.

In our study, we assumed hydromagnesite transforming into magnesite following the solvent-mediated mechanism. This assumption was based on the following:

- The process was performed in solution, where a solvent-mediated mechanism is expected to occur.
- The operating temperature was much below the melting point of hydromagnesite corresponding to 662°C.
- Hydromagnesite and magnesite have a very different crystal structure, i.e., layer-like in the first case and cubic-like in the second.
- The study carried out by Zhang (2000) where they observed a solvent-mediated transformation of hydromagnesite into magnesite in a system similar to ours, i.e., in brine with low ionic strength and with T between 110 and 150°C.

To model transformation, i.e., dissolution of hydromagnesite, we used a diffusion-controlled rate equation given by eq. 5.43, where the activity product $P$ is equal to $a_{Mg^{2+}}^5a_{H_2O}^6a_{CO_3^{2-}}^4$, and $\xi$ is 1/15, i.e., the inverse of the sum of the stoichiometric coefficients of reaction 5.3. This equation was already adopted in earlier works, e.g., by Fevotte et al. (2007b) to described transformation of citric acid from the anhydrous form to the stable monohydrated form and by Cornel et al. (2008a) to described polymorph transformation of the $\alpha$ form of L-glutamic acid into the stable $\beta$ form.
5.7 Modeling results and discussion

The parameter estimation technique presented in section 5.5 was used together with the population balance model described in section 5.6 and the experimental results of the runs listed in Table 5.1 to determine the nucleation and growth kinetics of magnesite (reported in sections 5.7.2 and 5.7.3) and nucleation, growth, and dissolution kinetics of hydromagnesite (section 5.7.3). All runs where used for the estimation of the model parameters and at each temperature and for each precipitation mechanism average value of the kinetics parameters was calculated together with its uncertainty. Induction time, \( t_d \), for magnesite and hydromagnesite was measured from the recorded Raman spectra, it decreased with supersaturation and temperature, and increased with Mg\(^{2+}\) ion concentration (section 5.4.2).

5.7.1 Parameter estimation

Two different optimization techniques were applied to estimate these parameters: The simplex method and the Newton-Gauss-Levenberg/Marquardt (NGL/M) methods, using the \texttt{fminsearch} and \texttt{lsqnonlin} function in MATLAB, both resulted in the same values of the parameters, but the simplex method was found to be most efficient in terms of computational effort and to be most robust. Additionally, simulated annealing, an approach that is known to be effective for finding a global minimum in the presence of several local minima, was used by employing the \texttt{simulannealbnd} function in MATLAB. Being this approach time consuming but more efficient in finding the optimum, it was applied initially to select the global minima, then starting from this optimal parameter value set the simplex method was used to calculate
5.7 Modeling results and discussion

the jacobian matrix. All algorithms were applied to the time-resolved baseline-corrected and normalized Raman spectra from the experiments. The part of the spectra between 1500-1050 cm$^{-1}$ was selected because in part of the Raman spectra the peaks of magnesite and hydromagnesite are well resolved and have a well-defined shape, in particular, their maxima are located at 1099 and 1100 cm$^{-1}$, respectively, and correspond to the symmetric C-O stretch of the CO$_3^{2-}$ molecule in the crystals (Edwards et al., 2005).

Once the parameters were estimated, their confidence intervals representing their sensitivity were calculated. The smaller the confidence intervals the smaller the sensitivity of the model to the parameters (Saltelli et al., 2000). Approximate confidence intervals can be calculated using the sensitivity matrix, or Jacobian, based on a linearized model in the vicinity of the estimated model parameters. This sensitivity matrix enables calculating the covariance matrix of the parameter estimates from which the correlation coefficients can be calculated (Beck and Arnold, 1977). The absolute values of the correlation coefficients varied between 0 and 0.95. The highest correlation coefficient value was between the preexponential and the exponential factors of a rate equation (see eqn. 5.39, 5.45, 5.46, and 5.47) indicating a poor identificability of those parameters. However, it is worth saying that the aim of this work was not to determine accurately physical parameters associated with nucleation and growth, such as surface tension $\gamma$, but to estimate the kinetics of the overall process. A further study might be carried out to investigate nucleation and growth kinetics by performing experiments targeted to characterize each process separately, e.g., seeded crystallization experiments for growth and T-mixer experiments for nucleation.

Each $i$th parameter value was associated with its standard deviation which is given by product of the square root of the $i$th diagonal element
of this covariance matrix \( (s_i) \) and the \( t \)-value \( (t_{\alpha,\nu}) \) of the \( t \)-distribution in the case of \( \nu \) degrees of freedom and the confidence level \( \alpha \) (Beck and Arnold, 1977). The degrees of freedom are given by the number of data points reduced by the number of the parameters, i.e., in this work they corresponded to \( 44954 \). The confidence level \( \alpha \) was equal to 0.05 that corresponds in a 95\% probability. Hence, the \( t_{\alpha,\nu} \) resulted equal to 1.645. Therefore, each model parameter in \( p \) was given as a sum of the estimated optimal values, \( p_i \), and its standard deviation:

\[
p = p_i \pm s_i t_{\alpha,\nu}.
\] (5.48)

At all investigated temperatures, we described growth through the B+S growth model because this model could capture at best the Raman spectroscopy measurements as shown in Figure 5.9 for experiment 11. For sake of simplicity, we adopted the same rate equation for hydromagnesite. Contrarily, Saldi et al. (2009) described magnesite growth with the spiral growth mechanism by using a simplified form of the BCF growth rate (eq. 5.45). However, their operating conditions were different from our case, in particular \( S_M \) varied between 4.5 and 6.2 and always supersaturated with respect to hydromagnesite, while in our study \( S_M \) was between 4 and 70 and \( S_H \) between 1.1 and 6. Spiral growth was indeed expected to be the controlling mechanism at low supersaturation values, while B+S at intermediate values, and mass transfer by diffusion at high supersaturation (Mersmann, 2001). In our work we expected convection to be not limiting because the suspension was well mixed and the crystals did not exceed 10 \( \mu \)m in size as one can see from the SEM pictures given in Figure 5.2.

The parameter were estimated with the following strategy. For the experiments where only magnesite precipitated \( k_{ho} \) and \( K_{ho} \) for homoge-
nous primary nucleation (eq. 5.39) and $k_{BS}$ and $K_{BS}$ for growth (eq. 5.46) were estimated simultaneously. For the experiments where magnesite and hydromagnesite precipitated simultaneously $k_{ho}$, $K_{ho}$, $k_{BS}$, and $K_{BS}$ were estimated for both crystals simultaneously using the Raman spectra recorded up to the onset of hydromagnesite transformation. From this time on, dissolution and secondary magnesite nucleation model parameters, i.e., $k_d$ (eq. 5.43), and $k_s$ and $n$ (eq. 5.41), respectively, were estimated keeping the other parameters fixed to the optimal values resulted from the fitting of the earlier Raman spectra.

The identificability of the nucleation and growth parameters for both magnesite and hydromagnesite was satisfactory, so was the one for the dissolution of hydromagnesite and the secondary nucleation of magnesite.
5.7.2 Kinetics of direct magnesite precipitation

In this section, the estimated parameters of nucleation and growth models for experiments where magnesite precipitated directly are listed. The optimal set of model parameter values averaged at each temperature and associated with their standard deviation is given below:

- **T = 90°C**, Nucleation: $k_{ho} = 2\cdot10^8 \pm 0.05$; $K_{ho} = 18 \pm 0.004$. Growth: $k_{BS} = 10^{-9} \pm 2\cdot10^{-7}$; $K_{BS} = 18 \pm 6\cdot10^{-5}$;

- **T = 120°C**, Nucleation: $k_{ho} = 5\cdot10^8 \pm 2$; $K_{ho} = 20 \pm 4\cdot10^{-4}$. Growth: $k_{BS} = 3.43\cdot10^{-8} \pm 9.3\cdot10^{-10}$; $K_{BS} = 20 \pm 2\cdot10^{-4}$;

- **T = 150°C**, Nucleation: $k_{ho} = 5\cdot10^8 \pm 5$; $K_{ho} = 20 \pm 2\cdot10^{-5}$. Growth: $k_{BS} = 5.27\cdot10^{-8} \pm 1.17\cdot10^{-10}$; $K_{BS} = 20 \pm 9.8\cdot10^{-6}$;

The estimated parameters are slightly temperature dependent and almost the same set of parameters could be used to describe all experiments indicating a much higher influence of supersaturation. No effect of the process variables such as $a_w$, $I$, pH, and $\text{CO}_3^{2-}$-$\text{Mg}^{2+}$ activity ratio was observed and a narrow uncertainty interval was calculated. However, supersaturation was intrinsically considered as a determining parameter of kinetics being the constitutive equations given in sections 5.6.2, 5.6.2, and 5.6.2 function of it. Regarding the effect of the concentration of magnesium ions, that has been observed to determine a change in the precipitation mechanism, has not shown to affect the kinetics parameters. However, it should be emphasize that the set of experiments discussed here were characterized by a similar $\text{Mg}^{2+}$ ion concentration and smaller than the threshold value over which the process changes from direct precipitation to simultaneous precipitation. Therefore, in this case such a non-sensitivity of the model to $\text{Mg}^{2+}$ ion concentration was expected.
Figure 5.10 shows the satisfactory agreement between measured and modeled data for experiment 11. To validate also the goodness of the geochemical model we compared the mass calculated with our model and the mass calculated with EQ3/6, being their values 0.81 g and 1.01 g, respectively, we considered the prediction quite satisfactory.

To verify the predictability of the model and of the optimal set of estimated parameters, we calculated matrix $A$ from experiment 11 (as described at the end of section 5.5) and we used it to reconstruct the spectra for experiment 6. Together with $A$ we use the optimal set of model parameter estimated for exp. 11. Figure 5.11 shows the results, in particular in the diagram measurements are shown together with predicted profiles (black solid line) and the profiles obtained by optimization of experiment 6 (gray solid line). The agreement between the prediction and the experimental data is reasonably good.
Figure 5.10: Concept of fitting multivariate Raman data for experiment 11 at 120°C. The measured Raman spectra acquired during precipitation of magnesite are shown in part a. The reconstructed Raman spectra upon parameter estimation are shown in part b. Part c plots the time-resolved peak maximum measured and associated with magnesite (1099 cm\(^{-1}\)) and part d plots the Raman intensity at different Raman shifts at the end of the experiment. Parts e and f display the modeled concentration profiles of Mg\(^{2+}\) and the magnesite mass.
Figure 5.11: Time-resolved peak maximum of magnesite measured during experiment 6. The prediction was performed using the optimal kinetics parameter set and matrix $A$ from the optimization of exp. 11.

It should be emphasized that given the correlation coefficient between the model parameters of nucleation and growth, in particular between the two preexponential factors $k_{ho}$ (in eq. 5.39) and $k_{BS}$ (in eq. 5.46) between 0.8 and 0.9, the values of estimated parameters cannot be used for physical properties determination of the system. As a matter of the fact, the objective of this work was not to provide the most accurate detailed process model for magnesite precipitation, but to demonstrate that application of spectroscopic monitoring tools coupled with multivariate kinetics modeling and PBE model can be used in a powerful manner to observe kinetics and to determine precipitation overall kinetics by fitting the time-resolved Raman spectra directly omitting extensive calibration efforts. However, as said above to better estimate accurately physical parameters associated with nucleation and growth, such as surface tension $\gamma$, experiments targeted to characterize each process separately, e.g.,
seeded crystallization experiments for growth and T-mixer experiments for nucleation, should be performed.

Moreover, we compared the growth rate equations estimated in this work \((G, \text{ m s}^{-1})\) with the one \((r_g, \text{ mol cm}^{-2} \text{ s}^{-1})\) derived by Saldi et al. (2009) at 100°C. However, to allow for direct comparison of our correlations with the growth rates given by Saldi et al. (2009), we applied the following conversion (Mersmann, 2001):

\[
r_g = \frac{3 k_v}{k_a} \rho G,
\] (5.49)

where \(k_v\) and \(k_a\) are the volume and shape factors for magnesite given by 1 and 6, respectively. Figure 5.12 compares the models in a low supersaturation range being the \(S_M\) in the work by Saldi et al. (2009) between 4.2 and 6.16. The spiral growth model at 100°C and the B+S model at 90°C are very similar, suggesting that at these temperatures and for low supersaturation ratio the two mechanisms would result in similar growth rates. While at higher temperatures, B+S model gives much higher growth rate values and a much more sensitive function to supersaturation, indicating that the model by Saldi et al. (2009) could not have been extrapolated at higher temperatures such as the ones applied in this work.

## 5.7.3 Kinetics of simultaneous precipitation of magnesite and hydromagnesite

Simultaneous precipitation of magnesite and hydromagnesite followed by transformation of hydromagnesite into magnesite occurred at 120 and 150°C, at high supersaturation with respect to magnesite, and at high concentration of Mg\(^{2+}\) ion in solution. A typical course of the solid
5.7 Modeling results and discussion

Figure 5.12: Comparison of B+S growth models estimated at 90, 120, and 150°C with the spiral growth model reported by Saldi et al. (2009) at 100°C upon conversion given by eq. 5.49.

Phase composition in solution is shown in Figure 5.5.b for experiment 13. At both operating temperatures simultaneous precipitation occurred above supersaturation values with respect to magnesite and hydromagnesite of 45 and 2.8, but the minimum Mg$^{2+}$ ion concentrations was different, at 120°C 0.2 m, and at 150°C 0.1 m. Moreover, at 150°C transformation of hydromagnesite occurred in a time span of a duration shorter than 6 minutes, while at 120°C transformation was much longer, namely between 86 and 145 minutes increasing with supersaturation and Mg$^{2+}$ concentration. Given the fast transformation time, the kinetics of hydromagnesite dissolution and secondary nucleation of magnesite were
5. Kinetics of magnesite and hydromagnesite precipitation

estimated only using experiments at 120°C.

The optimal set of model parameter values averaged and associated with their standard deviation is given below:

- **Magnesite**, Nucleation: $k_{ho} = 5 \cdot 10^6 \pm 5$; $K_{ho} = 24 \pm 2 \cdot 10^{-4}$; $k_s = 2 \cdot 10^6 \pm 5$; $n = 1.5 \pm 2 \cdot 10^{-4}$. Growth: $k_{BS} = 2.2 \cdot 10^{-7} \pm 10^{-9}$; $K_{BS} = 25.5 \pm 5 \cdot 10^{-3}$;

- **Hydromagnesite**, Nucleation: $k_{ho} = 10^{10} \pm 2$; $K_{ho} = 10 \pm 4 \cdot 10^{-4}$. Growth: $k_{BS} = 0.12 \pm 0.02$; $K_{BS} = 14.5 \pm 0.1$. Dissolution $k_d = 2 \cdot 10^{-7} \pm 5 \cdot 10^{-8}$.

Comparison of the parameter values for magnesite given above with the ones estimated when direct precipitation of this crystal occurred (section 5.7.2), highlights the hindered magnesite nucleation process during simultaneous precipitation with a similar growth rate.

5.8 Conclusion

This work evidences the effect of operating conditions on magnesite and hydromagnesite precipitation mechanism and kinetics at high temperature and high $P_{CO_2}$. The precipitation of magnesite resulted to be enhanced by temperature and supersaturation and hindered by Mg$^{2+}$ ions. Such an inhibiting effect led to simultaneous precipitation of magnesite and hydromagnesite followed by transformation of the latter into the former. Therefore, the proposed precipitation mechanism agrees with the general belief that dehydration of the cation is the rate-determining step in mineral precipitation.
5.8 Conclusion

Through the modeling of the process and of the geochemistry coupled with multivariate kinetics modeling of the Raman spectroscopy measurements, the kinetics parameters for nucleation, growth, and dissolution were estimated. These results can be used to predict Mg-carbonate formation during ex situ aqueous mineral carbonation and they can help to select operating conditions suitable for a direct and a fast magnesite precipitation.
5. Kinetics of magnesite and hydromagnesite precipitation
Chapter 6

Direct carbonation of APC residues

Direct gas-solid carbonation of alkaline residues from Air Pollution Control (APC) systems was investigated with the aim of evaluating its contribution as a CO₂ storage option. APC residues from a medical solid waste incinerator located in the vicinity of Rome were selected for performing carbonation experiments with pure CO₂ at reaction temperatures in the 200-500°C range. The extent of calcium conversion to the carbonate form was found to be negligible below 300°C, whereas the maximum conversion of 57% was already measured at 400°C. This implies a storage capacity of 0.12 kg CO₂ per kg dry solid. Considering that the APC residues production in the EU25 equals 1260 kt/year, this translates in a CO₂ storage potential for the European market of 0.15 Mt CO₂/year. These results indicate that accelerated carbonation of

\footnote{Most of this chapter has been published as Baciocchi et al. (2006)}
alkaline residues could be suitable to address the issue of CO$_2$ storage, especially for niche applications such as at steel plants and solid waste incinerators where both the residues and the CO$_2$ are present.

### 6.1 Introduction

As already mentioned in *Chapter 1*, during direct mineral carbonation CO$_2$ reacts with alkaline elements, namely Ca and Mg, forming the corresponding thermodynamically stable carbonates (Huijgen and Comans, 2003). The large worldwide availability of minerals rich in alkaline earth silicates provides a source of alkaline materials that exceeds that required for sequestering the total CO$_2$ emitted by the combustion of the available fossil fuels reservoirs (Huijgen and Comans, 2003). However, capture of CO$_2$ by mineral carbonation requires operation at high temperatures (180°C) and pressures (15 MPa) (Wolf et al., 2004a). Although several other options have been proposed (Huijgen and Comans, 2003), it is worth noting that the current stage of process development is still at the lab scale. An alternative source of materials is represented by alkaline wastes, which are available in relatively large amounts and are generally rich in Ca or Mg. Johnson (2000) proposed the use of several waste materials, including pulverized fuel ash (PFA) produced by coal fired power stations, ground granulated blast furnace and stainless steel slags (SSG) from the steel manufacturer industry, bottom and fly municipal solid waste incineration ashes (MSWI-b and MSWI-f), as well as deinking ash resulting from the waste produced during the recycling of paper. Carbonation of these waste materials, previously mixed with water at different water:solid (w:s) ratios, was carried out in a 100% CO$_2$ atmosphere at a pressure of 3 atm. The best performance was obtained with SSG, with a maximum 20% weight gain upon carbonation, achieved with
6.1 Introduction

a w:s ratio of 0.125. A lower but still notable weight gain of 13% was also observed for MSWI-f. More recently, Fernandez Bertos et al. (2004) investigated more specifically the carbonation behaviour of bottom ash and Air Pollution Control (APC) residues from different municipal solid waste incinerators located in the UK. The results from the experimental tests, performed at operating conditions very close to those reported by Johnson (2000), resulted in a 7% and a 3% weight gain for APC residues and bottom ash, respectively. A quite different approach was followed by Huijgen and Comans (2003); Huijgen et al. (2005), who performed the carbonation of steel slag slurries at a 10:1 w:s ratio. A 70% Ca conversion was obtained operating at 20 bar and 200°C in a 100% CO₂ atmosphere, on a solid fraction sieved below 106µm. Stolaroff et al. (2005) assessed the feasibility of extracting free calcium from steel slag and concrete waste by dissolution experiments in aqueous solutions. According to these authors, the solution containing free calcium could then be used in a carbonation process for capturing CO₂ directly from air. An alternative to the direct wet route is represented by direct gas-solid carbonation of alkaline residues. Such a carbonation route has been traditionally applied for the carbonation of raw materials, such as calcium and magnesium oxides (Bhatia and Perlmutter, 1983; Butt et al., 1996). Namely, Bhatia and Perlmutter (1983) investigated the kinetics of CaO carbonation by modified TGA experiments performed in a CO₂ stream at different operating temperatures, obtaining 70% calcium conversion at 500°C, but still reasonably fast process rate and high carbonation efficiency when operating at 400°C. More recently, Abanades and Alvarez (2003) proposed the use of CaO in a fluidized bed to capture CO₂ directly from combustion gases; up to 70% carbonation conversion was obtained for the fresh material, but a reduction in conversion yield was observed after several carbonation-calcination cycles, required to recover
the raw material from the process. The results obtained from direct gas-solid carbonation of natural alkaline oxides provide the basis for applying this route to the carbonation of alkaline residues as well. Such materials are mainly composed of calcium and magnesium oxides or hydroxides. The advantage of using alkaline residues rather than natural alkaline oxides is that, unlike the latter, they are not a raw material but a waste stream. Therefore, the process could be envisioned as a sequestration rather than a capture process. Besides, the carbonation process could at the same time improve the leaching properties of the waste material, potentially allowing for either utilization of the carbonated material for civil engineering application or mitigation of impacts at the final disposal site. Relevant work dealing with direct gas-solid carbonation of alkaline residues was performed by Jia and Anthony (2000), who performed pressurized TGA experiments of hydrated and non-hydrated fluidized bed combustion (FBC) ash, achieving CaO conversion efficiencies up to 60% when operating at temperatures above 400°C and in a 100% CO₂ atmosphere. The objective of the work reported here is to investigate the efficacy and efficiency of direct gas-solid carbonation of APC residues collected from a medical waste incinerator located near Rome. Carbonation experiments performed under different operating conditions in a modified muffle furnace are presented and discussed. The carbonation degree is then evaluated on the basis of different independent measurements (weight gain, calcination tests, TGA tests), made on the material before and after carbonation.

6.2 Material and method

APC ash was sampled at a medical solid waste incinerator located in the vicinity of Rome from the baghouse section following a contact reactor
for acid gases and organic micropollutants abatement using Ca(OH)$_2$ and activated carbon. When received at the laboratory, fresh APC ash was homogenized using a quartering procedure, oven-dried at 60°C to constant weight, and finally transferred into sealed containers where it was kept until the time of testing to prevent contact with atmospheric CO$_2$. Characterization of APC ash involved determination of element and major anion content, mineralogical composition, acid neutralization capacity (ANC), as well as leaching behaviour. The elemental composition of APC ash was determined using an alkaline digestion procedure with Li$_2$B$_4$O$_7$ in platinum melting pots at 1050°C, followed by dissolution of the molten material in a solution of 10% w/w HNO$_3$/nanopure water and measurement of element concentrations by means of an atomic absorption spectrometer equipped with air-acetylene flame. The concentration of chloride and acid-soluble sulphate was determined using the standard Italian UNI 8520 test procedures which involve dissolution with hot deionised water and 3% HCl, respectively. The mineralogical composition of the material was evaluated by X-ray diffraction (XRD) analysis using Cu K$_\alpha$ radiation, as well as by thermogravimetric analysis (TGA) and differential thermogravimetry (DTG). The acid neutralization behaviour of the material was evaluated through the ANC test as proposed by the Canadian Wastewater Technology Centre (Stegemann and L., 1991), which involves contacting eleven sub-samples of the material with HNO$_3$ solutions with increasing acid concentration. The leaching behaviour was evaluated from the results of the ANC test reported as heavy metal concentration-versus-pH curves, as well as by the ENV 12457-2 leaching test. The accelerated carbonation treatment was applied as direct gas-solid carbonation at different temperatures and contact times in order to evaluate the ash susceptibility to the process and the optimal operating conditions. The carbonation experiments were
conducted in a muffle furnace that was modified to allow for feeding a constant 100% CO$_2$ flow and for distributing uniformly the gas flow within the muffle chamber. Treatment temperature values of 200, 300, 400 and 500$^\circ$C were selected for the carbonation experiments and the treated samples were referred to as S2, S3, S4 and S5, respectively. Residence time was varied over the range 0.5 to 48 h. Due to the semi-batch configuration of the carbonation reactor and to the elevated treatment temperature, no adjustment could be made to the moisture content of the material, and this, although recognized as an important parameter for carbonation (Ecke et al., 2003; Fernandez Bertos et al., 2004) was not included among the process variables. Before the onset of the experiments, the carbonation chamber was flushed with 100% CO$_2$ for 10 min to purge air out from inside. Control experiments were also performed at the same operating conditions, but using an inert gas (N$_2$) flux. To evaluate the extent of carbonation, the treated material was characterized for weight gain upon carbonation and for final carbonate content, which was measured by means of calcimetry. This involved contacting the material with a standard volume of a HCl solution in a closed chamber and subsequently measuring the volume of CO$_2$ evolved from the reaction between carbonate phases and HCl. Additional information on the production of major mineral phases as a result of carbonation was derived from TGA/DTG analyses as well as from a TGA technique coupled with an on-line gas chromatograph for the determination of CO$_2$ in the gases evolved from the sample.
6.3 Results and discussion

6.3.1 Characterization of APC Residues

Table 6.1 reports the chemical composition of APC ash, while Figure 6.1 depicts the results from thermal analysis in terms of TGA and DTG curves as well as CO$_2$ evolution as a function of temperature. Chemical composition data reveal that the major constituents of APC ash are by far calcium and chlorine, accounting for more than 58% of the total mass of the residue. Relatively high concentrations were also measured for volatile heavy metals, such as Zn, Pb, Cu and Cd, which are present in APC residues as a result of volatile metals evaporation under the elevated temperature conditions of the incinerator. Additional information on the mineralogical characteristics of APC ash was derived from TGA/DTG analyses, which indicated the presence of two peaks on the DTG curve at temperatures of about 500 and 650°C, respectively, with relatively large related weight losses. The first DTG peak was associated to Ca(OH)$_2$, with a weight loss of 5.0%, corresponding to a Ca(OH)$_2$ content of 20.5%. The second peak, on the basis of the evidence from CO$_2$ evolution measurements, was associated to CaCO$_3$, the presence of which in APC ash is presumably a result of a certain degree of carbonation occurred before the time of testing, possibly in the APC system. The total volume of CO$_2$ measured for the second peak was 0.94 ml, which corresponds to a CaCO$_3$ content of 10.8%, in very close agreement with the amount calculated from the weight loss associated to the second peak, which was equal to 10.6%.

Tentative partitioning of Ca among the different chemical species was calculated on the basis of the data discussed above, XRD measurements, as well as ENV 12457 leachate composition. The calculations were done
Figure 6.1: Results of TGA/DTG analysis for sample S0: (a) sample weight (black solid line), derivative weight (gray solid line) (W0 = 5.33 mg; heating rate = 10°C/min) and (b) CO_2 concentration (dashed line) of gases leaving the TGA furnace (W0 = 38.83 mg; heating rate = 20°C/min; gas flowrate = 238 Nml/min).
to determine the amount of Ca available for the carbonation process (i.e., in the form of Ca(OH)$_2$/CaO) and the consequent Ca conversion yield. XRD analysis of untreated APC ash (not reported here) revealed the presence of crystalline phases including chloride (halite, NaCl, and sylvite, KCl) and sulphate minerals (anhydrite, CaSO$_4$) in addition to Ca(OH)$_2$. It was assumed that chloride species were completely solubilized during 24-h distilled water leaching. Under the hypothesis that Na and K in the eluate from the ENV 12457 leaching test were in the form of the corresponding chloride salts, the amount of NaCl and KCl in APC ash was calculated to be 16.8 and 0.2%, respectively. The assumption was then made that the residual chloride content (accounting for 20.5% of APC ash) was in the form of CaCl$_2$, while the entire sulphate content was present as CaSO$_4$. The amount of Ca remaining according to the above calculations (which was equal to 7.8%) was finally assumed to be in the form of CaO.
Table 6.2 summarizes the speciation of Ca determined, along with the hypotheses made for the calculations. The amount of chemical forms available for carbonation determined from Table 6.2 is thus 31.4% as Ca(OH)\(_2\) + CaO, or 18.9% as Ca. The presence of any Mg mineral potentially liable to carbonation was not considered in the present study because of the much lower Mg content (0.6%) in APC ash as compared to Ca content (27.6%).

<table>
<thead>
<tr>
<th>Species</th>
<th>Amount, % dry wt.</th>
<th>Measurement/assumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)(_2)</td>
<td>20.5</td>
<td>TGA/DTG analysis</td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>32</td>
<td>Indirect calculation based on Cl(^-) content and leaching results</td>
</tr>
<tr>
<td>CaCO(_3)</td>
<td>10.8</td>
<td>TGA/DTG analysis</td>
</tr>
<tr>
<td>CaSO(_4)</td>
<td>3</td>
<td>Direct calculation based on SO(_4^{2-}) content</td>
</tr>
<tr>
<td>CaO</td>
<td>10.9</td>
<td>Indirect calculation based on residual Ca</td>
</tr>
</tbody>
</table>

The ANC behavior of APC ash is shown in Figure 6.2. For the untreated material, the ANC curve indicates the presence of a very large plateau at a pH value of about 12.5 units, typical of solution pH control by Ca(OH)\(_2\), which was responsible for an acid neutralization capacity of about 8.8 meq/g of dry material. This corresponds to a Ca(OH)\(_2\) content of 17.6% (expressed as Ca), which is reasonably close to the value 18.9% determined using the approximate method described previously. From the ANC results it is also evident that the whole acid neutralization capacity of APC ash was dictated by Ca(OH)\(_2\); after solubilization of this phase no additional plateau was visible on the ANC curve reported in Figure 6.2, so that pH dropped steeply from 12.5 down to less than 1 unit upon the addition of about 3 meq H\(^+\)/g.
6.3 Results and discussion

6.3.2 Carbonation of APC Residues

The weight gain was found to be dependent upon the operating temperature, increasing from 3.1% for sample S3 to slightly less than 10% for samples S4 and S5. Conversely, exposing the APC residues to a nitrogen flow resulted in a reduction in sample weight that was slightly influenced by the operating temperature, increasing from 1.2% at 300°C, to about 2.5% at 400 and 500°C. Such a weight reduction was probably due to the dehydration process, involving loss of both sample humidity and bound water (e.g., in calcium hydroxide). Since it is reasonable to assume that the dehydration process still takes place during accelerated carbonation and that the extent of water loss is the same than under N$_2$ and CO$_2$ atmosphere, the actual weight gain upon carbonation was calculated using the principle of superimposition of the effects. The resulting actual weight change ranged from 4.4% at 300°C to about 12% at 400 and

Figure 6.2: ANC curves for untreated and carbonated APC residues.
500°C.

The CO₂ content of the APC residues before and after treatment in CO₂ atmosphere clearly confirmed the extent of the carbonation reactions. The CO₂ content did not notably increase after carbonation at 200°C, in agreement with the undetectable weight gain observed at this temperature. In contrast, the CO₂ content increased up to 18% at higher temperatures. Comparing the weight gain calculated from the difference in CO₂ content after and before the carbonation treatment with the actual weight gain. Although the quantitative agreement is not perfect, it is worth pointing out that the two independent measurements suggest that the weight gain of the APC residue may be entirely attributed to the increase in CO₂ content.

The TGA/DTG curves relevant to sample S3, reported in Figure 6.3, show that the first DTG peak at 500°C, associated to Ca(OH)₂, was smaller than that observed for untreated APC ash (sample S0, see Figure 6.1). Furthermore, a larger second peak at 650°C, associated to CaCO₃, was observed, with an estimated calcium carbonate content of 25.7% by weight (11.3% CO₂), which is in agreement with the data obtained from the calcimetry test and discussed above. The data obtained from the GC analysis, also shown in Figure 6.3, confirmed that the CO₂ amount in the S3 sample was higher than for the untreated fly ash (sample S0), although the quantitative agreement between TGA/DTG and GC data was in this case rather poor, the latter measurements providing a CO₂ amount of 18.1% by weight.

The TGA curve for sample S4, depicted in Figure 6.4, showed a different behaviour than those curves for samples S0 and S3, displaying a sudden 20% weight loss at temperatures between 20 and 120°C, ascribed to the loss of moisture that is probably more strongly retained in sample S4 due to a modification of the material porosity at the applied tempera-
6.3 Results and discussion

Figure 6.3: Results of TGA/DTG analysis for sample S3: (a) sample weight (black solid line), derivative weight (gray solid line) ($W_0 = 8.60$ mg; heating rate $= 10^\circ$C/min) and (b) CO$_2$ concentration (dashed line) of gases leaving the TGA furnace ($W_0 = 40.73$ mg; heating rate $= 20^\circ$C/min; gas flowrate $= 238$ Nml/min).
ture, i.e., 400°C. In addition, the DTG curve of Figure 6.4 shows no peak at 500°C, thus suggesting complete conversion of Ca(OH)$_2$, while the CaCO$_3$ peak corresponded to a higher associated weight loss when compared the other samples. The weight decrease at 650°C was equal to 14.7%; assuming total water content of 20% on the basis of TGA observations, implying that the CO$_2$ content of dry sample S4 was 18.4%, corresponding to 41.8% as CaCO$_3$. Such figures are in close agreement with those obtained from the integration of the CO$_2$ evolution diagram, also reported in Figure 6.4, indicating a 20.1% CO$_2$ content, i.e. a 45.6% CaCO$_3$ content. Finally, it is worth pointing out that even in this case the results obtained from TGA/DTG measurements provided similar values for the CO$_2$ content if compared to those determined by the calcimetry experiments.

On the basis of these results and relying on Ca speciation reported in Table 6.1, a 100 g APC residue sample contains roughly 0.27 mol of Ca. Carbonation of APC ash at 400°C results in a 12% weight increase, which, as confirmed by different independent measurements, may be entirely attributed to CO$_2$ uptake as CaCO$_3$. This corresponds to 12 g, 0.27 mol, of CO$_2$. Therefore, the Ca conversion yield is equal to 57%. A similar yield was obtained at 500°C and a smaller yield at 300°C. As suggested by Bhatia and Perlmutter (1983), the occurrence of incomplete conversion in gas-solid reaction may be attributed to the closure of small pores, which are characterized by a higher specific surface area, so that only the larger slowly reacting pores are left. The maximum conversion yield attainable depends on the cumulative small pores volume, i.e. on the solid properties. The limit conversion yield estimated by Bhatia and Perlmutter (1983) for CaO was found to be 71%. In a recent work, Abanades and Alvarez (2003) found an experimental maximum conversion yield for CaO powder of roughly 60-65%, depending
Figure 6.4: Results of TGA/DTG analysis for sample S4: (a) sample weight (black solid line), derivative weight (gray solid line) ($W_0 = 9.06$ mg; heating rate = $10^\circ$C/min) and (b) CO$_2$ concentration (dashed line) of gases leaving the TGA furnace ($W_0 = 65.81$ mg; heating rate = $20^\circ$C/min; gas flowrate = 238 Nml/min).
on the carbonation conditions. Both such figures are not far from that found for the APC residues investigated in this work; this suggests that the operating conditions adopted in the present work probably allowed the maximum conversion yield to be attained for the investigated materials when applying carbonation as a gas-solid reaction process. The results commented above and derived from weight change and calcimetric measurements as well as thermal analysis were confirmed by the acid neutralization behaviour of the accelerated carbonated material. It was found that the ANC of sample S2 was very similar to sample S0, as indicated by the presence of a plateau of comparable width at a pH value of 12.5; considering that, as observed earlier, such a pH plateau is the result of pH control by Ca(OH)$_2$, this is an additional indication of the very poor carbonation degree of sample S2. In the case of treatment at 300°C, a large initial pH plateau was still present, although with a lower width (6.4 meq H$^+$/g as opposed to 8.8 meq H$^+$/g for sample S0). This confirms that accelerated carbonation at 200 and 300°C was not capable of producing any macroscopic change in the mineralogical composition of APC ash. Conversely, the ANC behaviour was dramatically modified by the treatment at 400°C: while for sample S4 the plateau at pH 12.5 completely disappeared, indicating consumption of Ca(OH)$_2$ as a consequence of the carbonation treatment, another large plateau at pH values in the range 8.0 to 4.5 units (typical of the carbonate/bicarbonate buffer system) was visible on the ANC curve. The amount of acid required to overcome such a plateau was calculated to be 9.6 meq H$^+$/g, corresponding to a carbonate content of 28.8% as CO$_3^{2-}$, or 48.0% as CaCO$_3$. Considering the poor resolution of the titration curve as derived from the ANC test, this value is in reasonable agreement with that (43.5%) determined from TGA analysis.
6.4 Conclusion

Carbonation of APC residues was shown to be a viable process for the storage of CO$_2$, yielding almost 60% conversion of calcium available as calcium oxide or hydroxide and an uptake of around 120 g CO$_2$ per kg residue. Considering that the estimated production of APC residues in the 25 countries of the European Union (EU 25) from municipal, hazardous and hospital solid waste incinerators is approximately 1260 kt/year (Commission, 2005), the CO$_2$ storage capacity would amount to about 0.15 MtCO$_2$/year. This figure shall be compared with the CO$_2$ emission reduction expected from the application of the Kyoto protocol, about 8% of the 1990 CO$_2$ emissions, i.e. about 350 MtCO$_2$/year, or to the more realistic 19.7% reduction effort with respect to the actual 2010 emission baseline, i.e. about 800 MtCO$_2$/year. Thus, the APC residues produced from the existing incineration plants would cover only 0.2-0.5% of the total CO$_2$ European storage capacity required to comply with the Kyoto protocol objectives. Nevertheless, APC residues represent just a small fraction of alkaline residues available in the European Union, and that they could be effective as additional CO$_2$ storage capacity. Furthermore, they could be suitable for niche applications, such as at steel plants and municipal solid waste incinerators, where both the residues and the CO$_2$ are present (Huijgen and Comans, 2003).
6. Direct carbonation of APC residues
Chapter 7

Kinetics of direct carbonation of APC residues

The kinetics of the gas-solid carbonation of APC residues has been studied at different temperatures, CO$_2$ concentrations, and at atmospheric pressure in order to select the best operative conditions on the basis of CO$_2$ stored and reaction time. The samples were initially heated up to the operative conditions under argon atmosphere and then carbonated under a CO$_2$-argon atmosphere. All carbonation kinetics were characterized by a rapid chemically-controlled reaction followed by a slower product layer diffusion-controlled process. Maximum conversions between 60% and 80% were achieved, depending on the operative temperature and CO$_2$ concentration. Temperature did not notably affect the

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5 Most of this chapter has been published as Prigiobbe et al. (2009b)
maximum conversion obtained in the experiments performed at temperatures equal or above 400°C; the influence on the kinetics was masked by the change in initial composition due to dehydroxilation reaction and surface area while heating up to the operative temperature. A slight influence of CO$_2$ concentration on the kinetics was observed, whereas no influence on the maximum conversion was noticed. The obtained results suggest that the flue gases with 10 vol.% CO$_2$ concentration can be directly used to form stable carbonates, thus lumping capture and storage in a single step.

7.1 Introduction

Carbonation of residues from different industrial activities have been proposed because they are a valuable source of alkalinity: pulverized fuel ash produced by coal fired power stations, ground granulated blast furnace and stainless steel slags from the steel manufacturing industry, bottom and fly municipal solid waste incineration ashes, as well as deinking ash, resulting from the waste produced during the recycling of paper (Johnson, 2000). These materials contain alkaline elements in a more readily available form, so that carbonation could in principle take place at less severe operative conditions than the ones needed for silicate minerals. The amount of available alkaline residues is of a scale which will allow to store only a few hundreds MtCO$_2$/y, i.e orders of magnitude below the current CO$_2$ emissions (25 GtCO$_2$/y). Nevertheless, the process can substantially reduce the CO$_2$ emissions of specific industrial sectors (e.g. cement or steel industry) and can be a way to introduce the carbonation technology (IPCC, 2005). Moreover, carbonation might improve the environmental behavior of the residues allowing either for their reuse or make their disposal less expensive (Costa et al., 2007).
In particular, carbonation of alkaline residues can be performed by two different reaction routes: A dry and a wet gas-solid route (Costa et al., 2007).

In the dry gas-solid carbonation route, the alkaline solid is contacted with a gas containing CO$_2$ at atmospheric pressure and high temperatures. Gas-solid carbonation of pure calcium and magnesium oxides has been studied theoretically by Bhatia and Perlmutter (1983) and by Butt et al. (1996). Bhatia and Perlmutter (1983) investigated the kinetics of CaO carbonation by modified TGA experiments performed in a CO$_2$ stream at different operative temperatures, obtaining 70% calcium conversion at 500°C, but a still reasonably fast process rate and high carbonation efficiency when operative at 400°C. Butt et al. (1996) studied the gas-solid kinetics of Mg(OH)$_2$ carbonation. Under helium-CO$_2$ atmosphere in isothermal TGA experiments, they observed that dehydroxilation of brucite and precipitation of magnesite occurred simultaneously with the fastest kinetics at 375°C.

More recently, Abanades and Alvarez (2003) proposed the use of CaO in a fluidized bed to capture CO$_2$ directly from combustion gases. Up to 70% carbonation conversion was obtained for the fresh material, but a reduction in conversion yield was observed after several carbonation-calcination cycles, required to recover the raw material from the process. The results obtained from direct gas-solid carbonation of natural alkaline oxides, such as MgO and CaO, provide the basis for applying this route to the carbonation of alkaline residues, since such materials are largely composed of calcium and magnesium oxides or hydroxides. Steinfeld et al. (2007) investigated CaO and Ca(OH)$_2$ carbonation, observing that the addition of water vapor significantly enhances the reaction kinetics to the extent that, in the first 20 minutes, the reaction proceeds at a rate that is 22 and 9 times faster than that observed for the
dry carbonation of CaO and Ca(OH)$_2$. The first study dealing with direct gas-solid carbonation of alkaline residues was by Jia and Anthony (2000), who performed pressurized TGA experiments of hydrated and non-hydrated fluidized bed combustion ash, achieving CaO conversion efficiencies up to 60% when operative at temperatures above 400$^\circ$C and in a 100% CO$_2$ atmosphere. Nevertheless, in this work neither further independent evidence of the degree of carbonation was provided, nor was any information given on the effect of the carbonation reaction on leaching behavior of metals. In Chapter 6, the results of carbonation experiments performed on APC residues under 100 vol.% CO$_2$ atmosphere at atmospheric pressure and temperatures ranging between 300 and 500$^\circ$C are reported. Carbonation was observed to be effective above 400$^\circ$C, with a maximum Ca conversion of 60%. Neither evidence of the temperature effect on the reaction rate was provided nor the effect of CO$_2$ concentration was addressed. Both these issues are investigated in this chapter, with the aim of assessing the feasibility of APC residues gas-solid carbonation for a possible industrial application. In this view, the kinetics of the carbonation process is of paramount importance in order to design a proper gas-solid contacting system, which should guarantee an as low as possible residence time. Besides, the possibility of performing carbonation using flue gases rather than pure CO$_2$ as a reactant is also worth investigating, since this would allow to lump capture and storage in a single step. To this aim, carbonation kinetics studies of APC residues were performed in a TGA furnace under constant temperatures varying from 300 up to 500$^\circ$C and in atmosphere of CO$_2$-argon mixture of 10, 22, and 50 vol.% of CO$_2$. No water vapor was added to the gas mixture, in order to simplify the experimental procedure since in previous papers by Steinfeld et al. (2007), water vapor was observed to positively affect the carbonation kinetics, the results obtained in this
work provide a conservative estimate of carbonation using flue gases, where typically water vapor is also present. This range was selected based on previous study where carbonation was observed to be effective only above 300°C, whereas starting at 600°C CaCO₃ decomposition may take place. The material was characterized applying chemical elemental analysis, thermogravimetric analysis and X-ray diffraction, in order to quantify both the total calcium content and the corresponding calcium phases in the material before the carbonation experiments. The study of the chemical reaction pathways was also investigated and supported by SEM, X-ray diffraction analysis, thermogravimetric analysis, surface area and porosity measurement of untreated and treated APC residues.

7.2 Analytical methods

7.2.1 Materials and methods

APC residues were sampled at a hospital waste incinerator, located in the vicinity of Rome, from the bag-house section located downstream of a contact reactor for acid gases and organic micro-pollutants abatement, where Ca(OH)₂ and activated carbon are used as reactants. When the APC residues were received at the laboratory, they were homogenized using a quartering procedure, oven-dried at 60°C to constant weight, and finally transferred into sealed containers, where they were kept until the time of testing to prevent contact with atmospheric CO₂.

The characterization of the APC residues, whose detailed description is reported elsewhere (Baciocchi et al., 2007) is summarized in Table 7.1. The other main species include NaCl (approximately 9.5 % wt.) and KCl (approximately 1.0 wt.%). Their grain size ranged between
Table 7.1: Composition of the untreated fly ash and measurement methods (Baciocchi et al., 2007).

<table>
<thead>
<tr>
<th>Species</th>
<th>Mass fraction %</th>
<th>Type of measurement and assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)(_2)</td>
<td>37.8</td>
<td>Indirect calculation based on the difference between TG/DTA and calcimetry analysis and CaOHCl content.</td>
</tr>
<tr>
<td>CaOHCl</td>
<td>28.9</td>
<td>Indirect calculation based on Na(^+), K(^+) leaching values from EN12457-2 test, Cl(^-) content and XRD analysis.</td>
</tr>
<tr>
<td>CaCO(_3)</td>
<td>18.0</td>
<td>TG/DTA and calcimetry analysis.</td>
</tr>
<tr>
<td>CaSO(_4)</td>
<td>4.8</td>
<td>Direct calculation based on SO(_4^{2-}) content and XRD analysis.</td>
</tr>
</tbody>
</table>

10 and 40 \(\mu\)m while their mineralogy, obtained by X-ray diffraction, is characterized by the presence of: CaOHCl, Ca(OH)\(_2\), CaCO\(_3\), CaSO\(_4\), NaCl, and KCl. Among them, only CaOHCl and Ca(OH)\(_2\) can undergo a carbonation reaction. CaOHCl amount was calculated assuming that Cl was distributed among the three phases NaCl, KCl and CaOHCl, while Ca(OH)\(_2\) content was calculated from the TGA analysis of dry fly ash once the amounts of H\(_2\)O, carbon content, CaOHCl and CaCO\(_3\) were determined.
Table 7.2: Specific surface area of APC residues heated up to the applied operative temperatures.

<table>
<thead>
<tr>
<th>Heating temp., °C</th>
<th>BET, $m^2g^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>33.35 ± 0.61</td>
</tr>
<tr>
<td>400</td>
<td>29.01 ± 0.49</td>
</tr>
<tr>
<td>450</td>
<td>20.12 ± 0.42</td>
</tr>
<tr>
<td>500</td>
<td>15.90 ± 0.23</td>
</tr>
</tbody>
</table>

**X-ray diffraction.** XRD analyses were carried out by means of XPERT-PRO (PANALYTICAL), equipped with a copper anode (Cu K $\alpha$; $\lambda = 1.54056$ Å). The equipment’s operational conditions were 40 kV, 50 mA. The 2$\theta$ range between 5° and 109° was scanned at the rate of 0.2° min$^{-1}$. The database from the software TOPAS 2.0 produced by Bruker was used for the identification of the crystalline phases.

**Surface area.** BET measurements of dehydrated APC residue samples were carried out by means of Micrometrics Tristar 3000 in N$_2$ atmosphere. The samples were heated up to the applied operative temperatures (i.e., after steps 1 and 2 of the experimental procedure, shown in Figure 7.1 and described in paragraph 7.2.2) and then analyzed. The method and the interpretation of the data were implemented according to Sing et al. (1985). The results, reported in Table 7.2, showed that the specific surface area decreased with increasing temperature.

**Porosity.** The porosity and the pore size distribution were measured by mercury intrusion porosimetry using Micrometrics Autopore 9220 with the software Autopore II 9220 v2.03. This technique can be applied over a capillary range between 0.003 $\mu$m and 360 $\mu$m. Porosity measurements allowed identifying a change of the pore structure between the original sample, characterized by micro-porous structure (<14 $\mu$m) and the pre-heated samples (at the end of step 2), which were probably characterized
7. Kinetics of direct carbonation of APC residues

by a meso-porous structure (2-50 nm). Given the analytical method applied, the data obtained at different pre-heating temperatures did not allow assessing the effect of pre-heating temperature on the pore structure. On the contrary, BET surface area was observed to decrease with increasing pre-heating temperature. This behavior might be explained by a change of the pore structure towards the formation of larger pores with increasing pre-heating temperature or might suggest the occurrence of collapse of a fraction of the original pores.

Scanning Electron Microscopy (SEM). The morphologies of the APC residues were observed under a scanning electron microscope using Leo 1530 microscope (Zeiss/ LEO, Oberkochen, Germany).

7.2.2 Carbonation kinetics experiments

Carbonation experiments were carried out in a Thermogravimetric system (TGA, Netzsch STA 409 CD) coupled with Gas Chromatography (GC, 2-channel Varian Micro GC, equipped with a Molsieve-5A and a Poraplot-U columns) for measurement of the evolving CO$_2$. An average amount of 44 mg of APC residues was placed on an holder in a uniform layer of 3 mm and carbonated at different temperatures (300, 350, 400, 450, 500$^\circ$C), at a total pressure of 1 bar, and under different CO$_2$ concentrations obtained by mixing CO$_2$ (99.99 vol.%-purity) with argon, as reported below:

- 10 vol.% of CO$_2$ and 90 vol.% of argon and total flow rate 160.5 mL min$^{-1}$;
- 22 vol.% of CO$_2$ and 78 vol.% of argon and total flow rate 184.5 mL min$^{-1}$;
7.2 Analytical methods

- 50 vol.% of CO$_2$ and 50 vol.% of argon and total flow rate 239 mL min$^{-1}$.

Table 7.3 reports the operative conditions of the experimental runs, together with the main results, which are discussed in section 7.3. It is worth pointing out that tests performed at the same CO$_2$ partial pressure, but at different temperature, actually correspond to slightly different CO$_2$ concentration. Nevertheless, the difference in concentration is rather small: at 10% CO$_2$, it ranges from $1.95\cdot10^{-3}$ mol l$^{-1}$ at 350$^\circ$C to $1.5\cdot10^{-3}$ mol l$^{-1}$ at 500$^\circ$C, at 22% CO$_2$, it ranges from $4.3\cdot10^{-3}$ mol l$^{-1}$ at 350$^\circ$C to $3.5\cdot10^{-3}$ mol l$^{-1}$ at 500$^\circ$C, at 50% CO$_2$, it ranges from $9.8\cdot10^{-3}$ mol l$^{-1}$ at 350$^\circ$C to $7.9\cdot10^{-3}$ mol l$^{-1}$ at 500$^\circ$C. For sake of simplicity, and without any loss of generality, in the following, we will discuss all the experiments performed at constant CO$_2$ concentration as if they were performed also at constant CO$_2$ partial pressure. Before starting the experiment, the furnace was flushed with argon in order to achieve three volumes exchanges.

Figure 7.1 reports the weight variation observed during a typical carbonation experiment, showing clearly the three steps of the experimental procedure:

- **Step 1 Heating**: TGA furnace heated up to the desired operative temperature with a heating rate of 20 K min$^{-1}$ and under argon atmosphere; the weight loss observed during this step can be attributed mostly to the moisture and bond-water loss;

- **Step 2 Idle**: TGA furnace kept at the operative temperature for 15 min again under argon atmosphere;

- **Step 3 Carbonation**: A constant flow of the argon-CO$_2$ mixture was applied while keeping T constant until the carbonation
Figure 7.1: Typical weight variation (%) vs. time observed during carbonation.

completed (2 hrs).

After two hours at constant temperature and CO$_2$-argon flow, the CO$_2$ flow was switched off and the system was cooled down to room temperature keeping only argon flowing through the furnace chamber. The sample weight and CO$_2$ concentration in the off-gas line were measured over time during all the experiment using TGA and GC, respectively. The final solid product was analyzed with X-ray diffraction methods to assess the formation of CaCO$_3$ at the end of each experiment.
7.3 Results and discussion

7.3.1 Identification of reactants and reaction pathways

As shown in Figure 7.1, a weight decrease of the APC residue was typically observed at the end of step 1 and further also through step 2. This decrease was ascribed either to moisture loss or to the transformation of the existing phase, with water loss. Based on this evidence, and on the nature of the compounds present in the residues, it was supposed that the reacting phases available at the beginning of the carbonation experiments could be different from those present in the original material, depending on the operative temperature. X-ray diffraction analysis, SEM images and TGA measurements of the untreated material have been used as analytical techniques to identify the reactive phases at the applied operative temperatures and to describe the reaction pathways.

The identification of the reacting species by performing XRD analysis of pre-heated samples was carried out at different temperatures under helium atmosphere, i.e. 25, 300, 350, 400, 450, and 500°C. From the patterns shown in Figure 7.2, it can be noticed that the characteristic peaks of \( \text{Ca(OH)}_2 \) and \( \text{CaOHCl} \) are still present in the sample preheated at 300°C, suggesting that the mineralogy of the samples was substantially unchanged with respect to the as-received material, at least as far as \( \text{Ca(OH)}_2 \) and \( \text{CaOHCl} \) are concerned. On the contrary, XRD patterns of all the other samples, preheated at a temperature equal or higher than 350°C, showed the peaks of CaO; whereas those corresponding to \( \text{Ca(OH)}_2 \) and \( \text{CaOHCl} \) were not detected. However, \( \text{Ca(OH)}_2 \) and \( \text{CaO-HCl} \) could still be present in the material, but as amorphous phases that cannot be observed with X-ray analysis.
7. Kinetics of direct carbonation of APC residues

Figure 7.2: X-ray patterns of APC residues performed in helium atmosphere at: (a) ambient temperature, (b) 300°C, (c) 350°C, (d) 400°C, (e) 450°C, and (f) 500°C. Diamond symbols indicate CaO characteristic peak positions; upwards triangles indicate CaOHCl phase; and downwards triangles indicate Ca(OH)$_2$ phase.
The results of TGA of untreated APC ash under argon atmosphere at 20 K min$^{-1}$ from 25°C to 1000°C reported in Figure 7.3 clearly show two main weight changes. The first one took place between 300°C and 500°C, and it can be attributed to the dehydroxylation of both Ca(OH)$_2$ and CaOHCl to CaO in agreement with the findings of Allal et al. (1997). The second one, between 500°C and 700°C, is linked to CaCO$_3$ decomposition and confirmed the results already obtained in the study reported in the previous chapter. The total weight loss observed up to 700°C is equal to about 21%, it is very close to the stoichiometric weight loss expected from the dehydroxylation of Ca(OH)$_2$ and CaOHCl (reactions 7.1 and 7.2), equal to 12%, and from the CaCO$_3$ decomposition, equal to 8%, (reaction 7.5). The difference between the expected value from the dehydroxylation (12%) and the measured one (8%) suggests that a fraction of undecomposed hydroxides might still be present at 500°C.

Figure 7.4 reports the SEM images of APC samples. These measurements have been carried out in order to characterize the reacting phases
by the morphology of the samples. They correspond to the three experimental steps described in paragraph 7.2.2 during run 10, performed at 350°C. A visual analysis of these images leads to the following observations:

- The morphology of the untreated sample, shown in Figure 7.4(a), is layer-like which is the characteristic shape of CaOHCl and Ca(OH)$_2$;

- After dehydroxylation (step 2), shown in Figure 7.4(b), some crystals were observed, which could be attributed to CaO, characterized by an iso-rhombic-hexagonal morphology. Nevertheless, the layer-like morphology of Ca(OH)$_2$ and CaOHCl is still evident. This suggests that the sample still contains unreacted CaOHCl and Ca(OH)$_2$ at this temperature but part of the CaOHCl might have already been transformed into CaO;

- After the carbonation reaction (step 3) sample particles, shown in Figure 7.4(c), are more rounded and the layer-like structure disappeared completely. Such a variation can be attributed to the formation of CaCO$_3$, whose typical crystal shape is trigonal-hexagonal-scalenohedral.

The evidence gained from the different qualitative analysis suggests that Ca(OH)$_2$ and CaOHCl were only partially converted to calcium oxide, so that all three calcium species were present at the different operative temperatures, before the onset of the carbonation reaction. The amount of the calcium species available at the different operative temperature was estimated from the weight loss data measured in each experiment during steps 1 and 2. In doing this, the following assumptions were made:
7.3 Results and discussion

Figure 7.4: SEM pictures of APC residues before and after the carbonation experiment 10 at 350°C and applying 50 vol.% of CO$_2$. (a) Untreated sample; (b) dehydrated sample, at the end of step 2; (c) carbonated sample, at the end of step 3.
7. Kinetics of direct carbonation of APC residues

- The weight loss at the end of step 2 was assumed to be only due to the release of water from the following decomposition reactions (Allal et al., 1997):

\[
\begin{align*}
2\text{CaOHCl} & \leftrightarrow \text{CaCl}_2 + \text{CaO} + \text{H}_2\text{O} \\
\text{Ca(OH)}_2 & \leftrightarrow \text{CaO} + \text{H}_2\text{O}.
\end{align*}
\]

- Reactions 7.1 and 7.2 were supposed to occur in parallel and at the same rate. This assumption may not correspond to the physics, but is considered reasonable for the scope of this work.

Using these assumptions, the actual fraction of water loss was calculated as the ratio between the weight loss measured at the end of step 2 and the theoretical total water released as if CaOHCl and Ca(OH)$_2$ were dehydroxylated completely. These values are shown in Figure 7.5 for each applied temperature. The average water loss measured at 300°C was negligible in comparison to the total water content bound to Ca(OH)$_2$ and CaOHCl whereas it increased for temperatures from 300°C to 400°C, and stabilized at temperatures higher than 450°C. Given the assumption discussed above, the percentage of water loss with respect to the stoichiometric value was used to estimate through reactions 7.1 and 7.2 the percentage of Ca(OH)$_2$ and CaOHCl converted to CaO.

From these data, it was also straightforward to characterize quantitatively the composition of the sample at the beginning of step 3, in terms of CaOHCl, Ca(OH)$_2$, and CaO content, the latter one also reported in Figure 7.5.
Figure 7.5: Water weight loss (○) and mass of CaO (□) formed from Ca(OH)$_2$ and CaOHCl dehydroxylation for 100 g of untreated APC residues at different applied operating temperatures. The lines are only a visual guide.

### 7.3.2 Estimation of carbonation conversion

The thermogravimetry data corresponding to the carbonation reaction (step 3 in Figure 7.1) were analyzed assuming that all the three calcium species available could react with CO$_2$ simultaneously through the following gas-solid exothermic reactions:

\[
\begin{align*}
\text{CaOH}_2(s) + \text{CO}_2(g) & \leftrightarrow \text{CaCO}_3(s) + \text{H}_2\text{O}(g) & (7.3) \\
2\text{CaOHCl}(s) + \text{CO}_2(g) & \leftrightarrow \text{CaCO}_3(s) + \text{CaCl}_2(s) + \text{H}_2\text{O}(g) & (7.4) \\
\text{CaO}(s) + \text{CO}_2(g) & \leftrightarrow \text{CaCO}_3(s) & (7.5)
\end{align*}
\]

The conversion of the carbonation reaction was evaluated as the ratio between the measured weight increase, $\delta W(t)$ [g], and the maximum weight increase expected from the complete carbonation of the reacting phases, i.e. Ca(OH)$_2$, CaOHCl, and CaO, $\delta W_{\text{stoic}}^{\text{conv}}$ [g], calculated as
7. Kinetics of direct carbonation of APC residues

follows.

\[ \delta W_{\text{conv}}^{\text{stoic}} = n_{\text{Ca(OH)}_2}(\omega - \theta) + \frac{n_{\text{CaOHCl}}(\omega - \theta)}{2} + n_{\text{CaO}} \omega, \quad (7.6) \]

where \( \omega \) and \( \theta \) are the molecular weights of CO\(_2\) and water, respectively; \( n_{\text{Ca(OH)}_2}, n_{\text{CaOHCl}}, \) and \( n_{\text{CaO}} \) correspond to the moles of \( \text{Ca(OH)}_2, \text{CaOHCl}, \) and \( \text{CaO} \), respectively, at the beginning of step 3. This equation clearly shows that the weight change is due to the uptake of CO\(_2\), but also to the water loss because of the dehydroxylation of \( \text{Ca(OH)}_2 \) and \( \text{CaOHCl} \). This needs to be accounted for in order to evaluate the extent of the carbonation reaction, \( \eta^{\text{conv}}(t) \), correctly, which is given by:

\[ \eta^{\text{conv}}(t) = \frac{\delta W(t)}{\delta W_{\text{conv}}^{\text{stoic}}} \cdot 100. \quad (7.7) \]

The conversion measured at the end of step 3, which represents the maximum conversion of the carbonation reaction for each run, is reported for the different applied operative conditions in Table 7.3. The complete data of the carbonation kinetics in terms of conversion vs. time are reported in Figures 7.6 and 7.7.

### 7.3.3 Results of carbonation kinetics

Most of the kinetics of carbonation, reported in Figure 7.6, showed a similar shape, characterized by a first induction period corresponding to \( \text{CaCO}_3 \) nucleation, followed by a rapid growth reaction and by a slower final reaction stage at higher conversions. As suggested by Bhatia and Perlmutter (1983) for CaO carbonation, the initial rapid growth step increase can be assumed to be kinetically controlled by the carbonation reactions (reactions 7.3, 7.4, and 7.5) during which \( \text{CaCO}_3 \) crystals form a layer gradually reducing the porosity of the sample. This behavior is
Figure 7.6: Calcium conversion vs. time: (a) 10 vol.% of CO$_2$; (b) 22 vol.% of CO$_2$; (c) 50 vol.% of CO$_2$ at different temperatures: 350°C (- - -) runs 5, 8, and 9; 400°C (—) runs 11, 13, and 14; 450°C (···) runs 15, 17, and 19; 500°C (−·−·−) runs 21, 23, and 25.
Figure 7.7: Calcium conversion vs. time in the first 5 min: (a) 10 vol.% of CO₂; (b) 22 vol.% of CO₂; (c) 50 vol.% of CO₂ at different temperatures: 350°C (- - -) runs 5, 8, and 9; 400°C (—) runs 11, 13, and 14; 450°C (···) runs 15, 17, and 19; 500°C (−−−−) runs 21, 23, and 25.
7.3 Results and discussion

consistent with the observation that the residues are characterized by large pores (mesoporous structure), which exclude diffusion-controlled kinetics. After a given reaction time, the product layer hinders further diffusion of CO\textsubscript{2} into the material, switching the process to a diffusion-controlled one.

Looking at the results reported in Figure 7.6, it can be noticed that at $350^\circ$C the final Ca conversion values varied between 54 and 62%, and no trend could be recognized among the runs carried out at different CO\textsubscript{2} concentrations.

The experiments performed at $400^\circ$C (11, 13, and 14) showed a different characteristic shape of calcium conversion vs. time curves. Conversion was observed to increase very rapidly, reaching in few minutes approximately the maximum value, and to remain almost constant until the end of the run. Such a discontinuity in the reaction rate could be attributed to the particular physical changes of the particles, i.e. a sudden decrease in porosity, tortuosity and total pore size due to CaCO\textsubscript{3} precipitation, agglomeration of particles, sintering, etc. occurring only at this temperature value. During run 14 characterized by the fastest observed kinetics the curve reached a maximum value and then slightly decreased until a stable one. This behavior might be due to a buoyancy effect which takes place at the very beginning of step 3 when the total gas flux fed to the TGA furnace is suddenly increased since CO\textsubscript{2} is added to the Ar flow. For this reason, such an effect could be appreciated only in the experiment characterized by the fastest kinetics and not in the other ones. Also at this temperature calcium conversion, shown in Table 7.3, was not much affected by the applied CO\textsubscript{2} concentrations although the highest calcium conversion was measured at 10 vol.% CO\textsubscript{2} concentration (run 11).

At $450^\circ$C, the shape of the kinetics curves was characterized by a smooth
7. Kinetics of direct carbonation of APC residues

Table 7.3: Experimental conditions of the carbonation experiments. $t_{50}$ corresponds to the time needed to achieve 50% Ca conversion.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>T, °C</th>
<th>CO$_2$, vol.%</th>
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change between the chemically-controlled phase and the diffusion-limited one, as observed in the experiments performed at 350°C. The values of maximum conversion achieved were higher than at 400°C varying between 68 and 73%, with the highest value achieved in runs at 10 vol.% of CO₂ (15 and 16), while the conversion decreased as the applied CO₂ concentration increased.

Finally, at 500°C, the highest maximum extent of reaction was achieved although the carbonation kinetics was not the fastest one. That could be due to a faster CaCO₃ precipitation in the material pores that soon further hindered CO₂ diffusion into the material. Summarizing the main experimental evidence, it can be concluded that the operative temperature did not greatly affect the final maximum conversion of the reaction, despite the decrease of the material surface area with increasing temperature (see Table 7.2). The only exception was represented by the experiments performed at 350°C, where the maximum reaction conversion was lower than the one measured under other operative conditions. On the contrary, experiments at the same operative temperature but at different CO₂ concentrations did not show any special trend, although the highest conversion was obtained at 10 vol.% CO₂. This is an encouraging result, in the perspective of applying carbonation directly to the flue gases of a combustion plant whose composition is typically around 10 vol.% CO₂, thus opening the possibility of lumping both CO₂ capture and storage in a single-step process.

Finally, a deeper insight into the carbonation reaction was obtained by looking at the detail of the kinetics in the very first minutes of the reaction (Figure 7.7), and considering the t₅₀ values in Table 7.3 which correspond to the time required to achieve 50% of the final Ca conversion. Looking at Figure 7.7, it is evident that CO₂ concentration has an important effect on the first stage of the carbonation kinetics. The slope
of the chemically-controlled stage, during which the conversion increases rapidly and almost linearly with time, was observed to increase with increasing CO$_2$ concentration. This different behaviour is also reflected in increasing values of the time required to achieve 50% of the maximum conversion, $t_{50}$, reported in Table 7.3. On the other hand, the effect of temperature cannot be clearly assessed from the trend of both $t_{50}$ and $\eta^{conv}(t)$ during the first five minutes. That could be due to two main phenomena occurring during the experiments:

1. The composition of the material changed as the operative temperature changed, as highlighted above;

2. The specific surface area, reported in Table 7.2, decreased as the operative temperature changed;

Nevertheless, it is worth pointing out that the lowest $t_{50\%}$ values were observed in the experiments performed at 400°C, which was always characterized by the steepest conversion curve in the chemically-controlled stage. In view of a full scale application, a short residence time would be desired in order to reduce the reactor size. Therefore, the operative condition of $T = 400^\circ$C and CO$_2$ concentration 50 vol.%, where 1 minute is needed to achieved the maximum conversion, should be selected. However, this would require to capture CO$_2$ previously from the flue gases, where the typical CO$_2$ concentration is around 10 vol.%. An alternative approach would consist in performing the process at the same temperature but at 10 vol.% CO$_2$ concentration, which, despite of requiring a longer residence time (i.e., 2.5 min), would allow to lump capture and storage in a single step since flue gases could be directly used as the gas feed. It is worth pointing out that in real combustion flue gases, the presence of water vapor is actually expected to speed up the carbona-
7.4 Conclusion

Mineral carbonation is a CCS technology where CO$_2$ reacts with natural silicate and industrial alkaline materials and forms stable carbonate. Although the latter are available in smaller amount than the former, the use of industrial alkaline materials is attracting since they are very reactive and, most of the time, available at the CO$_2$ production. In this paper, we have reported the study of gas-solid carbonation of a type of alkaline material, APC residues. A fundamental study based on XRD, TGA and SEM analysis allowed to evaluate the composition of the APC residues after pre-heating under inert atmosphere and just before carbonation started. It was shown that, by increasing the pre-heating temperature, the weight fraction of Ca(OH)$_2$ and CaOHCl originally present in the material is reduced, whereas the CaO one is increased. In this way, the raw isothermal TGA data (weight vs. time), measured in a TGA furnace under a CO$_2$/Ar flux, could be transformed in terms of calcium conversion vs. time at different operating conditions. The results of carbonation kinetics, shown and discussed in this paper, confirmed that the carbonation process is effective at temperatures equal to or above 350°C. Maximum conversions between 60% and 80% were obtained, depending on the operative temperature and CO$_2$ concentration. The kinetics were characterized by a rapid chemically-controlled reaction followed by a slower product layer diffusion-controlled process. Apart from the tests performed at 350°C, the influence of temperature on the maximum conversion was negligible. Besides, the influence of temperature on the rate of the carbonation reaction was masked by the...
different composition and surface area of the residues at the tested operative temperatures. Kinetics was slightly affected by CO\textsubscript{2} concentration, although the fastest kinetics was observed at 400\textdegree C and 50 vol.% CO\textsubscript{2}. Reasonably fast reaction rates were observed at 10 vol.% CO\textsubscript{2} concentration. The data collected in this paper show for the first time that carbonation of APC residues, i.e. an alkaline residue rich of free calcium oxides and hydroxides, can be carbonated under a gas stream whose composition closely resembles that of combustion flue gases. The latter would also contain water vapor, but it is likely that this would actually speed up rather than slow down the carbonation kinetics. This makes possible lumping the capture and storage processes in a single step by directly contacting the flue gases with the residues. The required operative condition can be reasonably found along the flue gas pathway of any combustion plant, making the implementation of the process feasible. The APC residues produced from the existing incineration plants would cover only 0.02-0.05 % of the total CO\textsubscript{2} European storage capacity required to comply with the Kyoto protocol objectives. Nevertheless, the proposed carbonation route could be applied to other residues, such as Cement Kiln Dust, Paper mill residues and Stainless Steel Desulphurization slags, characterized by a high content of free calcium oxides and hydroxides, thus increasing the impact of this process option.
Chapter 8

Conclusions

Ex situ mineral carbonation of metal-oxide bearing materials such as olivine, serpentine, wollastonite and industrial alkaline residues is among the CCS technology the one with the safest implementation given the production of stable and environmental benign carbonates such as magnesite and calcite.

Two different process routes have been investigated: Aqueous mineral carbonation and direct carbonation. Although direct carbonation is a thermodynamically favored reaction and would require simple facilities, it is kinetically hindered, hence it can be performed only using very reactive materials such as industrial alkaline residues containing metals in form of oxide and hydroxides (e.g., CaO and CaOH). Aqueous mineral carbonation is a more complex process but would allow the treatment of silicate minerals that are worldwide available in larger amount.

Aqueous mineral carbonation reaction is kinetically controlled by dissolution and precipitation of anhydrous carbonates, while direct carbona-
tation is kinetically controlled by the chemical composition of the material and by its reactivity. The complexity of these processes makes necessary for an optimal process design to understand the thermodynamics and the kinetics of the underlying mechanisms. With the final aim to accelerate carbonation reaction, this thesis focused on the study of the thermodynamics and the kinetics of the elementary processes occurring during aqueous mineral carbonation and direct carbonation.

Regarding the dissolution of silicate, we investigated the role of inorganic and organic salts and CO$_2$ in enhancing the reaction of olivine applying operating conditions relevant to mineral carbonation, i.e., high temperature and high partial pressure of CO$_2$. We observed that the effects of CO$_2$, LiOH, HCl, NaCl and NaN$_3$ were important inasmuch as they affected the pH, but not directly and independently. Our investigations were carried out at 120°C, but our conclusions were general and could be applied to any temperature in the range between 25°C and 150°C, where the dissolution mechanism is the same. In case of the effect of organic salts, we observed that oxalate promoted olivine dissolution at 90°C and 120°C. At concentration of oxalate as large as 0.1 m the dissolution was enhanced of one order of magnitude with respect to an organic-free system. This occurred in a pH region suitable for direct and fast magnesite precipitation (i.e., pH between 5 and 6) opening the possibility to accelerate both olivine dissolution and magnesite precipitation in a single step mineral carbonation process.

As far as the precipitation of Mg-carbonate concerns, we studied the thermodynamics and the kinetics of Mg-carbonation precipitation. The magnesium carbonate system exhibits a complex behaviour due to the large number of possible hydrated and anhydrous phases and to the strong kinetic inhibitions that are dependent on temperature, partial pressure of CO$_2$, and solution composition. Thermodynamics can be
used to predict both the appearance of solid phases and the precipitation kinetics through the estimation of supersaturation with respect to Mg-carbonates. At low partial pressure of CO$_2$ and in a wide range of temperature, we observed the formation of hydrated form of Mg-carbonate. Their transformation into magnesite occurred only in the upper range of temperature and sped up with $P_{CO_2}$. At operating condition relevant to mineral carbonation process, i.e., high temperature and high partial pressure of CO$_2$ and at pH between 5 and 6, precipitation of magnesite was greatly enhanced when the solution was supersaturated with respect to magnesite and hydromagnesite. Under these conditions, and also with high concentration of Mg$^{2+}$, direct magnesite precipitation was hindered and it precipitated simultaneously with the most stable hydrated Mg-carbonate under those conditions, i.e. hydromagnesite, that then transformed into magnesite within few hours. Precipitation kinetics was characterized, nucleation was found to follow classical nucleation theory and growth the birth and spread mechanism. The applied method based on population balance modeling and multivariate kinetics modeling resulted to be a powerful tool in this context and the estimated parameters can be coupled with the dissolution kinetics for multi-step carbonation process simulation.

Direct mineral carbonation was studied using APC residues (fly-ash) and the kinetics of the carbonation reaction was investigated. A fundamental study based on XRD, TGA and SEM analysis allowed to evaluate the composition of the fly-ash and their reactivity under various operating conditions. The kinetics was characterized by a rapid chemically-controlled reaction at temperatures equal to or above 350$^\circ$C with maximum conversions between 60% and 80% followed by a slower product layer diffusion-controlled process. Fast reaction rates were achieved under a gas stream whose composition closely resembles that of combustion
flue gases (10 vol.% CO₂) and at 400°C making possible to lump capture and storage processes in a single step by directly contacting the flue gases with the residues.
Appendix A

Surface complexation model with the inhibition effect of bioxalate

This section reports a preliminary surface complexation model developed to model the enhanced and inhibited dissolution process of olivine.

A.1 Introduction

The model is based on the experimental data reported in Chapter 3 and on a new dataset reported in this Appendix. In particular, the inhibition part of the model is based on the experiments performed at 120°C and at pH values lower than 3.5 that showed specific dissolution rate lower than the one in an organic-free system. We initially assumed...
that the dissolution process was inhibited and we developed a surface complexation model based on the enhancement effect of protons and oxalate and on an inhibiting effect of bioxalate, being this species the dominant one in the pH region where inhibition was observed. Combing these experiments with the ones given in Chapter 3, the overall dissolution process was described with the population balance equation (PBE) model coupled with a mass balance equation and a surface-reaction controlled kinetics model based on the independent adsorption mechanism on two neighboring sites described by Langmuir adsorption isotherm. At 90 and 120°C (pH >3.5) the specific dissolution rate increased with salt concentration as already mentioned in Chapter 3, while at 120°C, pH <3.5 and with 0.1 m of sodium oxalate, the dissolution rate decreased with acid concentration. In an early stage of the surface complexation model development, we ascribed such a dissolution rate decrease to the formation of outre-sphere complexes on the olivine surface that impaired the proton effect.

Although this model was discarded in later stage of our study, this Appendix reports its development and guides to the decision to eliminate that dataset by assuming an oxalate decomposition phenomenon that affected the experiments.

This Appendix is structured as follows. Section A.2 reports the experiments carried at 120°C and at pH <3.5 at different oxalate concentrations and compares them with the ones already discussed in Chapter 3. Section A.3 describes the mechanism of enhancement and inhibition effect of oxalate during dissolution. Section A.4 reports the surface complexation model, i.e., the chemical reactions at the solid-liquid interface and implement them in a kinetics model to derive the dissolution rate equation.
A.2 Results

Experimental data of olivine dissolution experiments carried out at 120°C and pH <3.5 are reported in Table A.1. In particular, for each experiment, the applied operating conditions, i.e. $f_{CO_2}$, LiOH, HCl, and oxalate salt molalities, flow rate ($Q$), suspension volume ($V$), initial olivine mass ($m_0$), and duration of the experiment are listed together with the resulting specific dissolution rate ($r$), and the calculated pH. In Figure A.1, the logarithm of the specific dissolution rate of the experiments with 0.1 m of sodium oxalate which have been estimated as described in section 3.4, are shown over pH in comparison with literature data at 25°C, under atmospheric CO$_2$, and with $\sim$ 0.1 m of oxalic acid (Olsen and Rimstidt, 2008). The lines indicate the specific dissolution rate, mol cm$^{-2}$ s$^{-1}$, in absence of oxalate as already reported in Chapter 3.
Table A.1: Operating conditions and results of the olivine dissolution experiments at 120°C and pH <3.5.

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<th>T, °C</th>
<th>pH</th>
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<th>HCl, m</th>
<th>Na₂C₂O₄, Q, ml</th>
<th>V, ml</th>
<th>m₀, mg</th>
<th>Dura-, t, h</th>
<th>r, mol/cm²s x 10¹⁰</th>
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A.3 Mechanism of dissolution

As already mentioned in Chapter 3, at 90 and 120°C, and for pH values larger than 3.5, dissolution was enhanced by the presence of both citrate and oxalate, with an effect increasing with organic substance concentration. We associated the catalytic effect with the oxalate and citrate ions, namely C₂O₄⁻² and C₆H₆₂O₇⁻, respectively, since they are the dominant species in the pH region at both temperatures where olivine enhanced dissolution was observed.

At 120°C and at pH <3.5, dissolution was instead inhibited in presence of 0.1 m of sodium oxalate. Being bioxalate (HC₂O₄⁻) the dominant species in this pH region, we attributed the inhibiting effect to this ion. Concerning the citrate ion, since no experiments were performed with sodium citrate at pH<3.5, we could not argue about their effect on olivine dissolution kinetics under these conditions.

By comparing the time-resolved olivine equivalents in solution measured...
A.3 Mechanism of dissolution

![Graph showing pH vs. logr with different symbols and lines representing various conditions: 90°C, 0.1 m oxalate, 90°C, w/o oxalate**, 25°C, w/o oxalate, 120°C, 0.1 m oxalate, 120°C, w/o oxalate*, 25°C, ~0.1 m oxalate+ ++.](image)

Figure A.1: Logarithm of $r$ vs. pH at 25, 90, and 120°C in presence of CO$_2$. Symbols indicate: *, linear model for an organic-free solution at 120°C in presence of CO$_2$ (Prigiobbe et al., 2009a); **, linear model for an organic-free solution at 90°C (Hänchen et al., 2006); +, literature data (Olsen and Rimstidt, 2008); ++, model in a organic-free solution at atmospheric CO$_2$ (Olsen and Rimstidt, 2008).

during experiment 180 with 0.1 m sodium oxalate and experiment 27 without oxalate (Prigiobbe et al., 2009a) (see Figure A.2), the effect of the inhibitor appears in a later stage of the dissolution process. The diagram vertical axis is given in olivine equivalent divided by the actual initial mass of olivine used in the experiments to ensure proper comparison of the concentrations. Similarly, the diagram horizontal axis is given in dimensional time, where $\theta$ is the average hydraulic retention time, because of different flow-rate applied during the experiments. Initially, in experiment 180 the olivine concentration is much higher than in experiment 27, but then it decreases dramatically, and after 2-3 hours becomes much lower than in experiment 27. The estimated dissolution
rate in experiment 180 resulted therefore much smaller than in experiment 27.

![Graph showing Olivine equivalent over time measured during experiments 183 (this work) and 27 (earlier work (Prigiobbe et al., 2009a)) in presence of CO₂ and at 120°C. θ is the average hydraulic retention time and m₀ is the initial mass of olivine. The lines are only a visual guide.](image)

Figure A.2: Olivine equivalent over time measured during experiments 183 (this work) and 27 (earlier work (Prigiobbe et al., 2009a)) in presence of CO₂ and at 120°C. θ is the average hydraulic retention time and m₀ is the initial mass of olivine. The lines are only a visual guide.

However, the inhibiting effect might be also due to the presence Na⁺ ions as their adsorption is thermodynamically favored at low pH and at high temperature in comparison to H⁺, slowing down dissolution as reported in Sposito (2004). But, having observed in our earlier study (Prigiobbe et al., 2009a) no inhibited dissolution of olivine in presence of high concentration of Na⁺ up to 0.1 m, this type of ion could not have determined inhibition also in this case.

Given the observation above, two dissolution mechanisms were proposed:

1. Enhanced dissolution due to the simultaneous adsorption onto the
A.3 Mechanism of dissolution

olivine surface of a proton and of an oxalate ion. In particular, the proton is adsorbed on the oxygen atom bonded to the silicon atom and the magnesium atom (O(1)) (see Figure A.3.a) at the olivine crystalline surface (Pokrovsky and Schott, 2000) and the oxalate on the magnesium atom (Mg(1)) bonded to the protonated oxygen leading to the formation of inner-sphere complexes (defined as surface complexes where there is covalent bond between the oxygen atoms in the molecule of the adsorbed organic-species and the surface metal ion). Such a surface reaction leads to the weakening of the bond between O(1) and the silica group allowing the release of $\text{H}_4\text{SiO}_4$ to solution and Mg(1)-ligand complex as well (Olsen and Rimstidt, 2008; Liu et al., 2006);

2. The reactions that leads to inhibited dissolution occurs in parallel to the enhanced dissolution process. In our case, we assumed inhibited dissolution due to the adsorption of bioxalate ions onto the protonated oxygens at the olivine-solution interface by forming outer-sphere surface complexes (defined as surface complexes between hydrated mineral surface and the adsorbed organic-species therefore a hydrogen bond forms between the protonated oxygens atom at the mineral surface and the oxygen atoms in the organic molecule) that impair the proton effect and sterically hinder the formation of inner-sphere complexes between oxalate and magnesium on the olivine surface (see Figure A.3.b). A similar mechanism was proposed by Ganor et al. (1999) in the case of inhibited dissolution of gibbsite in a solution containing perchloric acid and at low pH.
A.4 Surface complexation model

A.4.1 Thermodynamic model

A surface complexation model was developed to describe olivine dissolution kinetics in a solution containing oxalate ions and in condition far from the equilibrium.

The model for enhanced dissolution combines the proton-promoted reactions formulated by Pokrovsky and Schott (2000) and the ligand-promoted reactions given by Wogelius and Walther (1991) together with the mechanism of the formation of the activated complex proposed by Olsen and Rimstidt (2008) and Liu et al. (2006). In the scheme shown in Figure A.3.a, the two sites correspond to O(1) (named site S) and Mg(1)
(named site M) belonging to the $\text{H}_4\text{SiO}_4(\text{s})$ and $\text{MgOH}^+_{2(\text{s})}$ surface groups and taking part in the formation of the activated surface complex.

The model for inhibited dissolution combines the enhanced dissolution model with the one based on independent adsorption of a catalyst and an inhibitor on the same neighboring sites formulated by Ganor and Lasaga (1998) and applied by Ganor et al. (1999) in the case of gibbsite. In the scheme shown in Figure A.3.b, this site correspond to $\text{O}(1)$-OH, named site S, as in the surface complexation model for the enhanced dissolution process since the inhibiting reaction blocks indeed this site.

The spatial distribution of the electrical potential at the particle interface was described by the 3-plane model (Tadanier and Eick, 2002).

In this, the two above mechanisms are discussed in the case of oxalate effect on the olivine surface complexation. They are described in the pH range lower than the $\text{pH}_{\text{pzc}}$ (pH of zero charge point) where the surface is positively charged (Pokrovsky and Schott, 2000).

At pH below $\text{pH}_{\text{pzc}}$, initially, an ion-exchange precursor reaction occurs. It is responsible for the rapid release of $\text{Mg}^{2+}$ in solution leading to the silica-enriched surface layer:

$$
\text{Mg}_2\text{SiO}_4(\text{s}) + 4\text{H}^+ \leftrightarrow \text{H}_4\text{SiO}_4(\text{s}) + 2\text{Mg}^{2+},
$$

$$
K_{\text{ex}} = \frac{a_{\text{Mg}^{2+}}^{\text{H}_4\text{SiO}_4(\text{s})}}{a_{\text{H}^+}^{\text{Mg}_2\text{SiO}_4(\text{s})}},
$$

(A.1)

where \{\text{i}_i\} is the concentration of species \text{i} at the olivine surface, (mol m$^{-2}$); $a_i$ is the activity of the subscripted species, (-), and $K_{\text{ex}}$ is the apparent equilibrium constant of the ion-exchange reaction. The $\text{H}_4\text{SiO}_4(\text{s})$ group polymerizes bringing together two isolated silica tetrahedra at the surface and forming silica dimers connected with each other by an oxygen atom (Si-O(1)-Si) which is linked to a magnesium ion Mg(1) deeper.
in the structure. On the bridging oxygen O(1) (site S), a H\(^+\) ion is adsorbed (protonation reaction) leading to the decomposition of the silica dimers and the release of the silicon group as H\(_4\)SiO\(_4(aq)\). The overall stoichiometry of the polymerization and protonation reactions is given by:

\[
H_4\text{SiO}_4(s) + n\text{H}^+ \leftrightarrow H_4\text{SiO}_4 - n\text{H}^+_\text{(s)}, \quad (A.2)
\]

\[
K_H = \frac{\{H_4\text{SiO}_4 - 0.5\text{H}^+_\text{(s)}\}}{a_{\text{H}^+}^{0.5} \{H_4\text{SiO}_4(s)\} e^{-\frac{F\Phio}{RT}}}, \quad (A.3)
\]

with the subsequent silicon group desorption reaction which controls the entire proton-promoted dissolution kinetics:

\[
H_4\text{SiO}_4(s) - n\text{H}^+ \leftrightarrow H_4\text{SiO}_4 + n\text{H}^+, \quad (A.4)
\]

\[
K = \frac{a_{H_4\text{SiO}_4} a_{\text{H}^+}^n}{\{H_4\text{SiO}_4(s) - n\text{H}^+_\text{(s)}\} e^{-\frac{F\Phio}{RT}}}. \quad (A.5)
\]

Parallel to proton adsorption, Mg atoms exposed at the surface undergo acid-base reactions (reactions A.6 and A.8) leading to the formation of MgOH\(_2^+\) surface group (named site M):

\[
\text{MgO}^-\text{(s)} + \text{H}^+ \leftrightarrow \text{MgOH}_{\text{(s)}}, \quad (A.6)
\]

\[
K = \frac{\{\text{MgOH}_{\text{(s)}}\}}{a_{\text{H}^+} \{\text{MgO}^-\text{(s)}\} e^{-\frac{F\Phio}{RT}}}, \quad (A.7)
\]

\[
\text{MgOH}_{\text{(s)}} + \text{H}^+ \leftrightarrow \text{MgOH}^+_{2\text{(s)}}, \quad (A.8)
\]

\[
K = \frac{\{\text{MgOH}^+_{2\text{(s)}}\}}{a_{\text{H}^+} \{\text{MgOH}_{\text{(s)}}\} e^{-\frac{F\Phio}{RT}}}. \quad (A.9)
\]

The MgOH\(^+\)\(_{2\text{(s)}}\) surface group forms inner-sphere complexes on the olivine surface adsorbing either water molecules or oxalate ions (X\(^2^-\)) (Wogelius
and Walther, 1991; Olsen and Rimstidt, 2008; Liu et al., 2006):

\[
\text{MgOH}_2^{+} + X^{2-} \leftrightarrow \text{MgX}^{-} + \text{H}_2\text{O}, \quad \text{(A.10)}
\]

\[
K_X = \frac{a_{\text{H}_2\text{O}}[\text{MgX}^{-}]}{a_{X^{2-}}[\text{MgOH}_2^{+}]} e^{-\frac{F\psi_o}{RT}}, \quad \text{(A.11)}
\]

Since the enhancement effect of oxalate ions is much higher than the one of water, in our model we considered only the adsorption reaction of the latter. Upon reaction A.10, the formed bonds between the organic oxygens of the ligand and the Mg(1) atom destabilize the one between O(1) and Mg(1) by bond polarization. Consequently, the silicon detaches as silicic acid (\(\text{H}_4\text{SiO}_4\)) (reaction A.4) and magnesium as magnesium oxalate complex (\(\text{MgX}\)):

\[
\text{MgX}^{-} \leftrightarrow >^- + \text{MgX}, \quad \text{(A.12)}
\]

\[
K = \frac{a_{\text{MgX}}[>]^{-}}{[\text{MgX}^{-}]} , \quad \text{(A.13)}
\]

where > indicates the surface.

In a ligand-free solution, the dissolution reaction is only proton-promoted and the desorption of silica group controls the entire kinetics.

At 120°C and pH $<3.5$, we observed inhibited dissolution. The inhibition mechanism might due to a combined effect of the highly positively charged olivine surface and the dominant species bioxalate in solution that favored the formation of outer-sphere surface complexes over site S impairing the proton effect and sterically protecting the M site from the catalytic surface complexation reaction with oxalate ions. We modeled the inhibited process through an adsorption reaction of bioxalate onto
A. Surface complexation model with the inhibition effect of bioxalate

the surface site S upon its protonation (reaction A.2).

\[
H_4SiO_4 - nH^+_{(s)} + HL^- \leftrightarrow H_4SiO_4 - nH^+_{(s)} \cdot HL^-.
\]  

(A.14)

\(H_4SiO_4 - nH^+_{(s)} \cdot HL^-\) outer-sphere surface complexes impaired the proton effect and inhibited dissolution. It is known that outer-sphere surface complexes are favored at low pH and their formation at mineral surface was observed with spectroscopic methods by Degenhardt and McQuillan (1999), Axe and Persson (2001), and Persson and Axe (2005). These type of surface complexes are known to have either a negligible or an inhibiting effect on dissolution (Johnson et al., 2004a; Yoon et al., 2005; Johnson et al., 2005). However, over time the outer-sphere complexes might undergo transformation into inner-sphere complexes and eventually decompose towards metal-liquid aqueous complexes (Johnson et al., 2004b).

Although on this surface site both oxalate ions and bioxalate could have been adsorbed, in the pH range where we observed inhibited dissolution, bioxalate ions were the dominant species therefore we considered only these ions to be responsible of inhibition. The equilibrium constant of reaction A.14 is give by:

\[
K_B = \frac{\{H_4SiO_4 - nH^+_{(s)}\}}{a_{HL}\{H_4SiO_4 - nH^+_{(s)} \cdot HL^-\}} e^{\frac{(\Psi_0 - \Psi_1)F}{RT}},
\]

(A.15)

where \(\Psi_1\) is the electrical potential of the 1-plane layer at which the outer-sphere complexes are bound (Tadanier and Eick, 2002).

Reactions A.2 and A.10 defined the model for enhanced dissolution and they combine the proton-promoted reaction formulated by Pokrovsky and Schott (2000) and the ligand-promoted reaction given by Wogelius and Walther (1991) together with the mechanism proposed by Olsen and
A.4 Surface complexation model

Rimstidt (2008) and Liu et al. (2006).

Reactions A.2, A.10, and A.14 defined instead the model for inhibited dissolution and they combine the enhanced dissolution mechanism and the inhibited dissolution mechanism proposed by Ganor et al. (1999) for gibbsite dissolution in presence of perchloric acid at low pH.

A.4.2 Kinetic model

In this section, we report the kinetic model developed to describe the catalytic and inhibiting effects of sodium oxalate on olivine dissolution based on the surface complexation reactions given in section 3.6.2.

We adopted however a simplified notation of surface complexes through the definition of the surface group $S_H$ corresponding to $\text{H}_4\text{SiO}_4-n\text{H}_+(s)$, a surface group $M_X$ corresponding to $\text{MgX}^-(s)$, and a surface group $S_B$ corresponding to $\text{H}_4\text{SiO}_4-n\text{H}_+(s)$·$\text{HL}^-$.

We considered dissolution due to three parallel reactions whose dissolution rates are proportional to the concentration of the adsorbed protons, the adsorbed oxalate ions, and the adsorbed bioxalate ions, consequently they are proportional to the concentration of the surface complexes $\{S_H\}$, $\{S_X\}$, and $\{S_B\}$. The resulting specific dissolution rate of olivine, $r$ (mol cm$^{-2}$ s$^{-1}$), is then given by the sum of the specific dissolution rates due to protonation, $r_H$, oxalate ion adsorption, $r_X$, and bioxalate ion adsorption, $r_B$:

$$
\begin{align*}
  r_H &= b_H \{S_H\}, \\
  r_X &= b_X \{M_X\}\{S_H\}, \\
  r_B &= b_B \{S_B\}, \\
  r &= r_H + r_X + r_B,
\end{align*}
$$

(A.16)  \quad (A.17)  \quad (A.18)  \quad (A.19)
where $b_H \text{ (s}^{-1})$, $b_X \text{ (cm}^2 \text{ mol}^{-1}\text{s}^{-1})$, and $b_B \text{ (s}^{-1})$ are the kinetic constants.

Combining eq. A.19 with the equation for the balance of the sites:

\[
\{S\} + \{S_H\} + \{S_B\} = \{S_o\}, \quad (A.20)
\]

\[
\{M\} + \{M_X\} = \{M_o\}, \quad (A.21)
\]

where $\{S_o\}$ and $\{M_o\}$ sum up to the total concentration of sites containing magnesium on olivine surface equal to $2.2 \times 10^{-5} \text{ mol cm}^{-2}$ (Wogelius and Walther, 1991; Pokrovsky and Schott, 2000), and eqn A.3 through A.15, $r$ becomes:

\[
r = \frac{b_H a_{H}^{0.5} K_H S_o}{1 + a_{H}^{0.5} K_H (1 + a_B K_B)} \left[ 1 + \frac{b_X}{b_H} \left( \frac{a_X K_X M_o}{1 + a_X K_X} \right) + \frac{b_B a_B K_B}{b_H} \right]. \quad (A.22)
\]

Defining:

\[
\beta_1 = \frac{b_X K_X M_o}{b_H}, \quad (A.23)
\]

\[
\beta_2 = \frac{b_B K_B}{b_H}, \quad (A.24)
\]

\[
r_H = b_H a_{H}^{0.5} K_H S_o, \quad (A.25)
\]

eq. A.22 rewrites as:

\[
r = \frac{r_H}{1 + a_{H}^{0.5} K_H (1 + a_B K_B)} \left( 1 + \frac{\beta_1 K_X a_X}{1 + a_X K_X} + \beta_2 a_B \right). \quad (A.26)
\]

Being $r_H$ the simplified kinetic equation of the specific dissolution rate due to only surface protonation, we substituted it with the Arrhenius equation already adopted in our earlier works (Hänchen et al., 2006,
2007; Prigiobbe et al., 2009a):

\[ r_H = a_H^n A e^{E_a/RT}, \]

with \( E_a = 52.9 \text{ kJ mol}^{-1} \), \( n \) the order of the protonation reaction, \((-)\), and \( A \) the preexponential factor, \((\text{mol cm}^{-2}\text{s}^{-1})\).

The model parameters are therefore \( \beta_1, \beta_2, K_B, K_X, \) and \( K_H \). By assuming the dissolution rate due to the inhibitor, \( r_B \), negligible (Ganor and Lasaga, 1998) the \( \beta_2 \) equals zero and eq. A.26 becomes:

\[ r = \frac{r_H}{1 + a_H^{0.5} K_H (1 + a_B K_B)} \left( 1 + \frac{\beta_1 K_X a_X}{1 + a_X K_X} \right). \] (A.27)

Moreover, by choosing the adsorption constant \( K_H \) in a way that the logarithm of \( r \) in absence of oxalate becomes pH independent at pH lower than 2 and decreases linearly with pH otherwise (Pokrovsky and Schott, 2000; Hänchen et al., 2006), \( K_H \) equals 0.2. Hence, the model parameters reduced to \( \beta_1, K_B, \) and \( K_X \). These parameters were estimated by a nonlinear least-squares minimization algorithm applied to eq. A.26 and the experimental data as explained in section A.6.

A.5 Discussion

A.6 Parameter estimation

Specific dissolution rate for experiments performed at 25, 90, and 120°C with 0.1 m sodium oxalate were fitted with eq. A.27 on the logr-pH plane. The model parameters \( \beta_1, K_B, \) and \( K_X \) were estimated using the optimization \textit{matlab} routine \textit{lsqcurvefit} and their optimal values
are reported in Table A.2. The high values of $R^2$ between 0.95 and 0.97 and the close correspondence between the best-fit functions and the experimental data for a broad pH range demonstrate the validity of eq. A.27 to describe the data (Figure A.4).

Figure A.4.c shows the profile of $r$ at 120°C together with the experimental data. It can be seen the model describes well the behavior of $r$: At pH $>3.5$ where dissolution is enhanced, at $2 < \text{pH} < 3.5$ where dissolution is inhibited, and at pH $< 2$ where dissolution is only proton-promoted, although no experimental data are available, due to the negligible concentration of oxalate and bioxalate.

Furthermore, Figure A.5 shows the experiments at 120°C and with increasing oxalate concentration. Within the experimental uncertainty of the data, the model describes the reduced enhanced and inhibited effect due to the organic salt.

Table A.2: Estimated optimal values of the parameters in eq A.27.

<table>
<thead>
<tr>
<th>T, °C</th>
<th>$\beta_1$, mol/cm²</th>
<th>$K_H$, (-)</th>
<th>$K_X$, (-)</th>
<th>$K_B$, (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>10</td>
<td>970</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>40</td>
<td>35</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>120</td>
<td>80</td>
<td>10</td>
<td>0.2</td>
<td>7000</td>
</tr>
</tbody>
</table>

The estimated adsorption constant of bioxalate ($K_B$) increased with temperature, and given the isothermic nature of the adsorption process we wondered if the assumed underlying mechanism was physically incorrect. Therefore, we excluded the experiments performed at 120°C and pH $< 3.5$ from the dataset on which afterwards we developed another surface complexation model. We considered these experiments affected by erroneous pH calculation as explained herein. The stability limit of oxalic acid is around 125°C (Benezeth et al., 1997) and decreases with
pH (Crossey, 1991), hence in our experiments where sodium oxalate was added the decomposition of oxalate ions determined a residual un-buffered sodium amount that raised the pH. Crossey (1991) estimated a decomposition rate constant of oxalate around $10^{-6}$ s$^{-1}$ between pH 4 and 6 and between 160 and 180$^\circ$C corresponding to a time for 50% reduction as long as 53 hours at pH 4. Extrapolating these results to our system, this translates into 10 hours for a 50% oxalate decomposition. However, from our calculations already a decomposition of 10 wt.% in the experiments at 120$^\circ$C and pH <3.5 would have raised the pH between 3.5-3.8 making uncertain therefore the pH calculation neglecting decomposition. Such an observation led us to exclude this group of experiments from the dataset used to formulate the surface complexation model in Chapter 3.

A.6.1 Effect of sodium oxalate and sodium citrate

To investigate the sensitivity of the system to increasing organic salt concentrations, experiments were performed in the pH range between 4.5-5.5 where the organic substances are expected to be more effective because the dominant species in the solution are the bidentate ligands (i.e., $\text{C}_2\text{O}_4^{2-}$ (oxalate) and $\text{C}_6\text{H}_6\text{O}_7^{2-}$ (citrate)) capable of strong promotional effect by forming mononuclear surface complexes (Stumm, 1992). At 120$^\circ$C and at pH 2 and 3, we measured an inhibited dissolution rate as shown in parts a and b of Figure A.6. At pH 2, we observed the strongest inhibition effect, log $r$ decreased about 15 times in presence of 0.1 m oxalate in comparison to an organic-free system, and at pH 3, log $r$ decreased linearly with oxalate concentration up to a third of the reference value (dashed line in the graph). In conclusion, an oxalate concentration threshold was required to either catalyze or inhibit disso-
lution, as observed in earlier studies (Drever and Stillings, 1997; Golubev and Pokrovsky, 2006b).

A.7 Conclusion

In this Appendix, we proposed a mechanism of independent adsorption on two neighboring sites described by Langmuir adsorption isotherm. However, the increasing value of the adsorption constant $K_B$ made this model questionable and the decomposition of oxalate at 120°C and pH $<3.5$ was proposed. Decomposition reduced the oxalate concentration by transforming them into formic acid and CO$_2$ and leaving 0.1 Na$^+$ ions buffering the solutions. In these experiments, pH was calculated by using EQ3/6 at the operating conditions neglecting decomposition, therefore its value was underestimated. Given the uncertainty on the experimental pH value of this dataset, we neglected it in a further development of the surface complexation model and we consider only the experiments reported in Chapter 3.
Figure A.4: Upper parts: Logarithm of the specific dissolution rate vs. pH and the best-fit of the functions given in eq. A.27. Lower parts: Speciation of oxalic acid, nominal concentration of 0.1 m. The discontinuity in the lines is due to $f_{CO_2}$ change: from 76 to 19 bar at 90°C and from 81 to 4 bar at 120°C. Simulations at 25°C are at $10^{-3.5}$ bar of CO$_2$. 
A. Surface complexation model with the inhibition effect of bioxalate

Figure A.5: Upper parts: Logarithm of the specific dissolution rate vs. pH and the best-fit of the functions given in eq. A.27 with increasing concentrations of oxalate at 120°C. Lower parts: Speciation of oxalic acid, nominal concentration of 0.001, 0.01, and 0.1 m. The discontinuity in the lines is due to $f_{\text{CO}_2}$ change from 81 to 4 bar.
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A. Surface complexation model with the inhibition effect of bioxalate
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2.6 Logarithm of \( r \) values plotted over pH for each run at 120\(^\circ\)C and linear model described in Eq. A.26. Namely, (○) experiments without CO\(_2\); (△) experiments with CO\(_2\), with or without LiOH; (▽) experiments with CO\(_2\) and NaCl; (♦) experiments with CO\(_2\) and NaNO\(_3\); (—) Eq. 2.20 with \( n = 0.52 \) and \( B = 7.59 \) (this work); (--) Eq. 2.20 with \( n = 0.46 \) and \( B = 8.05 \) (Hänchen et al., 2007). .................. 48
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- Prigiobbe, V., Mazzotti, M. Precipitation kinetics of magnesite and hydromagnesite. In preparation.
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