

METHOD DEVELOPMENT FOR CHEMICAL SYNTHESIS OF CALCIUM-BASED DOUBLE CARBONATES

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**by
Gasham HAJIYEV**

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We approve of the thesis of **Gasham HAJIYEV**

Examining Committee Members:

Prof. Dr. Ekrem ÖZDEMİR

Chemical Engineering, Izmir Institute of Technology

Prof. Dr. Fikret İNAL

Chemical Engineering, Izmir Institute of Technology

Assoc. Dr. Canan URAZ

Chemical Engineering, Ege University

23 May 2025

Prof. Dr. Ekrem ÖZDEMİR

Supervisor, Chemical Engineering,
Izmir Institute of Technology

Prof. Dr. Funda TIHMINLIOĞLU

Head of the Department of Chemical
Engineering

Prof. Dr. Mehtap ENES

Dean of Graduate School of
Engineering and Sciences

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ABSTRACT

METHOD DEVELOPMENT FOR CHEMICAL SYNTHESIS OF CALCIUM-BASED DOUBLE CARBONATES

The aim of this study was to develop chemical synthesis methods for calcium-based double carbonates under low temperature and pressure conditions. The aimed double carbonates to synthesize were $\text{BaCa}(\text{CO}_3)_2$, $\text{CoCa}(\text{CO}_3)_2$, $\text{SrCa}(\text{CO}_3)_2$ and $\text{MgCa}(\text{CO}_3)_2$. Two synthesis methods, direct mixing and batch reactor were used. $\text{M}^{2+}/\text{Ca}^{2+}$ ratios of 0.5, 1.0 and 2.0 were used in direct mixing method. Concentration of 0, 3, 5 and 10 mM $\text{Ca}(\text{OH})_2$ solutions were used in batch reactor. The crystal structure and compositions were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The saturation index values of relevant mineral phases were calculated using PHREEQC, while Medusa & Hydra was used to visualize the distribution of aqueous species as a function of pH. Double carbonates were obtained for Ba^{2+} and Sr^{2+} , however, double carbonates could not be obtained for Co^{2+} and Mg^{2+} . It was concluded that ionic radius is one of the factors for the synthesis of calcium based double carbonates. The particles obtained are important in alternative materials for the industrial use.

ÖZET

KALSIYUM BAZLI ÇİFT KARBONATLARIN KİMYASAL SENTEZİ İÇİN YÖNTEM GELİŞTİRME

Bu çalışmanın amacı, düşük sıcaklık ve basınç koşullarında kalsiyum bazlı çift karbonatların kimyasal sentez yöntemlerini geliştirmektir. Sentezlenmesi hedeflenen çift karbonatlar $\text{BaCa}(\text{CO}_3)_2$, $\text{CoCa}(\text{CO}_3)_2$, $\text{SrCa}(\text{CO}_3)_2$ ve $\text{MgCa}(\text{CO}_3)_2$ 'dir. Sentez için doğrudan karıştırma ve kesikli reaktör olmak üzere iki yöntem kullanılmıştır. Doğrudan karıştırma yönteminde $\text{M}^{2+}/\text{Ca}^{2+}$ oranları 0.5, 1.0 ve 2.0 olarak belirlenmiştir. Kesikli reaktörde ise 0, 3, 5 ve 10 mM $\text{Ca}(\text{OH})_2$ çözeltileri kullanılmıştır. Kristal yapı ve bileşimler X-ışını kırınımı (XRD), taramalı elektron mikroskobu (SEM) ve enerji saçılım spektroskopisi (EDX) ile analiz edilmiştir. İlgili mineral fazlarının doygunluk indeksi değerleri PHREEQC kullanılarak hesaplanırken, sulu türlerin dağılımını pH'ın bir fonksiyonu olarak görselleştirmek için Medusa & Hydra kullanılmıştır. Ba^{2+} ve Sr^{2+} iyonları için çift karbonatlar elde edilebilmiş, ancak Co^{2+} ve Mg^{2+} iyonları için çift karbonatlar elde edilememiştir. Kalsiyum bazlı çift karbonatların sentezinde iyonik yarıçapın belirleyici faktörlerden biri olduğu sonucuna varılmıştır. Elde edilen partiküller, endüstriyel kullanım için alternatif malzemeler açısından önem taşımaktadır.

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CHAPTER 1

INTRODUCTION

Carbonates are crucial minerals, prevalent in nature and extensively utilized in industrial applications. They play significant roles in geological and biological processes, making them the subject of extensive research. Carbonate minerals typically crystallize in trigonal and orthorhombic systems, with variations arising from the type of cation and its ionic radius. The carbonate ion (CO_3^{2-}) features a central carbon atom bonded to three oxygen atoms, forming a trigonal planar geometry. This structure plays a decisive role in the chemical and physical properties of carbonates. These minerals exhibit diverse properties, including variations in solubility, thermal stability, and reactivity. Studies in the 20th century indicated that carbonates of alkaline primarily exhibit two crystal structures: calcite (rhombohedral) and aragonite (orthorhombic).¹ Recent studies have extended this understanding by identifying double carbonate structures between alkaline earth and transition metal carbonates.²

Natural dolomites can be categorized in two groups such as dolomitic sediments settling at the bottom of the water column or as dolomite acting as cement within pre-existing gaps while secondary dolomites were produced through the process of replacing calcite or aragonite precursors (dolomitization).³ Mineral Ca based double carbonates are defined by the formula $\text{M}(\text{CO}_3)_2$, where M^{2+} denotes Ba, Mg, Sr and etc. In the carbonate structures mentioned, Ca-based double carbonates containing alkaline-earth and transition metals were targeted. These crystals attracted considerable interest in the field of materials science and engineering because of their fascinating characteristics and several potential uses. Dolomite is a distinctive carbonate mineral. While it frequently occurs in ancient platform carbonates, it is rarely found in Holocene sediments.⁴

Different characterization techniques such as X-ray diffraction (XRD) analysis provide valuable information on the crystal structure and composition of mineral carbonates⁵. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have provided detailed information on morphological properties.⁶ The findings have potential

applications that will enhance advances in the development of new materials for catalysis, energy storage, construction, ceramic production, environmental remediation and nuclear waste treatment. The aim of this thesis was to develop methods for chemical synthesis and characterization of calcium-based double carbonates at room temperature and atmospheric pressure. Cobalt (Co^{2+}), Magnesium (Mg^{2+}), for those the ionic radius was lower than that of Calcium (Ca^{2+}), and Strontium (Sr^{2+}) and Barium (Ba^{2+}) for those the ionic radius were higher than that of Ca^{2+} were investigated. Co^{2+} did not produce double carbonate, however, they oxidized to produce nano Co_3O_4 nano particles. Dolomite can be partially synthesized under mild conditions in our developed experiments. Both $\text{SrCa}(\text{CO}_3)_2$ and $\text{BaCa}(\text{CO}_3)_2$ could be synthesized with the developed methods. It was concluded that double carbonates could be synthesized under mild conditions with the alkali-earth metal elements having ionic radius higher than that of the Ca^{2+} ion.

CHAPTER 2

LITERATURE REVIEW

2.1. Definition and Properties of Calcium Based Double Carbonates

Dolomite ($\text{MgCa}(\text{CO}_3)_2$) is an idealized anhydrous carbonate mineral composed of calcium magnesium carbonate⁷ and it has several uses, including the production of refractory materials the neutralization of soil acidity in agriculture, the addition of minerals to food and medicine. The mineral dolomite was initially characterized in 1792 by the Swiss naturalist Nicolas de Saussure.⁸ One of the best ways to understand the crystal structure of dolomite is to compare it with CaCO_3 structure.

In Figure 1, the crystal structures of dolomite and CaCO_3 are shown in comparison and the differences are declared. Calcite has a crystal structure consisting of alternating layers of calcium cations (Ca^{2+}) and carbonate anions (CO_3^{2-}) aligned perpendicular to the c-axis. In this structure, the carbonate groups in adjacent layers are oriented in opposite directions.⁹ Dolomite crystallizes in the rhombohedral system, adopting a structure that is a modification of the calcite lattice. In dolomite, the unit cell comprises alternating layers of magnesium cations (Mg^{2+}) and calcium cations (Ca^{2+}), interleaved with carbonate anions (CO_3^{2-}). These carbonate ions are oriented perpendicularly to the c-axis. The ordered alternation of Ca^{2+} and Mg^{2+} in the dolomite lattice disrupts the c-glide plane symmetry inherent in the calcite structure, resulting in a unique deviation from the idealized calcite symmetry and giving rise to the characteristic dolomite crystal arrangement.¹⁰

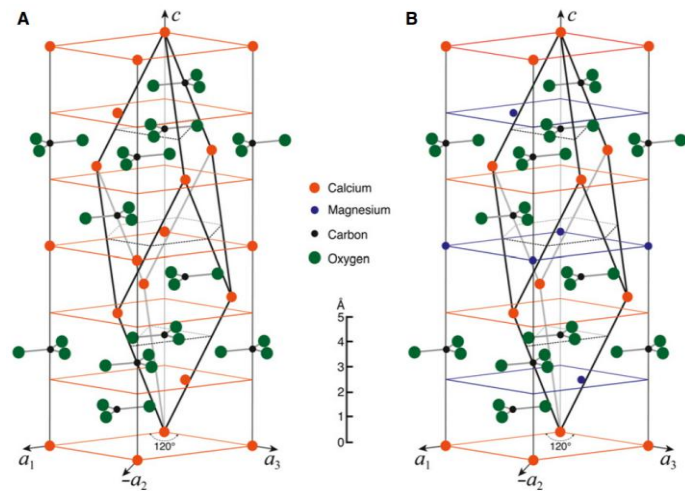


Figure 1. Crystal Structure of (a) calcite and (b) dolomite.¹⁰

The processes and rates of dolomite formation in natural environments, as well as its artificial synthesis in laboratory environments, continue to be discussed. To date, a substantial amount of research has been devoted to the synthesis of dolomite under laboratory conditions. The sparse occurrence of newly formed dolomite in natural settings stands in stark contrast to its prevalence in older marine sedimentary rocks, giving rise to enigma termed the dolomite problem.^{11–13} Dolomite observed to form in diverse environments, including lakes, on or beneath shallow seafloors, in areas of brine reflux, and throughout early to late stages of burial.¹⁴

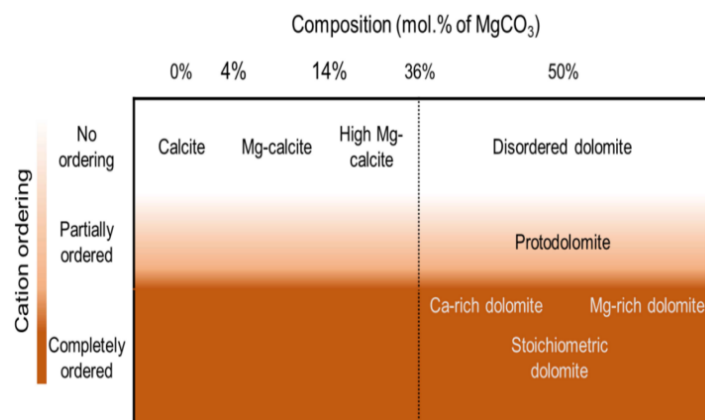


Figure 2. The different stages involved in the formation processes of the dolomite mineral, preceding or transforming the dolomite itself.¹⁵

Dolomite is divided into two groups according to its formation.¹⁶ Primary dolomite, which is precipitated from aqueous solution and is rare, and secondary dolomite, which is formed by the replacement of CaCO_3 in liquids carrying magnesium ions.¹⁷ Figure 2, dolomite and the phases preceding the formation of dolomite indicate the different stages involved in the growth processes of dolomite, which precede or transform dolomite itself. Gregg et al.¹⁰ uses this term to describe a component containing between 4-36% magnesium carbonate (MgCO_3), also protodolomite; a type of dolomite that also contains more than 36% magnesium carbonate but shows a partial cation ordering. Fang et al.¹⁸ defines the type of dolomite that contains more than 36% magnesium carbonate (MgCO_3) but does not show cation ordering as disordered dolomite. Sedimentary dolomite¹⁹, dispersed dolomite and high-magnesium calcite (HMC)^{20,21} are considered as precursor phases for sedimentary dolomite.

In moving from dolomite to other double carbonates, it is important to understand the similarities and differences in the formation, structure and industrial relevance of barium-containing calcium-based double carbonate, $\text{BaCa}(\text{CO}_3)_2$. The mineral was first discovered at the Brownley Hill lead mine near Alston, England, in 1834.²² Its initial description in scientific literature was provided by Johnson and Thomson.²³ $\text{BaCa}(\text{CO}_3)_2$ double carbonates naturally presents in three various polymorphic forms²⁴ which are monoclinic barytocalcite, alstonite and paralstonite.²⁵ The crystal structure of barytocalcite (Figure 3) was first proposed by Dickens et al.²⁶ The crystal structure of paralstonite was analyzed and introduced to the literature by Effenberger H.²⁷ Barytocalcite found to have a very regular structure in each chemical composition (1:1 ratio of barium and calcium carbonate) and this mineral undergoes a structural change (phase transition) when heated to 525°C. Spahr et al.²⁸ have obtained a fourth synthetic polymorph using precipitation, high-temperature reaction of the constituent carbonates and mechanochemical activation and describes C2 space group symmetry. This new polymorph was refined via Rietveld analysis of X-ray powder diffraction data and its structure is markedly different from the existing barytocalcite, paralstonite and alstonite polymorphs.

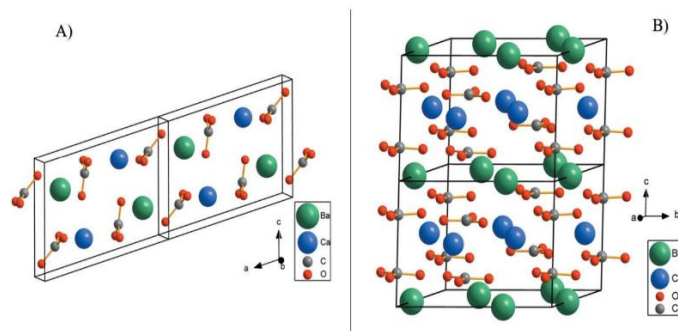


Figure 3. Crystal structure of $\text{BaCa}(\text{CO}_3)_2$ polymorphs. a) barytocalcite and b) paralstonite (P321 and Z3).^{26,27}

Alstonite has a more irregular structure and resembles aragonite.^{29,30} Bindi et al.³¹ recently proposed a new structural model based on the P31m space group with a unit cell volume of about 1614 Å³. This model allows us to better understand the structural complexity of alstonite by emphasizing the specific arrangements of Ba^{2+} and Ca^{2+} within the carbonate layers. The coordination of Ba^{2+} and Ca^{2+} ions contribute to the unique properties of the mineral. Ba^{2+} generally shows ten-fold coordination, while Ca^{2+} exhibits a more variable coordination environment. The carbonate groups in alstonite are organized in layers where Ba^{2+} and Ca^{2+} ions form a pseudo-hexagonal arrangement. This structural formation is important for the stability and properties of alstonite. Furthermore, the twinning of alstonite, often described as hidden complex twinning, adds additional complexity to its crystal structure, challenging the conventional understanding of carbonate minerals.

Recent studies using advanced crystallographic techniques have provided an understanding of the lattice parameters and atomic positions of alstonite, confirming the complex nature of its crystal structure. This information is critical for potential industrial applications and further research on similar carbonate minerals. The refinement and experimental data confirm that the P31m space group model is a reliable representative of the crystal structure of alstonite, providing good agreement with the observed physical and chemical properties.

Kutnohorite is a dolomite-type double carbonate mineral with the general formula $\text{CaMn}(\text{CO}_3)_2$, medium density and vivid orange-red cathodoluminescence color.³² This double carbonate was proposed by Bukowsky in 1901 as a Mn-containing double carbonate member of the dolomite group. The presence of kutnohorite in various geological conditions provide a

good comparison and model to investigate dolomite isomorphism. This mineral consists of coarse-grained aggregates. The grains can often grow up to 3 cm in size and have slightly curved fracture surfaces, showing a pearly luster. In thin sections, the large grains appear wavy and consist of small grains connected to each other in a lobate shape.^{33,34}

These small grains have only slightly different crystal orientations, forming the micro block structure of the whole grain. In addition, in some sections recrystallized carbonate veins and edges can also be observed. Suitable sections show a distinct pleochroism ranging from colorless to light pink, gray.³⁵ Figure 4 shows the crystal structure of kutnohorite.³¹ In the structure of double carbonate minerals, the arrangement between layers of Ca^{2+} and other cations (Mg^{2+} , Fe^{2+} , Mn^{2+} and Zn^{2+}) is more regular than in calcite. This causes a decrease in symmetry compared to the calcite structure. Irregular structures of kutnohorite at low temperatures have been reported. It shows that the large ionic diameter of Mn^{2+} causes distortion of calcium and manganese octahedrons in dolomites, which may affect the low sorting potential.³⁶

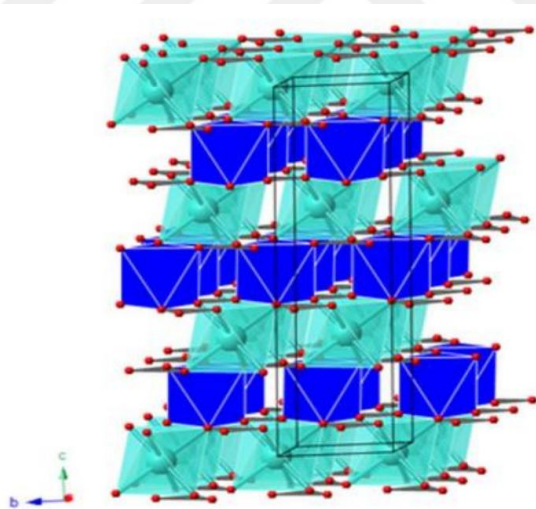


Figure 4. Crystal structure of kutnohorite.³¹

Ankerite is an iron carbonate mineral commonly found in soil and a mineral from the dolomite group with a trigonal carbonate structure³⁷ (Figure 5) that is described by the formula $\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$.³⁸ This mineral is found in many clay-containing matrices and, when

dissolved, leads to the formation of another iron mineral called goethite (α -FeO(OH)).

Ankerite ($\text{CaFe}(\text{CO}_3)_2$) has the same crystal structure as dolomite ($\text{CaMg}(\text{CO}_3)_2$) and is considered a member of the dolomite mineral group because it shares many similarities with siderite (FeCO_3).³⁸ In a review of the existing literature, a characterization and mineralogical change study on iron/bentonite interaction at 80°C and in a seawater environment was conducted and because of the study, siderite and ankerite were identified as iron corrosion products formed because of iron exchanges.³⁹

Rosenberg et al.⁴⁰ describes a hierarchy of stabilities, but the relative stabilities cannot be solely attributed to octahedral distortion.

$$\text{Mg} \gg \text{Mn} > \text{Zn} > \text{Fe} > \text{Co} > \text{Ni} \gg \text{Cu} \quad (1)$$

Octahedral distortion may explain the instability of $\text{CaFe}(\text{CO}_3)_2$. It may explain the differences that make solid solutions of calcite (CaCO_3) and siderite (FeCO_3) energetically more stable over ankerite containing more iron than about 70 mol% in $\text{CaFe}(\text{CO}_3)_2$. Further work on Fe-containing carbonates is needed to solve this long-standing problem⁴¹. Iron-rich ankerite is enriched with higher amounts of Fe^{2+} than Mn^{2+} and Mg^{2+} and it could be called ferroan dolomite.⁴² Ferroan dolomite, thus pure iron analog of dolomite is understood with less information and more theoretical modeling because it is a non-naturally occurring and non-synthesized mineral.⁴³ However, according to Chuliá-Jordán, R et al.⁴² revealed only a disordered structure, and thermodynamic models predict that at temperatures below 450°C, ordered $\text{CaFe}(\text{CO}_3)_2$ can exist in a stable phase.

Dolomite's one of the natural analog is minrecordite ($\text{CaZn}(\text{CO}_3)_2$).⁴⁴⁻⁴⁶ Minrecordite is a rare double carbonate in the nature. This mineral was thought to be unstable in nature, however, Carlo G. Garavelli et al.⁴⁷ found it in association with zinc-containing dolomites, thus proving its existence in nature. Two different types of minrecordite variants (Type A and Type B) identified. Type A-Pure minrecordite, contains Ca^{2+} and Zn^{2+} and varies with small amounts of Mg^{2+} , Fe^{2+} and Mn^{2+} . Type B-Magnesian minrecordite, contains Mg^{2+} , cell parameters are large, density is low and refractive index is low.

The major differences between these two variants are the color, shape, size and luster of the crystals. Type A has larger and more distinct crystals, while type B has a more opalescent appearance.⁴⁷ Liu et al.⁴⁸ calculated phase diagrams to understand the conditions

under which zinc-containing carbonate minerals such as minrecordite can form and found that minrecordite has a metastable structure and a positive ΔE_f value, which proves that the minrecordite structure is not stable but can exist under certain conditions.

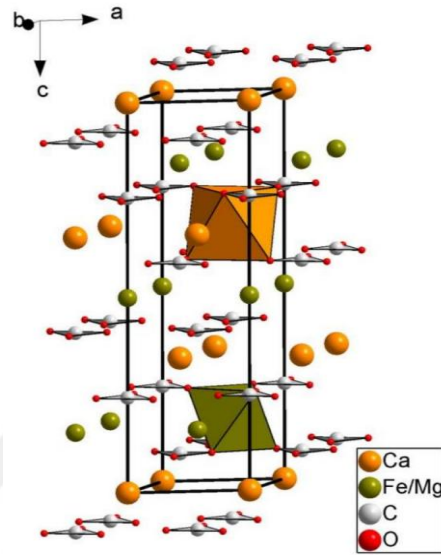


Figure 5. Crystal structure of iron-rich $\text{CaFe}(\text{CO}_3)_2$.⁴⁰

2.2. Overview of Chemical Synthesis Methods

2.2.1 Reported Synthesis Approaches for $\text{MgCa}(\text{CO}_3)_2$

Synthesis of dolomite ($\text{MgCa}(\text{CO}_3)_2$) under mild conditions (at low temperature and low pressure), which is one of the biggest challenges in dolomite synthesis. It is unsuccessful in experiments for many years leading to the production of aragonite and calcite.^{9,18}

Even under supersaturation conditions ($\text{SI} > 0$) in solution, experimental studies have shown that more stable carbonate phases such as aragonite and calcite are precipitated instead of dolomite. For instance, in a long-term series of 43 experiments by Land (1998) starting from 1968 and lasted 32 years in total (Figure 6), natural carbonates were continuously vibrated in 200 ml of pure distilled water in 250 ml Erlenmeyer flasks. In Figure 6, there is a significant increase in the Mg^{2+} content in the solution. This increase is

attributed to the release of extra Mg^{2+} into the solution because of slight evaporation occurring during the experiment, leading to calcite precipitation. As time progresses, a decrease in the Mg^{2+} content is observed. This decrease is due to the precipitation of the Mg-silicate phase called ‘sepiolite’ in solution. The precipitation of sepiolite causes the ratio to decrease by taking Mg out of the solution. The horizontal line on the graph represents the equilibrium value at which the solution composition is assumed to be in equilibrium with calcite, amorphous silica and sepiolite precipitates.⁴⁹

One of the main reasons for this failure is the strong interaction of the Mg^{2+} ion with water and its high hydration energy. The studies of Noyes in 1962 revealed that Mg^{2+} ion has higher enthalpy values compared to other binary charged ions and forms a high hydration level by binding strongly with water molecules. This situation prevents the formation of dolomite crystals by creating additional kinetic barriers in the partial dehydration stage required for crystallization of Mg^{2+} ion.^{50,51}

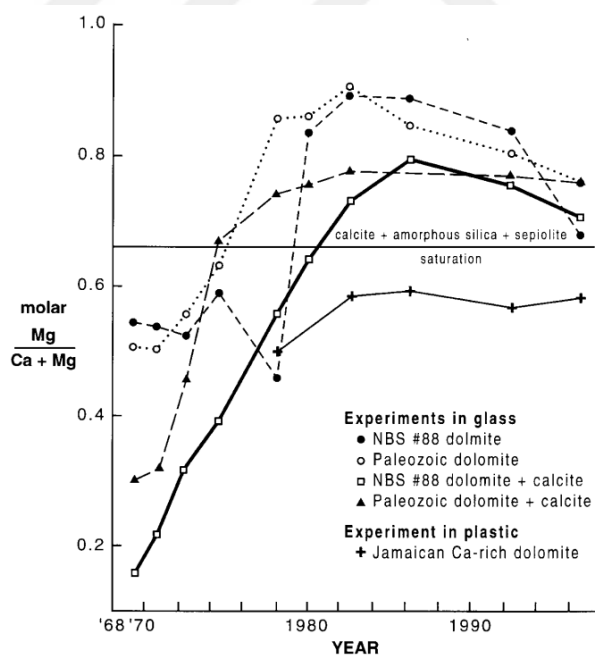


Figure 6. Change in mol $\text{Mg}^{2+}/(\text{Mg}^{2+} + \text{Ca}^{2+})$ ratio with time in dolomite experiments and related solution reactions.⁴⁹

Recent experimental studies have tried to elucidate the formation mechanism of such phases by examining in detail the solubility product and growth kinetics of hydro magnesite,

one of the hydrated Mg carbonates in solution. The studies of Gautier et al.⁵¹ showed that the growth kinetics of hydrated Mg carbonates depend on the dehydration process of Mg^{2+} ion in experiments carried out at temperatures between 25-75°C, which supports the difficulties in synthesizing anhydrite phases such as dolomite under low temperature conditions.

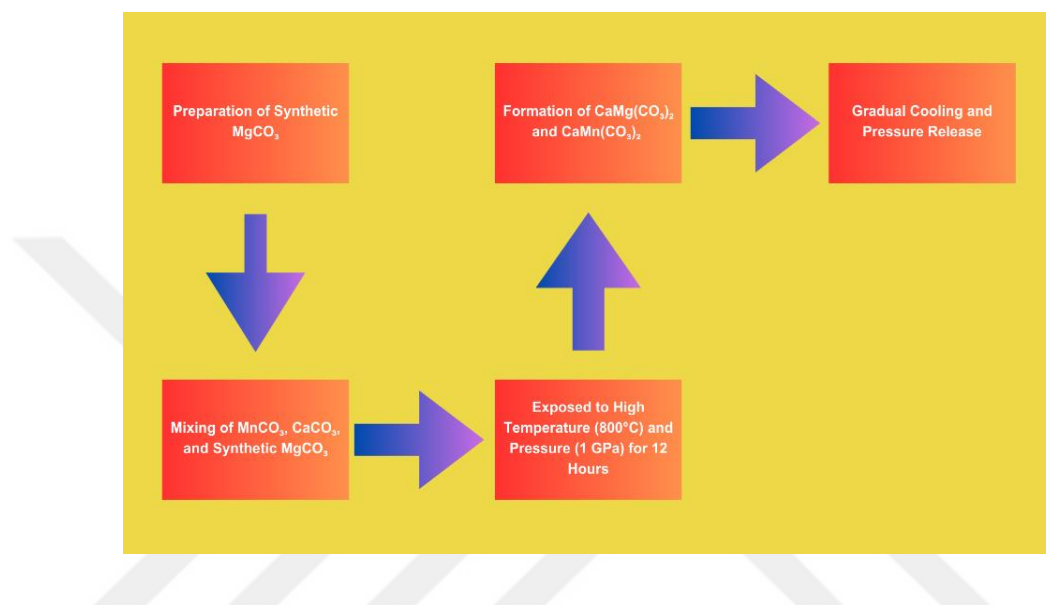


Figure 7. Flowchart of the synthesis method at high temperature and pressure for $\text{MgCa}(\text{CO}_3)_2$ and $\text{MnCa}(\text{CO}_3)_2$.⁵²

Montes-Hernandez et al.⁵³ carried out a study to determine the factors that promote the formation of dolomite at low temperature by investigating the synthesis of dolomite at different temperature and solution. In this study, calcite and MgCO_3 (magnesite) were used as starting materials. Calcite was prepared as nano-sized (<100 nm) and submicrometric (<1 μm) particles by dissolution of portlandite ($\text{Ca}(\text{OH})_2$). Magnesite was dissolved in $\text{Mg}(\text{OH})_2$ (synthetic brucite) solution and reacted with CO_2 to obtain dypingite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$). In the study, dolomitization experiments were carried out at five different temperatures, 50, 75, 100, 150 and 200° C, and the duration of each experiment was determined as three months. Alkaline solutions with high carbonate content were used in the experiments. CO_2 in the solution was prepared by adding to 2M NaOH solution. The experiments were carried out in two different solutions: High carbonate alkaline solution and pure water.

The results of the study show that temperature and carbonate alkalinity are critical factors in dolomite formation. High carbonate content, especially from 100° C, was determined as a promoting factor for dolomite precipitation. This study provides a new insight into the kinetic mechanisms of dolomite synthesis under hydrothermal conditions and provides important data for understanding dolomite formation in natural systems. However, the long duration of the experiment and the limited ability to synthesize dolomite at low temperatures are factors that complicate the applicability of the method on an industrial scale.

Table 1. Amounts of solvents and reagents used in the experiment.⁵³

Solvents and reagents	
250 ml	Purity Water
0.25 mol	NaOH
0.25 mol	MgCl ₂ ·6H ₂ O
0.25	Ca(OH) ₂

Unlike the previous study, it was conducted at a higher temperature and in a shorter time Montes-Hernandez et al.⁵⁴ the solvents were added together with the reagents to a Hastelloy C22 autoclave with an internal volume of 0.6 L and continuous mechanical stirring at 400 rpm. The temperature suddenly increased to 26°C, which is due to the dissolution of NaOH. Then, 0.62 mol CO₂ is added to the reaction medium under 44 bar pressure. The decrease in pressure and increase in temperature is due to the exothermic reaction. After 1 hour of reaction, the temperature rose to 29°C. After 24 hours of reaction, heated aging steps to 200°C, 250°C, and 300°C were applied. At each temperature condition, sampling was taken out at intervals of 1, 3, 5, 8, 24 and 48 hours. The duration of the experiment at 200°C was extended up to 72 hours. The collected samples were cooled using water circulation, followed by centrifugation at 12,000 rpm for 30 min. The supernatant solutions were decanted, and the solid product was subjected to redispersion and centrifugation twice to remove soluble salts. The solid product was then dried at 90°C for 24 hours. The dried product was stored in plastic vials and prepared for characterization.

According to Land L.⁴⁹, there may be a yet unidentified catalyst. Fang et al.¹⁸ reported, recent experiments for at irregular dolomite precipitation at lower temperature with

the presence of the catalysts used.

Nowadays, many successful synthesis attempts have been made to precipitate dolomite at lower temperatures with the presence of catalysts in the system.⁵⁵ The catalysts used have low dipole moment or OH⁻ groups to form hydrogen bonds with CO₃²⁻ on carbonate surfaces, e.g. polysaccharides, dioxane, dissolved sulfides, EPSs and aqueous Si(OH)₄.^{56,57} It has been shown that the main factor in dolomite growth at low temperature is not only the hydration problem but also cation properties and disorder in lattice confinement.^{58,59}

Matsumoto et al.⁶⁰ was developed microbubble injection technique method, to recover Ca²⁺ and Mg²⁺ ions from seawater and convert it into an alternative mandate. The importance of this method is to find a way to crystallize CaMg(CO₃)₂ under low temperature and pressure conditions. As an alternative to traditional high temperature and pressure methods, this method offers a more economical and environmentally friendly solution. Therefore, it stands out as an innovative approach for the recovery and upgrading of Ca²⁺ and Mg²⁺ contained in concentrated brine originating from seawater. In this study, microbubbles with a diameter less than <<50 μm were used to accelerate mass transfer and reactive sorption and thus concentrate on high reaction rate, high efficiency and lower energy consumption. This allows the synthesis of dolomite particles, which are double carbonate with a higher Mg²⁺/Ca²⁺ ratio.⁶¹

One of the by-products of salt production in Japan is brine, which can be used for dolomite synthesis. It is very important to understand the content of the brine as it is the chlorite salts of the metals Mg²⁺, Ca²⁺ and Na⁺ and is the factor that affects the quality of the final product.⁶¹

In the experiment, microbubbles with an average bubble size (d_{bbl}) of 40 μm in diameter were used. Bubbles of other sizes d_{bbl} =200, 300, 800, 2000 μm were produced with a dispersive type of generator. Bubble diameters (d_{bbl}) were measured using a laser particle size analyzer and a digital microscope. Managing bubble generation methods and experimental conditions is critical to improve the efficiency of the crystallization process. Throughout the experiment, CO₂ bubbles of various sizes were continuously introduced into 300 mL of concentrated brine. A thermostat was used to control the temperature of the reaction, and the temperature was maintained at 293 K. NaOH was added to keep the pH constant (pH=6.8). After a certain reaction time (up to 120 min), the mixture was filtered. The solid products were washed, dried at 373 K and analyzed.⁶²

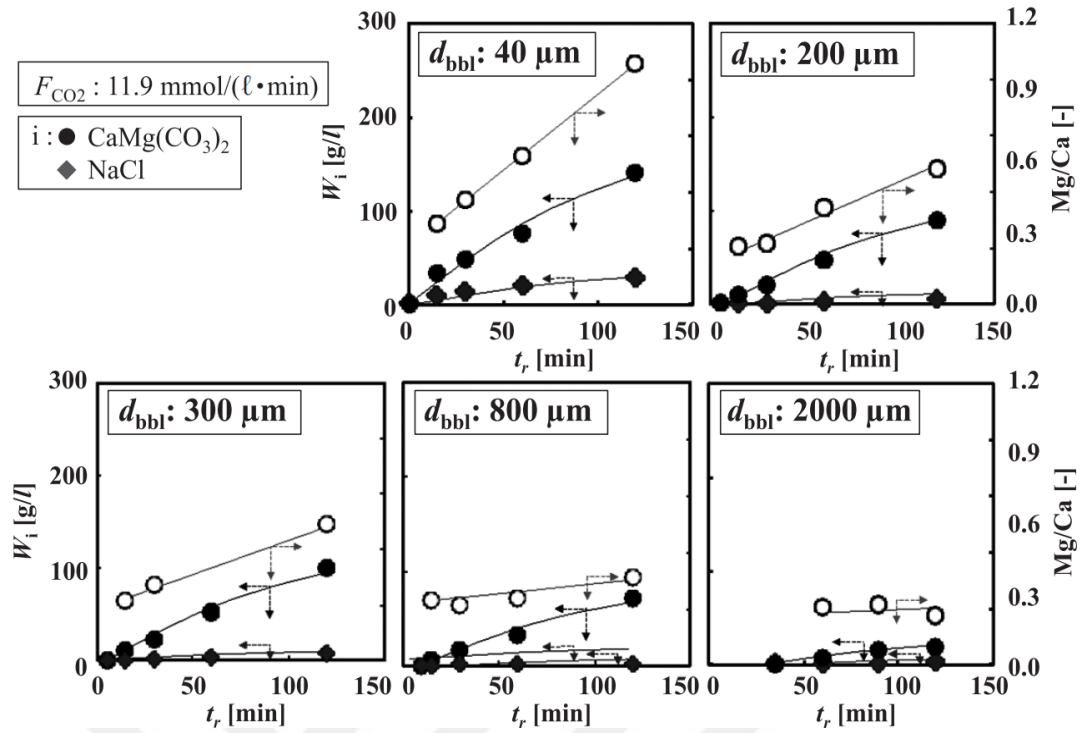


Figure 8. Time variations on $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio and product weight.⁶⁰

Figure 8, it was reported in the produced weight of $\text{CaMg}(\text{CO}_3)_2$ generally increases with reaction time for all bubble sizes. Smaller microbubble sizes result in higher produced weights compared to larger microbubble sizes. The formation time of crystalline nuclei decreased as d_{bbl} became smaller. This suggests that smaller microbubbles improve the crystallization process due to increased surface area for mass transfer and more efficient gas-liquid contact.⁵⁴ As for the Mg/Ca ratio, the ratio increases from larger microbubbles to smaller microbubbles ($2000 > 800 > 300 > 200 > 40 \mu\text{m}$). It can be concluded that the effect of CO_2 microbubbles on the crystallization of dolomite depends on the size of the microbubble. Smaller microbubbles (40 and $200 \mu\text{m}$) seem to increase both the crystallization rate and the selectivity towards magnesium-rich phases. However, the decrease in both weight and $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio with increasing bubble size can be attributed to lower mass transfer rates and less effective mixing, resulting in less uniform crystal growth and lower Mg incorporation.⁶²

Sono chemical synthesis method developed by Kamei et al.⁶³ used K-bittern as a raw material in their study, likely due to its rich mineral content. The mineral composition of K-bittern is provided in Table 2. In the synthesis process described by Kamei et al. Na_2CO_3

and NaHCO_3 solutions were added to removed-K bittern, and ultrasonic irradiation was applied. The reaction conditions were maintained at 25°C to 65°C without cooling, lasting 20 minutes at 20 kHz and 40 W. After the reaction, the samples were filtered, washed, and dried.

Table 2. Concentrations of the ions in removed-K bittern.⁶³

Ions	Concentrations ($\text{mmol}\cdot\text{dm}^{-3}$)
Ca^{2+}	670
Mg^{2+}	2,100
K^+	100
Na^+	1,100
SO_4^{2-}	4
Cl^-	6,300

2.2.2 Reported Synthesis Approaches for $\text{BaCa}(\text{CO}_3)_2$

Different methods have been tried in the synthesis of $\text{BaCa}(\text{CO}_3)_2$. For instance, low-temperature precipitation, mechanosynthesis and high temperature reactive sintering are depicted in Figure 9. Massoni et al.⁶⁴ carried out precipitation experiments by introducing $\text{Ba}^{2+}/\text{Ca}^{2+}$ salts in the form of nitrate (NO_3^-) or chloride (Cl^-) into Na_2CO_3 solution at room temperature and investigated the yield of $\text{BaCa}(\text{CO}_3)_2$ by mechanosynthesis and high temperature sintering.

Similarly, Spahr et al.²⁸ also considered precipitation, mechanosynthesis and reactive sintering methods; however, they reported that a new polymorph called ‘C2 phase’ can occur, especially with the precipitation or high temperature approach, whereas monoclinic barytocalcite is formed by hydrothermal synthesis. Therefore, although both groups apply the same general synthesis strategies, the difference in parameters such as experimental conditions and cooling rate significantly affects the resulting $\text{BaCa}(\text{CO}_3)_2$ polymorph and crystal structure.

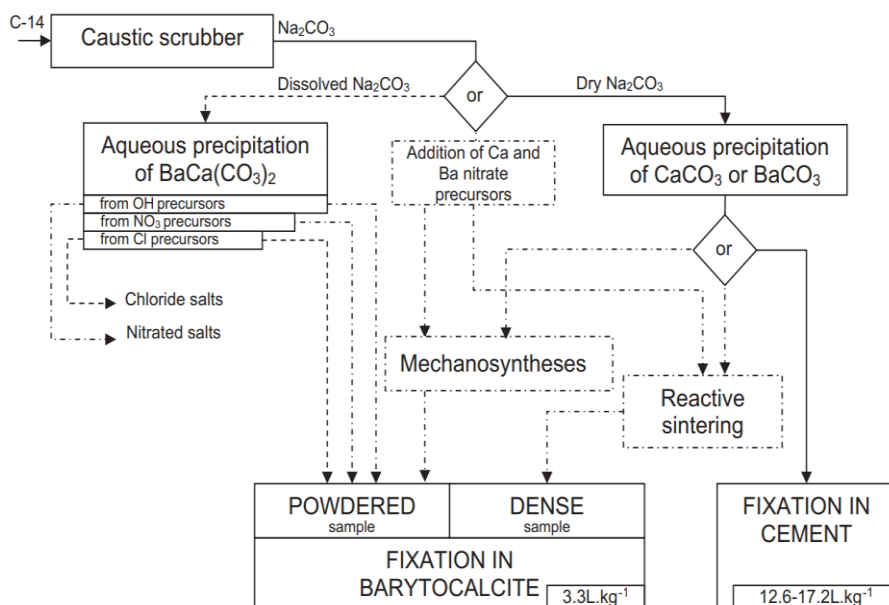


Figure 9. Schematic representation shows different routes of synthesis of $\text{BaCa}(\text{CO}_3)_2$.⁶⁴

These results showed that although similar general synthesis strategies were applied in both studies, the difference in experimental parameters can seriously affect both the crystal structure of $\text{BaCa}(\text{CO}_3)_2$ and the choice of polymorph. Low-temperature methods can often produce finer-grained or alternating phases, whereas reactive sintering at high temperature both increases the grain density and alters the probability of the appearance of new polymorphs or classical barytocalcite depending on the conditions.

2.2.3 Reported Synthesis Approaches for $\text{MnCa}(\text{CO}_3)_2$

Li et al.⁵² synthesized kutnahorite ($\text{CaMn}(\text{CO}_3)_2$) under high pressure and temperature conditions (Figure 7). Manganese carbonate (MnCO_3), CaCO_3 and synthetic MgCO_3 were used as starting materials. Synthetic MgCO_3 was obtained by first heating $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (magnesium oxalate dihydrate) at 600°C , 1 GPa for half an hour. MnCO_3 and CaCO_3 (or MgCO_3) were then mixed in a 1:1 molar ratio and kept at 800°C and 1 GPa for 12 hours. These high temperature and pressure conditions promote the formation of double carbonates such as $\text{CaMg}(\text{CO}_3)_2$ and $\text{CaMn}(\text{CO}_3)_2$. Once the reaction was complete,

the pressure and temperature were slowly reduced to maintain the integrity of the sample.

Win⁶⁵ reported the synthesis of 20% mol Mn²⁺ doped CaCO₃ ceramics. CaCO₃ and MnO₂ were used as starting materials. The aim was to synthesize Ca_{0.80}Mn_{0.20}(CO₃)₂ thin film by thermal diffusion method on n-Si substrate. The starting materials (CaCO₃ and MnO₂) were powdered and mixed according to the stoichiometric formula. These homogeneous powders were annealed and sintered at 1000°C for 1 hour. Then the sintered Ca_{0.80}Mn_{0.20}(CO₃)₂ was ground in an agate motor for 10 hours to homogenize it.

Massoni et al.⁶⁶ employed both low-temperature precipitation and high-temperature reactive sintering approaches for the synthesis of MnCa(CO₃)₂, in a manner analogous to their work on BaCa(CO₃)₂. The low temperature method involves the controlled addition of salts containing Mn²⁺ and Ca²⁺ to Na₂CO₃ solution at room temperature. The solid formed at the end of the reaction is obtained by filtration and drying. In addition to, MnCa(CO₃)₂ can also be obtained by heat treatment of carbonate precursors such as MnCO₃ and CaCO₃ mixed in the solid state in the high temperature approach (600-800°C). Massoni et al. (2015) also investigated the densification of the obtained powdered MnCa(CO₃)₂ by techniques such as spark plasma sintering and showed that sintering can proceed simultaneously with decarbonation, but this loss can be limited when appropriate pressure is applied (40-90 MPa).

2.2.4 Reported Synthesis Approaches for FeCa(CO₃)₂

Goldsmith et al.⁶⁷ and Rosenberg P. E.⁶⁸ studies of the ankerite mineral (FeCa(CO₃)₂) under high temperature and pressure conditions have demonstrated that carbonate solutions do not form complete solid solutions. Specifically, Goldsmith et al. aimed to determine the stability of CaFe(CO₃)₂ in the calcite structure and suggested that this solution may be stable above 800°C and under a pressure of 15 kbar, but becomes unstable at lower temperatures (300°C). Following the work of Goldsmith et al. and Rosenberg et al. explored the synthesis of ankerite under high temperature and pressure conditions and found that carbonate solutions do not form complete solid solutions, the work of Morlidge et al.⁶⁹ built on these findings. The recent study provides more detailed information on the synthesis conditions and structural properties of ankerite and related minerals than ever before. Study conducted by Morlidge et al. provides information about the synthesis conditions and structural properties of various minerals. When the details for

the synthesis of ankerite are investigated, it is seen that the synthesis is synthesized under high pressure and temperature conditions. As starting materials, CaCO_3 (aragonite) and FeCO_3 (siderite) minerals were mixed in stoichiometric ratios. This mixture was kept in a piston-cylinder apparatus at a pressure of 1.5 GPa and a very high temperature of 850°C for 24 to 48 hours. The mixture was then placed in a graphite capsule. The purpose of using a graphite capsule is to minimize side reactions and to ensure oxygen evolution. The particles obtained because of the synthesis were characterized by appropriate characterization techniques. The synthesis of $\text{FeCa}(\text{CO}_3)_2$ usually requires high pressure and temperature, but is experimentally difficult to observe as completely stable; in practice it is found as disordered ankerite or as mixtures containing a little $\text{Mg}^{2+}/\text{Mn}^{2+}$.

2.2.5 Reported Synthesis Approaches for $\text{SrCa}(\text{CO}_3)_2$

Studies on the synthesis of $\text{SrCa}(\text{CO}_3)_2$ are quite limited according to the literature. A study by Terada et al.¹ focused on the synthesis of barium and strontium double carbonates by precipitation. Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) and calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) are dissolved in water, followed by the addition of sodium carbonate (Na_2CO_3). The reaction proceeds under continuous stirring to ensure homogeneous mixing and the formation of a double carbonate precipitate. The chemical reaction can be represented as follows:



The precipitate obtained at the end of the reaction is filtered, washed and dried to obtain the solid precipitate after washing. According to the experimental report, in $\text{SrCa}(\text{CO}_3)_2$ double carbonate, precipitated samples containing SrCO_3 with mole percentages below 40% usually occur together with solid solutions of SrCO_3 and aragonite.

2.2.6 Reported Synthesis Approaches for $\text{ZnCa}(\text{CO}_3)_2$

Despite several experimental attempts, minrecordite ($\text{CaZn}(\text{CO}_3)_2$) could not be synthesized under laboratory conditions, a situation previously reported by Fazeli et al.⁷⁰

2.3. Investigation of Characterization Techniques

Characterization of double carbonates is critical for understanding their structure, characteristics, and uses. It allows for the identification of their structure, phases, and chemical, and mechanical properties, which aids in optimizing synthesis processes and analyzing environmental effects.⁷¹ Characterization also adds to the understanding of geological importance, such as formation mechanisms and the potential for carbon dioxide sequestration.⁷²

Since the discovery of X-rays significant innovations have been made across all scientific disciplines. X-ray-based experimental methods used in materials science and engineering.⁷³ X-ray diffraction (XRD) is a successful method used to determine the microstructural crystalline properties and atomic arrangement within the crystals^{74,75}. A 3-dimensional (3D) image of the electron density in a nanoparticle crystal is obtained in terms of the diffracted angle and the intensity of diffracted beams.⁷⁶

XRD peaks and Lattice Parameter data of $\text{BaCa}(\text{CO}_3)_2$ ⁷⁷, $\text{MnCa}(\text{CO}_3)_2$ ⁷⁸, $\text{MgCa}(\text{CO}_3)_2$, and $\text{FeCa}(\text{CO}_3)_2$ ⁷⁹ obtained from the American Mineralogist Crystal Structure Database (AMCSD) shown in Table 3.

Table 3. Barytocalcite, kutnohorite, dolomite and ankerite lattice parameters, respectively.^{77–}

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Lattice Parameters	Lattice Parameters	Lattice Parameters	Lattice Parameters
BaCa(CO ₃) ₂	MnCa(CO ₃) ₂	MgCa(CO ₃) ₂	FeCa(CO ₃) ₂
a = 8.1118(6) Å	a = 4.9171(6) Å	a = 4.8220(1) Å	a = 4.8270(1) Å
b = 5.2386(3) Å	b = 4.9171(6) Å	b = 4.8220(1) Å	b = 4.8270(1) Å
c = 6.5519(4) Å	c = 16.607(4) Å	c = 16.0995(9) Å	c = 16.1475(8) Å

Scanning electron microscopy (SEM) is used to image the surface morphology and microstructure of organic and inorganic materials on the nanometers(nm) and micrometers (µm) scale at high resolution. SEM can reach 1000000x magnification and depicts very precise images of even materials with complex content.⁸⁰ In the literature, various SEM images of many double carbonates, both in pure form and in different forms reported.

2.3.1. Characterization of MgCa(CO₃)₂

Peaks reported for dolomite are illustrated in Figure 10. In the Kulikova et al.⁸¹ report, it was determined that the initial dolomite sample consists of 3 main phases: dolomite, calcite and periclase. Dolomite (a) [CaMg(CO₃)₂, 2.88, 2.19, 1.79 Å] calcite (b) [CaCO₃, 3.04, 2.28, 2.09 Å] and periclase (c) [MgO, 2.11, 1.49 Å]. When dolomite is calcined at 720 °C, MgCO₃ and magnesium oxide (MgO) are transformed and CaCO₃ is partially transformed into calcium oxide (CaO). When the sample is calcined at 750 °C, both MgCO₃ and CaCO₃ are completely transformed into MgO and CaO.

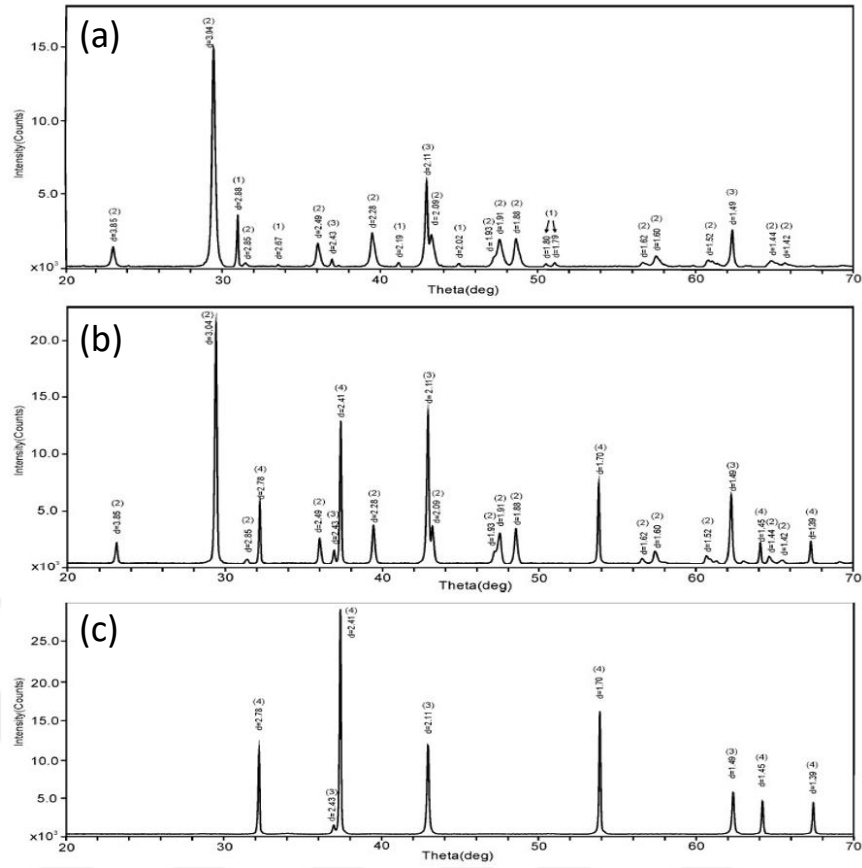


Figure 10. XRD peaks of a) dolomite, b) calcite and c) periclase.⁸¹

Zhang et al.⁵⁷ published a report presenting XRD results obtained from an attempt to synthesize dolomite under mild conditions using a polysaccharide-based catalyst. The diffraction peaks of synthetic carbonates produced in the presence of carboxymethyl cellulose are systematically shifted to higher angles. This slip is due to the reduction of lattice parameters resulting from the integration of Mg^{2+} into the crystal lattice.

In addition, XRD patterns of irregular dolomite obtained by precipitation synthesis of irregular dolomite using another catalyst and XRD patterns of irregular dolomites formed at different pH values (8; 8,5; 9) using sulfide catalyst are discussed comparatively (Figure 11, a). XRD peaks of irregular dolomite and aragonite crystals are shown and the difference between a) final pH of 9.0, b) final pH of 8.5 (reduced by adding HCl) final pH of 8.0. Based on the data reported in the literature, XRD analysis of dolomite shows that the main peaks are observed at 2.88 Å, 2.19 Å, and 1.79 Å, and that the d (104) value varies between 2.91 Å and 2.94 Å depending on the $MgCO_3$ content.⁸²

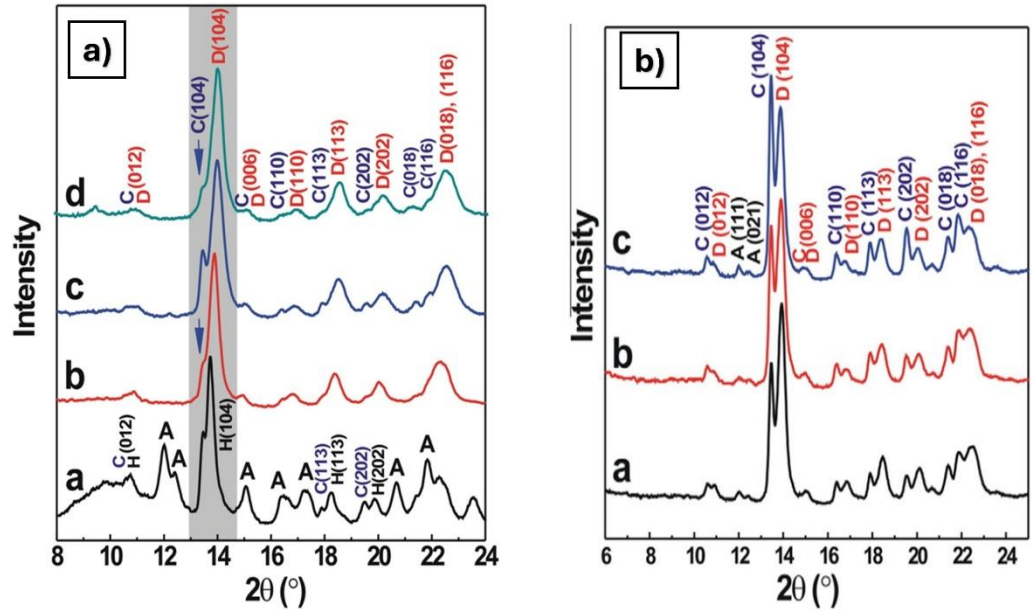


Figure 11. XRD models of dolomite synthesized using catalysis.⁵⁷

The mineral dolomite occurs as particles with irregular morphology and therefore does not have a distinct crystal morphology. Within the scope of Figure 12, SEM images of dolomite crystals of different sizes and various formations are presented. Based on the 100 μ m and 1 μ m morphology of dolomite (a,b) in the paper published by Pesonen et al.,⁸³ it is observed that dolomite crystals are mostly irregular in shape. This irregular structure is usually due to variations in crystal growth during the formation process of dolomite. When the image is zoomed in (1 μ m scale), it is seen that the dolomite has an irregular and layered structure on the surface.

In the study executed by Rodriguez-Blanco et al.⁸⁴ the precursor phase of dolomite, protodolomite (c,d), was critically analyzed through SEM images, playing a critical role in deepening our understanding of the irregular morphological structure of dolomite crystals. The particles appear to be interconnected and exhibit a rough surface texture characteristic of the first stage of crystal growth of dolomite. Since protodolomite is known to have a spherical morphology and a less organized structure than dolomite, the spherical structures seen are indicative of early-stage mineral formation.

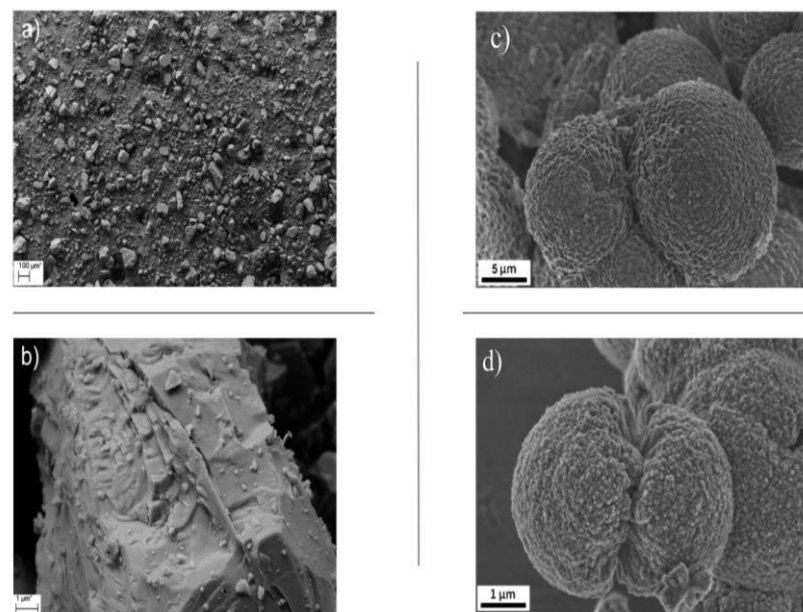


Figure 12. SEM images of dolomite.^{83,84}

2.3.2. Characterization of $\text{BaCa}(\text{CO}_3)_2$

Barytocalcite, paralstonite, and alstonite are the three polymorphs of $\text{BaCa}(\text{CO}_3)_2$ that have been discovered thus far. The crystal structure data of these compounds were given in Table 4.²⁴

Table 4. Data of crystal structure for $\text{BaCa}(\text{CO}_3)_2$ polymorphs.²⁴

	Barytocalcite†	Paralstonite‡	Alstonite§
Crystal system	Monoclinic	Trigonal	Triclinic
Space group	$P2_1/m$	$P321$	$C1$ or $C\bar{1}$
a (Å)	8.092 (1)	8.692 (3)	30.14
b (Å)	5.2344 (6)	8.692 (3)	17.40
c (Å)	6.544 (1)	6.148 (4)	6.12
α (°)	90	90	90
β (°)	106.05 (1)	90	90
γ (°)	90	120	90
Z	2	3	24
V (Å ³)	266.4	402.26	3161.59
ρ (g cm ⁻³)	3.71	3.68	3.69

$\text{BaCa}(\text{CO}_3)_2$ has different multiple polymorphic forms. Chuliá-Jordán et al.²⁴ report compared the performance of two different structural models (P31m and P321) to determine the crystal structure of the mineral alstonite (Figure 13, a) and the XRD results of a powder sample of alstonite under different pressures (Figure 13, b) were compared. Both structural models show a similar peak over the entire 2θ range. However, a significant difference is observed in the $29\text{--}32^\circ$ range (with Cu $K\alpha$ wavelength). Zone marked with a green rectangle the P321 model better explains the 31.6° peak in the experimental diffraction pattern. In the XRD patterns obtained under high pressure, we see that the diffraction peaks shift to higher angles under pressure. The reason for this is that as the pressure increases, the distance between atoms decreases, which causes the diffraction angles to increase. It was observed that alstonite remained stable up to 19 GPa.

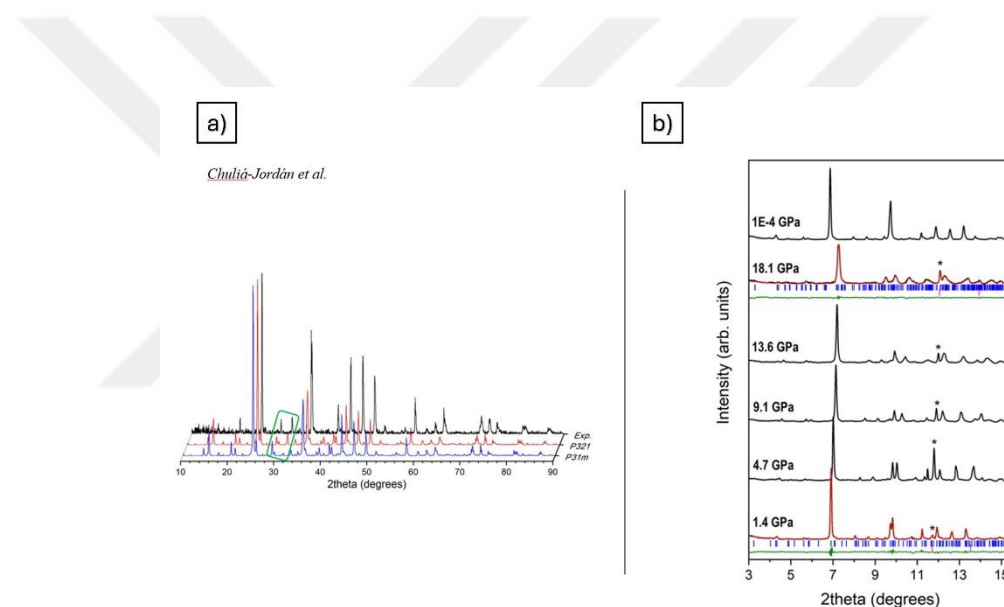


Figure 13. XRD patterns of alstonite.²⁴

As previously mentioned, Spahr et al.²⁸ succeeded in synthesizing a new synthetic barytocalcite with a different morphology from the 3 known types of barytocalcite and named it the C2 phase. Analysis by XRD and Rietveld refining confirmed that the C2 phase has a different crystal structure. Comparative XRD results of barytocalcite and C2 phase are reported in Figure 14, (a). There are many reflection peaks in the range of $30\text{--}40^\circ$ 2θ angles under Cu $K1$ radiation, referring to the reflection peaks of (100) 11.33° , (001) 14.05° and (101) 15.42° of barytocalcite. Based on the results of the precipitation experiments, it is reported that no matter which method is used, the product obtained is a single-phase C2 phase. However, the precipitation with nitrates gave the best results in terms of crystallinity and

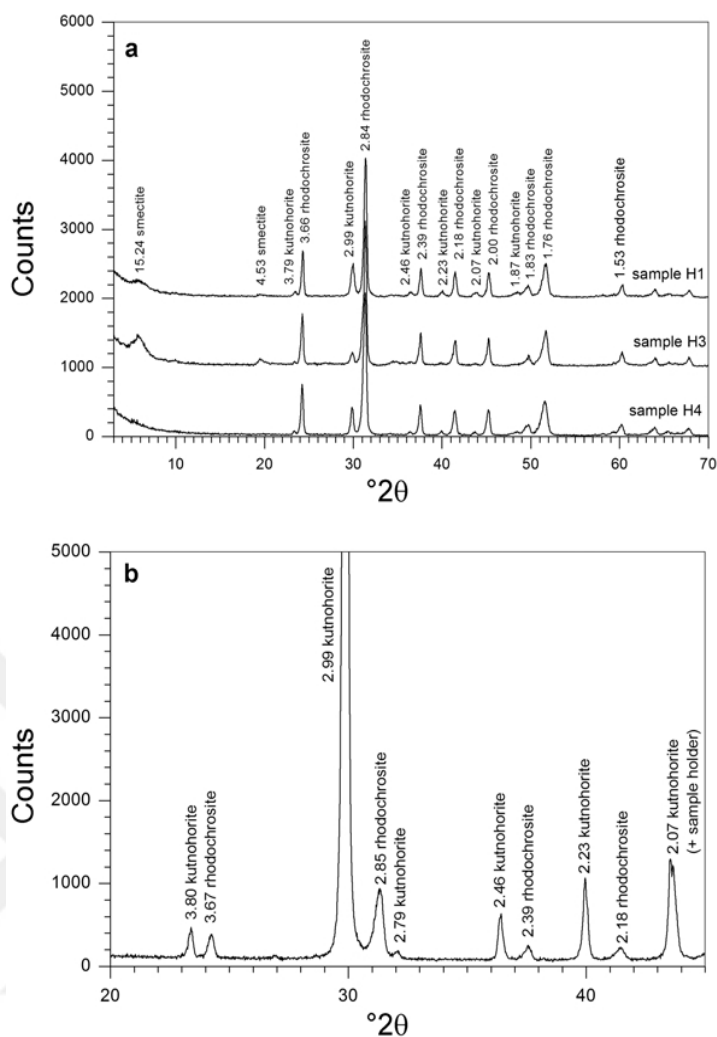


Figure 15. XRD patterns of kutnohorite.³²

It has also been reported that the temperature range of irregularity of kutnohorite starts at about 450°C; it is less sensitive to pressure compared to dolomite.⁶⁹ In the crystal morphology of $(\text{Ca}_{1-x}\text{Mn}_x)\text{CO}_3$ solid solutions synthesized with increasing Mn^{2+} incorporation (Figure 16), it was observed that much smaller spherical crystals were obtained than block-shaped spherical crystal aggregates. Due to the almost equal proportions of Mn^{2+} and Ca^{2+} in the crystals obtained from the initial aqueous solutions, XRD analyses revealed a pronounced oscillatory concentric zoning pattern and double peaks corresponding to calcite and rhodochrosite peaks. This reveals that the central region of the crystal is moderately Mn-rich, while Ca-rich and Mn-rich rings are successively located around the center. In addition, the synthesized calcite formed crystals of standard rhombohedral morphology characterized by $\{104\}$ planes with a size of about 10 μm , while the diameter of the $(\text{Ca}_{1-x}\text{Mn}_x)\text{CO}_3$ solid solutions decreased with increasing Mn^{2+} concentration. As the

Mn^{2+} content increased, these solid solutions evolved from block crystal morphology to spherulite and peanut-like aggregates.⁸⁵

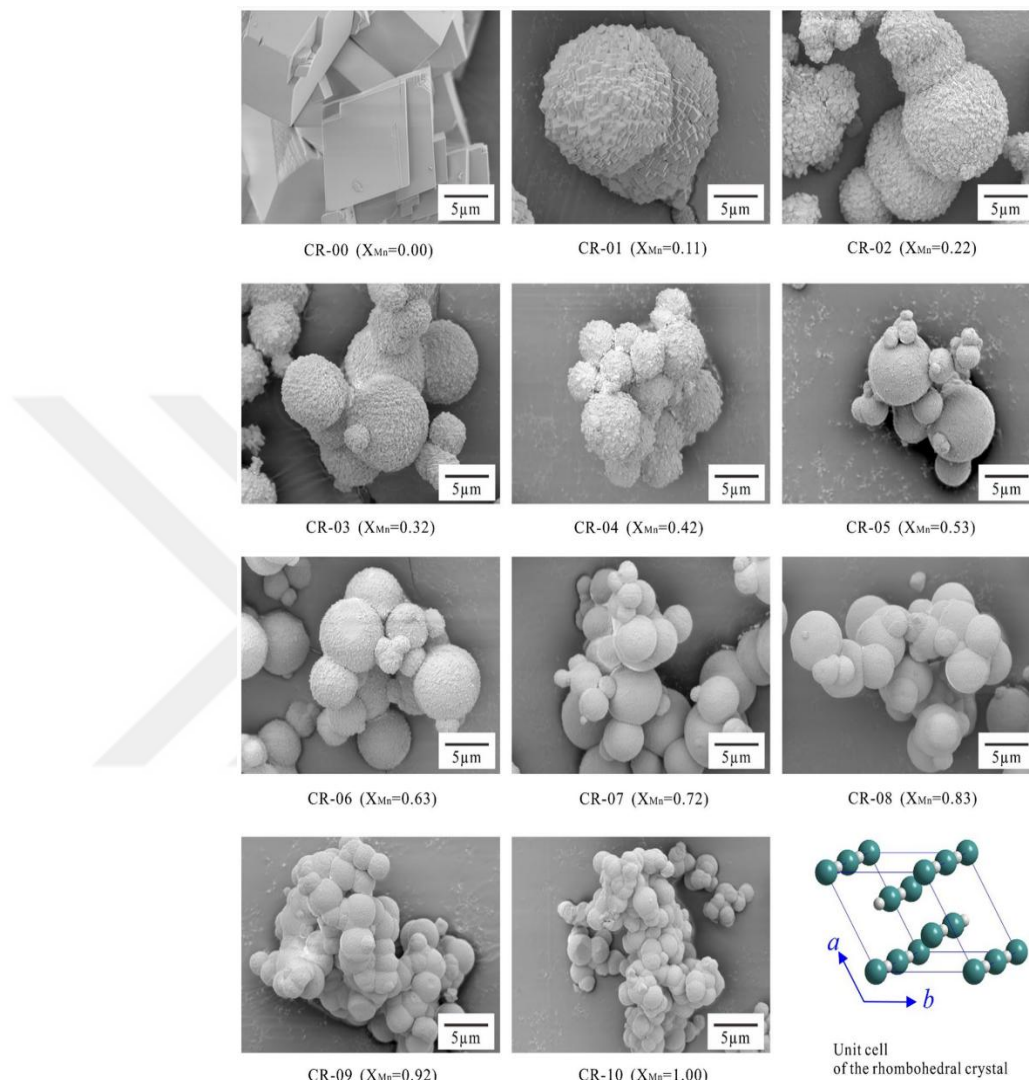


Figure 16. SEM images of the $(\text{Mn}_x\text{Ca}_{1-x})\text{CO}_3$ solid solutions.⁸⁵

2.3.4. Characterization of $\text{FeCa}(\text{CO}_3)_2$

Based on the Chuliá-Jordán et al.⁴² describing how the ankerite crystal changes under different pressures (Figure 17). A new peak appeared in the XRD pattern above 4 GPa pressure in the crystal structure. The new peak (210) corresponds to a reflection of the solid

phase CO₂-I. Since a Cu catalyst was used in the experiment, it was also reported that CO₂ was formed at room temperature due to the catalyst, whereas normally high temperature is required for CO₂ formation. The crystal structure remained stable up to a pressure of 12 GPa and no new peak was detected. Predicated on the reported lattice parameters, there is a slight narrowing of the a and c axis lengths as the pressure increases. For example, the a-axis length of 4.8361(12) Å at 0 GPa decreased to 4.7560(14) Å at 12.1 GPa and the c-axis length decreased from 16.185(7) Å at 0 GPa to 15.125(11) Å at 12.1 GPa. This narrowing reflects the decrease in the distance between the atoms. It also reflects a decrease in the unit cell volume (Å³). The unit cell volume of 327.83(15) Å³ at 0 GPa decreased to 296.28 Å³(17) at 12.1 GPa. This decrease indicates that the crystal structure is compressed under pressure and the space between atoms is narrowed.

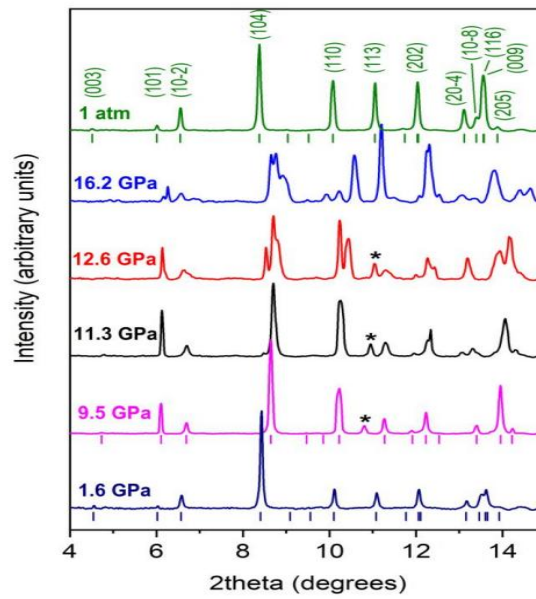


Figure 17. XRD patterns of FeCa(CO₃)₂ under on the different pressure.⁴²

2.4. Recent Application Areas of Double Carbonates

2.4.1 Application Areas of $\text{MgCa}(\text{CO}_3)_2$

Dolomite has a wide range of applications because of its versatile physical and chemical properties. Figure 18 provides a summary of the wide range of uses of dolomite.

Dolomite has been used in the synthesis of PCC (nano-precipitated calcium carbonate), PCC/PMMA (precipitated calcium carbonate/poly methyl methacrylate) and CaO/MgO and $\text{CaZrO}_3/\text{MgO}$ nanocomposites. Abeywardena et al.⁸⁶ succeeded in synthesizing PCC (nano-precipitated calcium carbonate) nanostructures from dolomite. The obtained nanostructures are capable of being used in various industrial applications. Mantilaka et al.⁸⁷ synthesized PCC/PMMA (precipitated calcium carbonate/poly (methyl methacrylate)), a valuable nanocomposite material from dolomite. The privilege of this synthesis method is that instead of expensive raw materials used in other PCC/PMMA synthesis methods, dolomite, which is a cheaper raw material, was used as an alternative. The nanocomposite material produced showed properties suitable for several important industrial applications, such as acid resistance and good dispersibility in the organic phase. CaO/MgO and $\text{CaZrO}_3/\text{MgO}$ nanocomposite materials synthesized using dolomite with high temperature resistance properties were successfully realized by Suzuki et al.⁸⁸. They are deformable and machinable at high temperatures. $\text{CaZrO}_3/\text{MgO}$ nanocomposite was synthesized from a mixture of dolomite and zirconia. Unlike other nanocomposites, it shows quasi plastic deformation even at room temperature.

Boudchicha et al.⁸⁹ focused on the production of glass ceramics with a mixture of dolomite and kaolin ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$). The materials used are the raw materials used to form the CMAS system (CaO, MgO, Al_2O_3 , SiO_2). Binary glass ceramics based on cordierite ($(\text{Mg,Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18}$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) were synthesized using the CMAS system. Anorthite crystals were formed at 850°C and cordierite crystals were formed at 950°C. The best density and hardness values of the glass ceramics were achieved at 950°C. As a result, dolomite played an important role in the synthesis of the ceramic to increase the mechanical strength.

Also, dolomite is used as bioceramic. Amirthalingam et al.⁹⁰ used dolomite in the

synthesis of hydroxyapatite (HAp), an important bioceramic used in tooth and bone tissue repair. The mechano-chemical method was used, and the temperature was studied between 950°C and 1250°C. It was confirmed that at 950°C the hydroxyapatite phase is formed and at temperatures above 1050°C phases such as β -tricalcium phosphate (β -TCP) and monetite are formed.

The gradual depletion of fossil fuel reserves worldwide has led to an increasing focus on switching to renewable energy sources such as biodiesel as a viable alternative. In order to increase the biodiesel production rate and reduce its negative impact on the environment, catalysts and environmentally friendly additives are required. Dolomite as a catalyst is an alternative material that can be used as a catalyst in various application areas, for example, in the synthesis of biodiesel and the synthesis of the by-product glycerol carbonate. In the study conducted by Sendžikienė et al.⁹¹ dolomite was calcined (850°C) and used efficiently as a catalyst in transesterification reactions. In the transesterification of sunflower oil with methanol (Fatty Acid Methyl Esters (FAME) were synthesized) 8:1 methanol/oil molar ratio, 6% catalyst amount, 5 hours reaction time and 60°C reaction temperature. To make the biodiesel usable in summer, 500 ppm Ionol antioxidant was used to increase the oxidation stability of the biodiesel, and 500 ppm Infineum R-442 was used to reduce the Cold Filter Plugging Point (CFPP). Although the catalytic activity of dolomite was maintained twice in reuse, a decrease in yield was reported in 3 uses.

A similar study to the one conducted by Sendžikienė et al.⁹¹, was published by Correia et al.,⁹² and Olivia et al.,⁹³. Each study focused on biodiesel production using dolomite as a heterogeneous catalyst. One of the main differences is that Sendžikienė et al., used only sunflower oil, Correia et al., used both canola oil and sunflower oil, and Olivia et al., used only palm oil. According to the reported results, a biodiesel conversion rate of 98.81% was obtained for canola oil, 96.52% for sunflower oil and 78.09% for palm oil. Another important difference is that Sendžikienė et al., used Ionol antioxidant and Infineum R-442 depressant to improve the oxidation stability and CFPP of biodiesel, whereas Correia et al. and Olivia et al., add any additives.

The use of Ni modified Malaysian dolomite as a catalyst in the deoxygenation reaction of waste cooking oil into green fuel was investigated by Hafriz et al.⁹⁴. In the report, it was reported that the Ni/CMD900 catalyst obtained by precipitation method provided a higher conversion (68% waste cooking oil conversion and 36.4% pyrolysis oil yield). Coke formation was found to be less than 32%. Another conclusion is that this catalyst produces long alkene chains and may be a suitable by-product for plastic production.

In the use of calcined dolomite as a catalyst, Algoufi et al.⁹⁵ calcined dolomite at 800°C to obtain a mixed oxide of CaO and MgO and used it as a catalyst to produce glycerol carbonate via transesterification of glycerol, a biodiesel by-product. This catalyst was found to provide high efficiency in the conversion of glycerol-to-glycerol carbonate. Some decrease in the activity of the catalyst was observed after use, but the activity of the catalyst was maintained by recalcination.

Dolomite is also an example of an alternative catalyst used in organic synthesis. Yang et al.⁹⁶ studied the catalytic activity under mild conditions using calcined dolomite (700°C) for Knoevenagel condensation in organic synthesis. The reaction conditions between aldehydes and active methylene compounds (malononitrile and ethyl cyanoacetate) were analyzed and one of the most important findings was that the catalyst was four times recyclable and environmentally friendly. This simple method can be considered as a very interesting strategy for α , β -unsaturated carbonyl compounds. The obtained α , β -unsaturated carbonyl compounds are very important products in areas such as pharmacy and polymer production.

The pursuit for efficient and cost-effective solutions in environmental cleaning technologies brings the use of dolomite-based photocatalysts to the forefront. Tian et al.⁹⁷ developed composite microspheres with low Ag_2CO_3 content, economically producible and high photocatalytic performance using dolomite as core material. Dolomite was combined with Ag_2CO_3 and converted into $\text{CaMg}(\text{CO}_3)_2@\text{Ag}_2\text{CO}_3$ composite microspheres by a rapid ion exchange process and a superior photocatalytic performance was obtained. In the study, it was reported that the optimal ion exchange time was 4 hours, and the temperature was 40°C. The use of dolomite in this field is important in terms of showing how it can be used in photocatalytic processes by going beyond its classical applications.

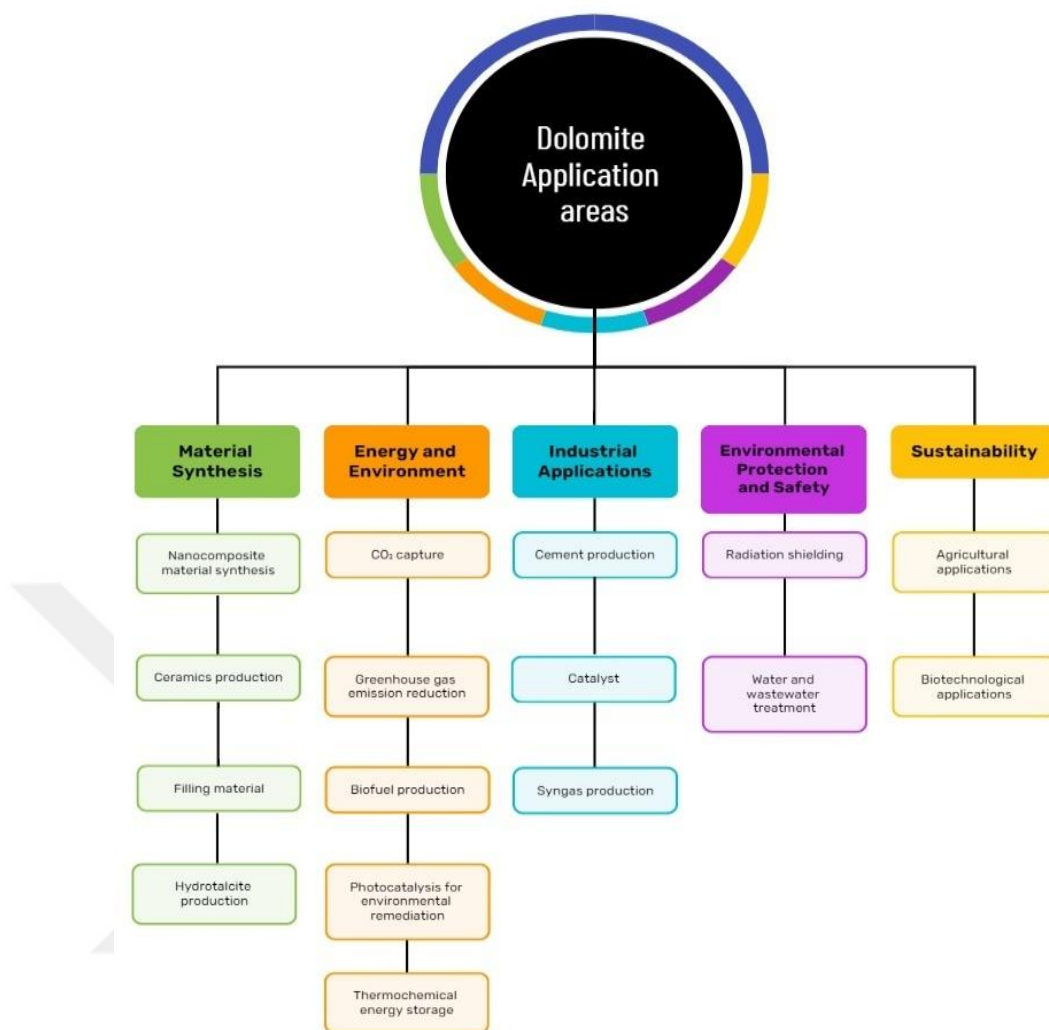


Figure 18. Summary application areas of dolomite.

There has been extensive research in recent years on the versatile effects of dolomite nanoparticles in agriculture, biotechnology and medicine. In agricultural applications, the effects of dolomite NPs on seed germination and early plant development were investigated by Hann et al.⁹⁸, Zhang et al.⁹⁹, and Pražák et al.¹⁰⁰. Hann et al. reported that the germination rate of rice seeds to which 1% dolomite NPs were added was 30% higher compared to the control group. Similarly, Zhang et al. evaluated the effects of biochar nanoparticles on plant growth and reported that they may play a role in soil improvement and nutrient absorption. In the field of biotechnology, Hann et al. detailed the antibacterial and cytotoxic properties of dolomite nanoparticles. It was observed that it provided growth inhibition against Gram-negative *E. coli* bacteria and suppressed human ovarian cancer (SKOV3) cells. However, Pražák et al., evaluated the effects of AgNPs (silver nanoparticles) on green bean

germination and bacterial symbiosis under different temperature conditions, indicating that nanoparticle-based treatments may alter plant-microbial interactions.

Yu et al.¹⁰¹ demonstrated that it is possible to produce magnesium phosphate cement (MPC) at lower cost and higher performance than other raw materials (e.g. magnesite) by calcining dolomite and quartz in appropriate proportions. The thermal decomposition, which takes place between 550°C and 750°C, allows MgO to be released and CaO to combine with quartz. However, a suitable calcination temperature and dolomite-quartz ratio must be selected to ensure that the MgO obtained by fully calcining the dolomite is sufficiently abundant and reactive. In this study, dolomite was calcined at temperatures between 1100°C to 1300°C. The effect of these temperatures was analyzed on the CaO and MgO content of the calcined cement and the mechanical properties of MPC. After calcination, the effects of dolomite-quartz powders on the performance of MPC pastes, compressive strength, phase evolution, setting time and microstructure of hydration products were evaluated. Acetylene sulfide (C₂S) and CaO were added to the hydration reactions and struvite crystals and a small amount of portlandite were detected as the main hydration products. The obtained struvite crystals showed large plate-like structures. This made the microstructure of the product more stable. MPC prepared with T1250-R1.5 sample calcined at 1250°C was found to have a setting time of 16 minutes and a compressive strength of 63 MPa at the end of 7 days of curing and showed sufficient durability. As a result, the use of dolomite as an alternative raw material to magnesite offers a critical advantage in terms of both low cost and sustainable production.

Another study on the effect of dolomite on cements was conducted by Xu et al.¹⁰². The study compares the reaction mechanisms of dolomite and limestone powders in Portland cement, showing that the use of dolomite at elevated temperatures can improve the mechanical properties of cement. In particular, the calcite and hydrotalcite formations obtained with dolomite provide important information on how this material can be effective in applications with strength and microstructure improvements. Based on the main findings, dolomite showed higher chemical reactivity with increasing temperature compared to limestone. In general, dolomite improved the long-term compressive strength of Portland-dolomite cement (PDC) compared to Portland-limestone cement (PLC).

Amid the ongoing advancements in sustainable material production techniques and the growing emphasis on environmental awareness, research on the regeneration of various wastes to produce both new and existing materials continues to progress steadily. One of the related studies was carried out by Abbass et al.¹⁰³ to convert dolomite waste into a sustainable

katoite-based binder and minimize its carbon footprint. It offers an alternative approach for the conversion of dolomite waste into an environmentally friendly binder and sustainable cement production. The study aims to a sustainable katoite based binder was synthesized through ion-exchange reactions between sodium aluminate (NaAlO_2) solution and dolomite waste powder (DW). Katoite is the basic binder phase of calcium aluminate cement (CAC). Calcium aluminate cement (CAC) is characterized by excellent mechanical performance^{104,105} and resistance to high temperatures.¹⁰⁶ Additionally, the influence of sodium oxide (Na_2O) content and silicate-rich wastes (perlite waste and concrete waste) on the binder's performance was meticulously scrutinized. Increasing the concrete waste content increased the compressive strength while decreasing the pore volume and drying shrinkage. However, perlite waste had the opposite effect and negatively affected the mechanical performance of the material. The reaction between sodium aluminate and dolomite waste led to the formation of the katoite phase, with its development being notably enhanced by increased Na_2O content. Despite the high magnesium concentration in the dolomite waste, only trace amounts of Mg were detected within the katoite phase.

Innovative approaches to reduce carbon emissions offer environmentally friendly strategies that improve the performance of sorbents, enable efficient use of materials derived from natural resources and contribute to sustainable energy solutions. The work of Filitz et al.¹⁰⁷ presents an innovative approach to CO_2 capture methods used to reduce carbon emissions, while the work of Li et al.¹⁰⁸ aims to bring a new dimension to this technology with the integration of solar energy. While the use of synthetic dolomite provides a much more efficient CO_2 capture capacity compared to natural limestone, recent studies show that such sorbents can be made even more efficient by supplementing them with solar energy. Li et al., showed that Mn^{2+} and Fe^{2+} doped dolomite-derived sorbents have great potential for both high CO_2 capture capacity and solar absorption capacity. In line with the findings of Filitz et al., study, a Ca-rich synthetic dolomite with CO_2 sequestration capacity at elevated temperatures has been successfully developed. Although natural dolomite has a CO_2 sequestration capacity that remains constant with the number of cycles, its total CO_2 sequestration capacity is low due to its high MgCO_3 content. MgCO_3 does not contribute to the active CO_2 capture capacity by breaking down at lower temperatures during calcination, which reduces the overall performance of dolomite. In contrast, the enhanced Ca-rich dolomite was able to maintain its CO_2 capture capacity through repeated cycles of calcination and carbonation, minimizing the performance degradation during cyclic use. These sorbents were found to provide up to 100% higher CO_2 sequestration capacity

compared to natural limestone. Li et al. synthesized unit and dual-doped dolomite-derived sorbents by combustion method using cigarette butts. For Mn-doped sorbents, it was observed that the solar absorption capacity increased with increasing Mn doping ratio. Ca/Mg-Mn₁₀ had the highest average solar absorption (63.6%), while Ca/Mg-Mn₃ showed the best cyclic CO₂ capture capacity (74.8%, cycle 20). Among the dual-doped sorbents, Ca/Mg-Mn₅-Fe₅ had a higher average solar absorption (76.7%), but the cyclic CO₂ capture capacity remained slightly lower. Ca/Mg-Mn₅-Cu₅ showed the lowest performance. The results show that the Mn/Fe doped dolomite-derived sorbent have significant potential for application in direct solar-driven calcium cycling systems.

In the face of accelerating global warming, strategies to reduce greenhouse gas emissions are key to a sustainable future. Dolomite applied to agricultural soils plays an important role in this process. In the study by Umair Hassan et al.¹⁰⁹ the effect of dolomite on greenhouse gas emissions was discussed in detail and its potential in combating climate change was emphasized. Dolomite improves productivity in acidic soils by regulating soil pH¹¹⁰ and affects greenhouse gas emissions. According to the results of the meta-analysis, dolomite application increased CO₂ emissions by 30.34%, CH₄ emissions by 4.91%, and decreased N₂O emissions by 54.88%. It is also emphasized that the increase in soil pH significantly increases CO₂ and N₂O emissions, while decreasing CH₄ emissions. These data can not only help us understand the impacts of dolomite application on greenhouse gas fluxes, but also enable us to make better predictions on how it can be used as a strategic tool to combat climate change in agricultural soils.

The use of dolomite as a filler in polymer matrices presents several challenges, especially in terms of improving mechanical properties.¹¹¹ Therefore, studies on the modification of dolomite have aimed to improve the performance of composites. Use of physically and chemically modified dolomite applications, physically modified dolomite, Ahmad Saidi et al.,¹¹² used dolomite as filler in composites with polybutylene terephthalate (PBT) matrix. While the tensile strength increased up to 10% dolomite loading, it decreased after 15% loading. Dolomite induced crack formation in the PBT matrix, reducing the impact strength. Ridhwan et al.¹¹³ studied the effect of different dolomite sizes on the tensile properties of Malaysian rubber and epoxidized natural rubber composites. Dolomite particles smaller than 63 µm were better dispersed and therefore showed better tensile performance compared to those larger than 75-150 µm. At low dolomite loadings (up to 15 phr), dolomite was better dispersed in the polymer matrix. Osman et al.¹¹⁴ dolomite prevented from agglomeration by tip-sonication in thermoplastic starch matrix improved the mechanical

properties. The small dolomite particles were better dispersed and formed a stronger bond with the matrix, improving the tensile and tear properties of the composite. Fauzi et al.^{115,116} they found that ultrasonically modified dolomite improved the performance of composites with Polyethylene vinyl acetate (PEVA) matrix. Ultrasonication improved the mechanical properties by dispersing the dolomite particles. Furthermore, the best tensile properties were obtained with 1% dolomite loading in the PEVA matrix. Syed Bakar et al.¹¹⁷ studied the effects of different sizes of dolomite in recycled polypropylene matrix (rPP). The rPP composites containing 300 μm dolomite showed higher tensile strength than those containing smaller sizes of dolomite. However, at high dolomite loadings, agglomeration occurred, and tensile performance decreased.

In a review of studies with chemically modified dolomite, Manni et al.¹¹⁸ show that the addition of dolomite to silane-modified dolomite and polyamide 11 (PA11) composite improves the thermal stability of the composite. Silane strengthened the bonding between dolomite and polymer, resulting in better dispersion of dolomite particles in the matrix. Ghada et al.,¹¹⁹ used dolomite filler in polyvinyl chloride (PVC) composite. However, tensile strength and elongation at break decreased at higher dolomite loadings (≥ 10 phr), which is due to the agglomeration of dolomite particles within the matrix. Sönmez et al.¹²⁰ used titanium and silicon modified dolomite as photocatalyst filler in poly-dimethyl siloxane matrix. This modification improved the mechanical and photocatalytic properties of the dolomite filler.

In studies using unmodified dolomite, Adesakin et al.¹²¹ investigated the mechanical properties of polyester/dolomite composite material. As the amount of dolomite in the content increased, tensile strength decreased, but modulus and hardness increased. A 211.3% increase in hardness was recorded with 30% dolomite loading. Mohd Din et al.¹²² analyzed a polypropylene/dolomite composite and found that the addition of dolomite decreased the tensile strength but increased the flexural modulus. Thermal durability and flame-retardant properties were improved by the addition of dolomite. Furthermore, dolomite acted as a crystallizing agent, increasing the crystalline structure of polypropylene. Ali et al.,¹²³ prepared and characterized a polyurethane/dolomite composite. Tensile strength decreased with increasing dolomite loading, but compressive strength increased. With 45% dolomite loading, the compressive strength doubled.

In studies on the use of dolomite as a hybrid filler, Ni et al.¹²⁴ used palygorskite and dolomite as hybrid fillers in a waterborne polyurethane matrix. Both mechanical and thermal properties were improved more than those obtained when using dolomite or polyurethane

alone. Tensile strength increased by 178% at 10% hybrid filler loading.

Shamsuri et al.¹²⁵ used dolomite as a hybrid filler with low-density polyethylene (LDPE) and kenaf core fibre. The addition of dolomite increased the tensile modulus, tensile stress and impact strength of the LDPE/kenaf composite. Dolomite provided mechanical interlocking by reducing the sliding effect of kenaf core fibre. Verma et al.^{126,127} used *Grewia optiva* and glass fibre as hybrid fillers in an epoxy matrix with dolomite. As the loading of dolomite increased (up to 15 wt%), the stiffness and impact strength of the composite increased, while the tensile and flexural strength decreased. This decrease can be explained by the agglomeration of dolomite particles and the increase of voids within the matrix. Saleh et al.^{128,129} used dolomite and carbon nanotubes (CNT) as hybrid fillers in epoxy matrix. Dolomite and CNTs were combined by chemical vapor deposition (CVD), which prevented CNT agglomeration and ensured a homogeneous distribution in the epoxy matrix. The composites obtained by CVD method showed 67% and 28% increase in tensile strength and modulus. Less effective results were obtained with the physical hybrid method.

Ubiquitous minerals such as dolomite present a novel approach to thermochemical energy storage technologies by offering low-cost and environmentally friendly energy storage solutions. In related subjects, Humphries et al.¹³⁰ proves that dolomite exhibits higher performance when used in concentrated solar power systems with NaCl and MgCl₂ additives. On the other hand, the study by Srinivasan et al.¹³¹ examines the energy storage capabilities of dolomite from phosphate mines in Florida compared to commercial dolomite, showing that these minerals have great potential. Humphries et al. identified dolomite as a promising, cost-effective material for thermochemical energy storage in concentrated solar thermal power systems. In this process, a new melt salt mixture was used by adding a mixture of NaCl and MgCl₂ to dolomite samples. The use of this salt mixture increases carbon dioxide absorption. Three different sources of dolomite (industrial, raw and synthetic) were used and analyzed separately. The industrial dolomite source showed the lowest performance in terms of thermochemical energy storage due to the high amount of impurities. These impurities, which caused the formation of a very high amount of calcium silicate (Ca₂SiO₄), reduced the CO₂ absorption capacity of dolomite by removing calcium from the activated carbonate/oxide component. Therefore, they prevented the calcium in the dolomite structure from efficiently participating in the carbonation cycle, negatively affecting its thermochemical energy storage capacity. Despite being produced with high purity, synthetic dolomite exhibited rather poor performance. It showed high levels of agglomeration and phase separation between CaCO₃ and MgO, reducing the reversible CO₂

capacity. High phase segregation limited the CO₂ absorption capability of dolomite. One of the main reasons for the limitation of CO₂ absorption capacity is the absence of impurities in the dolomite and therefore, dolomite particles adhere to each other and form less active surface area. Compared to the other 2 dolomite samples used, raw dolomite, it exhibited the best thermochemical cycling properties in its unrefined form. Quartz impurity in the crude dolomite prevented the agglomeration of dolomite and reaction products (CaCO₃ and MgO). The raw dolomite showed stable performance for 10 cycles with 50% CO₂ capacity. Moreover, this dolomite sample has high porosity, which shortened the gas-solid reaction pathways and accelerated the carbonation process. This research provides a fundamental resource for future research into the utilization of dolomite and other metal carbonate systems for thermochemical energy storage. Humphries et al. have made significant advances in thermochemical energy storage using additives. However, the potential of dolomite in its natural form cannot be ignored. At this point, the study conducted by Srinivasan et al., with dolomite from Florida phosphate mines shows that even in its raw form, dolomite can offer an effective solution for sustainable energy storage. Selected raw dolomite samples demonstrated significant potential for thermochemical energy storage due to their 36% large surface area and lower crystallinity compared to commercial dolomites. Both Humphries et al and Srinivasan et al. show that dolomite can be used as a low-cost energy storage material. However, the study of Srinivasan et al. suggests that natural dolomite samples have higher stability, while Humphries et al concluded that additives added to dolomite increase the CO₂ capacity.

The use of environmentally and sustainable friendly materials for the removal of toxic pollutants in wastewater treatment is becoming increasingly important.¹³² Especially natural mineral source such as dolomite has adsorption capability due to its surface area and calcite and magnesite composition and thus offers promising solutions for the removal of heavy metals, microorganisms and pH neutralizers in wastewater.^{133,134} Pesonen et al.⁸³ investigated the effects of calcination temperatures of dolomite on phosphate (PO₄³⁻) and ammonium (NH₄⁺) removal in wastewater, while Zahuri et al.¹³⁵ investigated the potential of dolomite for decolorization and chemical oxygen demand reduction in textile dye wastewater depending on activation temperature. These studies provide important findings supporting the versatile use of dolomite in wastewater treatment. Pesonen et al. explored the removal of PO₄³⁻ and NH₄⁺ from synthetic diammonium phosphate (NH₄)₂HPO₄ solution and agricultural sludge using dolomite calcined at 650°C, 750°C and 950°C and commercial MgO. Dolomite calcined at 750°C was the most suitable precipitant for struvite precipitation.

Zahuri et al. carried-out experiments on the treatment of textile dye wastewater using dolomite as a 'green' adsorbent for low cost and sustainable environment. Dolomite activated at 300°C, 700°C and 900°C adsorbed synthetic textile dye wastewater under various conditions. The highest decolorization rates were obtained using dolomite activated at 700°C and 900°C, and 78% and 98.7% decolorization of synthetic textile dye wastewater was achieved, respectively. In addition, a 73.9% and 66.7% reduction in chemical oxygen demand was also observed at these temperatures, indicating that dolomite is an effective treatment agent.

Baldauf-Sommerbauer et al.¹³⁶ state that the production of carbon monoxide (CO) through reduced calcination of magnesite and dolomite has significant potential for syngas production. Conversion of CO₂ to CO during calcination with hydrogen enables sustainable recovery of carbon-containing products. Syngas is a gas mixture containing H₂, CO and a small amount of CO₂¹³⁷. The study shows that more than 70% of the CO₂ released during the reduced calcination of magnesite can be converted to CO at moderate temperatures and without the addition of a catalyst.

Zakaly et al.¹³⁸ highlight the superior radiation damping properties of dolomite-doped borate glasses. The high atomic number of dolomites allows us to use this mineral as a radiation absorber. Dolomite components with different dolomite glass compositions (40-x) B₂O₃-40PbO-20ZnO-x were synthesized for the experiments. In the study, as the dolomite content increased, the radiation attenuation capacity of the glasses improved in direct proportion. A total of 4 different glass samples DG-0 to DG-4. The first sample, DG-0, does not contain dolomite. That is, it contains only borate (B₂O₃), lead oxide (PbO) and zinc oxide (ZnO). Since dolomite is not added, the density and gamma shielding ability of this glass is lower. DG-1 contains 1% by weight of dolomite. With the addition of dolomite, the density of this glass is slightly higher than DG-0. Radiation attenuation properties also show improvement compared to DG-0. DG-2 contains 2% by weight of dolomite. With the increase in the amount of dolomite, the density and radiation shielding capacity of the glass has further improved. Improvements in optical properties are also observed due to the dolomite additive. DG-3 contains 3% by weight of dolomite. As the dolomite content increases, the physical and armoring properties of the glass improve markedly. DG-3 has higher density and better gamma shielding capabilities than DG-2. DG-4 contains 4 wt% dolomite. This sample is the glass with the highest dolomite content. As the amount of dolomite increases, the density of the glass increases and the radiation shielding capability reaches the maximum level. DG-4 exhibits the highest radiation shielding performance and

optical properties compared to the other samples. These contributions of dolomite in terms of gamma radiation attenuation are guiding the development of new materials in the field of nuclear radiation protection.

2.4.2 Application Areas of BaCa(CO₃)₂

Nuclear waste management and radiation protection was reported by Massoni et al.^{66,139} that BaCa(CO₃)₂ has the potential to be used in the immobilization of carbon-14 due to its low specific volume of carbon and relatively good sinter ability properties. It has been observed that when barytocalcite encounters water, it dissolves faster than expected and as a result, simple compounds such as CaCO₃ and BaCO₃ begin to precipitate. However, it has been found that this precipitation process greatly limits the loss of carbon, i.e. it can help to keep carbon-14 safe in the long term.

The potential use of barytocalcite as a carbon-bearing compound in the Earth's lithospheric layer was investigated by Chuliá-Jordán et al.¹⁴⁰ The study investigated the phase change of barytocalcite at high and low pressures and found that at a high pressure of 5.7 GPa, the barytocalcite transitioned to a new phase thus post-barytocalcite, which was structurally more compact and resulted in an increase in the coordination number of calcium and barium atoms. The transformation of the low-pressure phase barytocalcite to the post-barytocalcite phase at high pressure was observed to reduce the volume of the structure by 1.4%. This phase transformation resulted in a structurally more tightly packed structure.

While the effect of barium hydroxide Ba(OH)₂ on the binder phases in lime-based mortars was investigated by Karatasios et al.¹⁴¹ it was observed that barium hydroxide changes the mineral structure of the mortar by promoting the formation of BaCa(CO₃)₂ by participating in the carbonation process. It was determined that BaCa(CO₃)₂ strengthened the microstructure of the mortar binder and formed a more homogeneous carbonate phase. Experimental analyses revealed that BaCa(CO₃)₂ formation can prevent sulphation-induced deterioration of lime mortars by increasing their resistance to sulphate ions. Especially in restoration applications, mortars containing BaCa(CO₃)₂ are more stable against environmental effects and can contribute to the protection of historical buildings exposed to air pollution, sulphate and acidic conditions.

2.4.3 Application Areas of $\text{MnCa}(\text{CO}_3)_2$

In the study of Lièvremon et al.,¹⁴² the effects of the mineral kutnohorite ($\text{CaMn}(\text{CO}_3)_2$) on arsenic removal were demonstrated. While kutnohorite effectively absorbed arsenate (As(V)) ions, the same degree of effect on arsenite (As(III)) was not observed. In the experiments, bacterial oxidation process was used for arsenic removal and kutnohorite acted as an adsorbent in this process. The results showed that kutnohorite is an effective material for arsenate removal.

Massoni et al.⁶⁶ scrutinized the sintering behavior and carbon-14 capture potential of kutnohorite as well as barytocalcite. The main differences are thermal stability, densification and carbon content. Kutnohorite, it experiences carbon loss and the formation of intermediate phases such as CaCO_3 and MnO is observed during sintering. This carbon loss limits the immobilization process. It undergoes carbon loss during the densification process and this process occurs in parallel with densification, which reduces the carbon content in the matrix. Compared to barytocalcite, kutnohorite contains more carbon (11.1%), but losses occur during sintering and the carbon content decreases. According to the results, barytocalcite is a more effective option for C-14 immobilization compared to kutnohorite.

May Sandar Win.⁶⁵ investigated the use of kutnohorite as a thin film material for electronic devices. It was coated as a thin film on N-Si substrate and its current-voltage (I-V) characteristics were investigated under different illumination conditions under light. The film, which stands out as a quite important material in the development of photoelectric devices, draws attention with its photosensitive properties. It was reported in the report that the I-V characteristics showed diode characteristics and maximum output currents were recorded under different lighting conditions.

2.4.4 Application Areas of $\text{FeCa}(\text{CO}_3)_2$

In paper production, it is very important to both increase the quality and reduce the cost. For this reason, manufacturers use fillers such as precipitated calcium carbonate (PCC) to improve printing performance in paper production and to achieve better quality paper thickness¹⁴³. The properties of these fillers used in paper production vary according to the

type of raw material and production method. At this stage, PCC obtained from natural carbonate minerals such as ankerite is important due to its cost-effectiveness and high quality. Ankerite-based PCC attracts attention with the obtaining of homogeneous crystals in nano size. The obtained PCC has a rhombohedral cubic structure because of morphological analysis and the average crystal size was calculated as 43.85 nm. Thanks to these properties, it improves the optical and mechanical properties of paper by increasing the light emitting ability of PCC in applications such as paper.¹⁴⁴

Since it is a double carbonate containing iron in its chemical structure, it is a considerable attractive option to be investigated for next generation energy storage technologies. Ankerite has the potential to be used as a cathode in calcium-based rechargeable batteries. Such batteries are being investigated as an alternative to lithium-ion batteries. Based on density functional theory (DFT) calculations, the theoretical capacity of ankerite is 250 mAh/g with an average operating voltage of 3.8 V.³¹

Dabbas et al.¹⁴⁵ studied ankerite, particularly in the context of the effect of high-level radioactive waste on glass corrosion. In experiments with ankerite, it was observed that the durability of glass is enhanced through pH regulation and Mg-Si precipitation. Ankerite mixes with the environment around the glass, stabilizing the pH and reducing the solubility of the glass. Based on experimental findings, ankerite shows a protective effect against the corrosive effects of glass and significantly reduces the corrosion rate of glass, especially during long-term radioactive waste disposal.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Reagents including $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 98\%$), $\text{Ca}(\text{NO}_3)_2$, Na_2CO_3 ($\geq 99.5\%$), CaCl_2 ($\geq 98\%$), $\text{Ca}(\text{OH})_2$ ($\geq 96\%$) and $\text{Ba}(\text{OH})_2$ ($\geq 98\%$) were purchased from Merck, Germany with analytical grade and used without further purification. The solutions were prepared in ultrapure deionized (DI) water (H_2O) obtained from Milli-Q water purification system (Millipore) with a resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$. Calibrations of pH and conductivity probes were performed using standard pH buffer and conductivity solutions.

3.2 Experimental Setup for Direct Mixing Method

The experimental setup for direct mixing of solutions is shown in Figure 19. Solutions of nitrate salts of the appropriate metals ($\text{M}^{2+} = \text{Ba}, \text{Mg}, \text{Sr}, \text{Co}$ and Ca) and solutions of Na_2CO_3 were prepared with ultrapure deionized (DI) water. Metal ions and $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions added to a batch reactor, 100 ml each, and then 200ml of Na_2CO_3 solution, unless otherwise stated, so that the $\text{M}^{2+} / \text{Ca}^{2+}$ ion molar ratio were adjusted to 0.5, 1 and 2. A glass pH electrode and a metallic conductivity probe were placed in the reactor, and measurements were recorded every 5 min using a Thermo Scientific Orion 5-Star meter (Thermo Scientific, Inc.). The Orion 5-Star meter software continuously recorded the sensor signals displayed on the computer screen. The mouth of the reactor was closed to seal it from atmospheric CO_2 . The experiment was carried out at atmospheric pressure and a room temperature of $24 \pm 1^\circ\text{C}$.

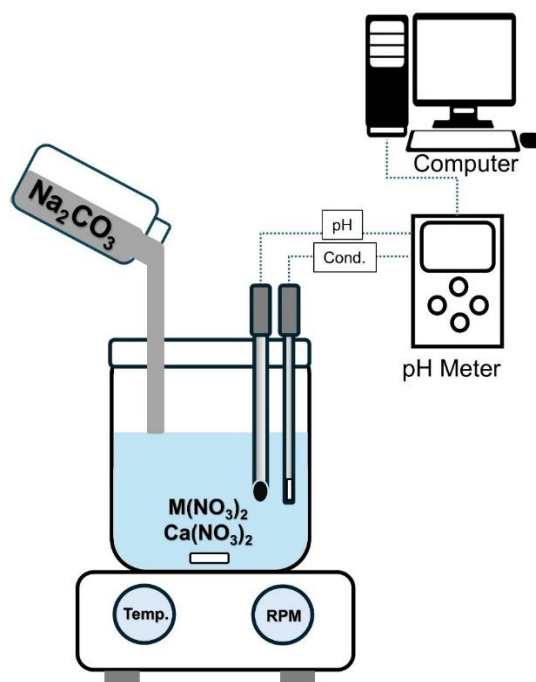


Figure 19. Experimental setup for direct mixing.

3.3 Experimental Setup for Batch Reactor Experiment

Experimental setup for batch reactor is shown in Figure 20. Stock solutions of calcium chloride ($CaCl_2$) and sodium carbonate (Na_2CO_3) were prepared in glass bottles at 25 mM concentration and isolated from atmospheric CO_2 . Solutions of nitrate salts of the metal ions ($M^{2+} = Mg, Ba, Sr, Co$ and Ca) were prepared together with $Ca(OH)_2$ stabilizing solution prepared at 4 different concentrations of 0, 3, 5 and 10 mM.

Firstly, 200ml of the nitrate salt of the metal ions was added to the batch reactor, then 50ml of $Ca(OH)_2$ was added to the specific concentration. Equal concentrations of $CaCl_2$ and Na_2CO_3 solutions were taken from the stock solutions using a peristaltic pump at a constant flow rate of 15 mL/min each and reacted in the tubular reactor. The total flow rate of the reaction mixture in the tubular reactor was kept constant at 30 mL/min. In the tubular reactor, the content precipitated $CaCO_3^0$, Ca^{2+} , CO_3^{2-} and other ions such as $CaOH^+$, $CaHCO_3^+$, Na^+ and Cl^- and added into the batch reactor containing the stabilizing solutions. The experiment was carried out for 7 minutes at atmospheric pressure and room temperature of 24 ± 1 °C.

In a separate study, concentrations of $M(NO_3)_2$ and $Ca(OH)_2$ solutions were adjusted to 5 mM each. pH and conductivity of the stabilizing suspension were measured continuously using a glass pH electrode and a metallic conductivity probe connected to a Thermo Scientific Orion 5-Star meter. The Orion 5 Star meter software allows a continuous record of the sensor signals displayed on the computer screen.

For the synthesis of $BaCa(CO_3)_2$, 10mM 250ml $Ba(OH)_2$ solution and 75mM stock solutions of $CaCl_2$ and Na_2CO_3 were used in the same experimental system. The experiment was carried out at atmospheric pressure and room temperature of 24 ± 1 °C for 10 min.

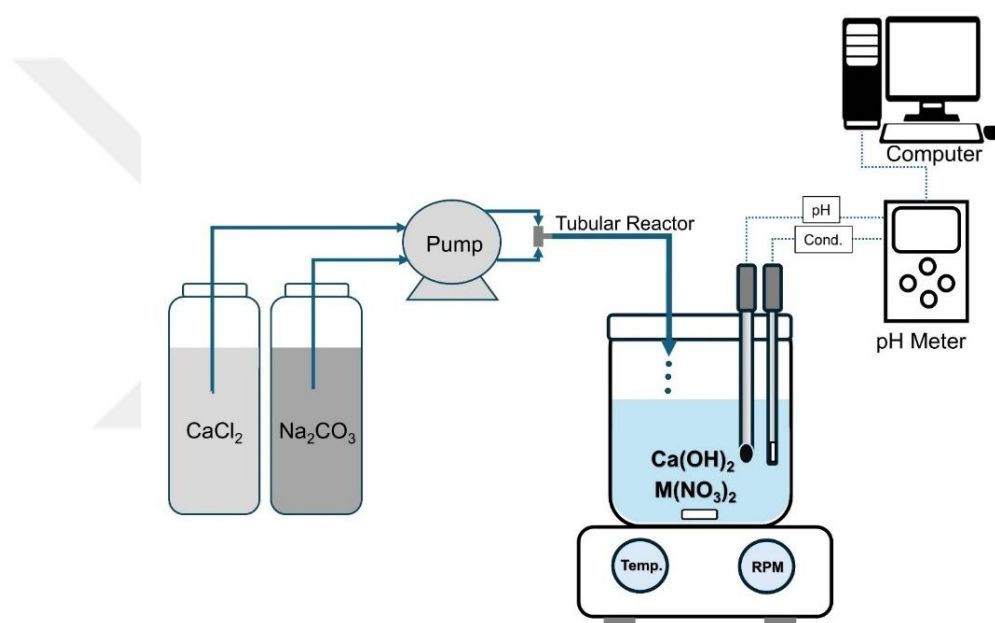


Figure 20. Experimental setup for batch reactor.

3.4 Particle Characterization

The crystal form, morphology and elemental distribution of the solid particles were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDX), respectively. The samples obtained were centrifuged at 9000rpm for 20 minutes to settle the solid particles. The solid particles were vacuum dried at 80°C overnight to remove moisture.

X-ray diffraction (XRD) analysis with Cu-K radiation was used to determine the particle forms. There was a step size of 0.013 degrees between 2θ scans in the range of 10 to 80 degrees. The Rietveld refinement was used to enhance the data using X'Pert Highscore Plus and refined the diffraction data to determine the relative amount of each crystalline phase in the samples.

Scanning electron microscopy (SEM) (Carl Zeiss 300VP) was used to study the morphologies of the particles.

Energy Dispersive X-ray (EDX) analysis was carried out to determine the chemical distribution and the percentages by weight of the elements in the samples. This analysis was performed using the EDX detector integrated with the SEM instrument and the homogeneity of the elements was confirmed by spectra taken from specific areas.

3.5 Crystallite Size Measurement

The crystallite size of the synthesized materials was determined using X-ray diffraction (XRD) data and calculated based on the Scherrer equation¹⁴⁶:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Where:

- D is the crystallite size (nm),
- K is the Scherrer constant (typically 0.89 for spherical particles),
- λ is the X-ray wavelength (Cu-K α radiation, $\lambda = 1.5406 \text{ \AA}$),
- β is the full width at half maximum (FWHM) of the diffraction peak (radians),
- θ is the Bragg angle (degrees).

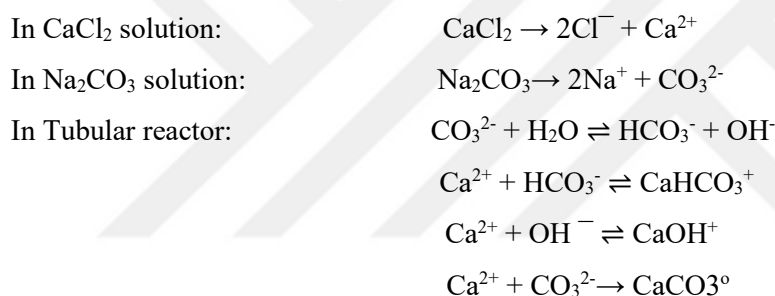
Full width at half maximum (FWHM) values for crystallite size estimation were obtained from XRD patterns using HighScore'Plus software and corrected for instrumental broadening before calculation.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Crystallization in Tubular Reactor

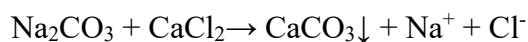
Sodium carbonate (Na_2CO_3) and calcium chloride (CaCl_2) solutions were prepared at a concentration of 25 mM. The two solutions were fed to the tubular reactor through a peristaltic pump are sealed and connected to a peristaltic pump through a separate pipe.



The ions rapidly react in the solution and calcium carbonate (CaCO_3^0) precipitate:



The overall reaction becomes



Due to this action in the tubular reactor nuclei of CaCO_3 such as the metastable phases amorphous calcium carbonate (ACC) or vaterite form rapidly¹⁴⁷. Due to regular flow and short-lived mixing in the tubular reactor, nucleation may take place. The final solid phase may be predominantly calcite or vaterite (some aragonite can also be formed) depending on parameters like pH, temperature, ionic strength, type of stirring, etc. These nuclei of CaCO_3 are then withdrawn from the precipitation medium and introduced

dropwise into the batch reactor. So, the flow into the batch reactor is mostly non-suspended CaCO_3 particles and ions which have not outgassed but all the time should be maintained in the liquid phase. Na^+ , Cl^- , CO_3^{2-} , CaHCO_3^0 , HCO_3^0 or Ca^{2+} .

Increasing the pH of the medium with Ca(OH)_2 increases CO_3^{2-} and OH^- ions and makes $\text{Ca}^{2+}/\text{CO}_3^{2-}$ precipitation dominant and increases the supersaturation required for the precipitation of CaCO_3 nuclei added to the medium. As pH increases, supersaturation increases, nucleation and growth kinetics change. Therefore, even if $\text{M(NO}_3)_2$ is added, CaCO_3 becomes the most stable phase and grows. In the experiments without Ca(OH)_2 , the pH level is low due to the limited amount of OH^- . Since CaCO_3 nuclei from tubular reactor do not raise the pH sufficiently in batch reactor, CaCO_3 growth or the formation of additional phases such as $\text{MCa(CO}_3)_2$ may not be possible.

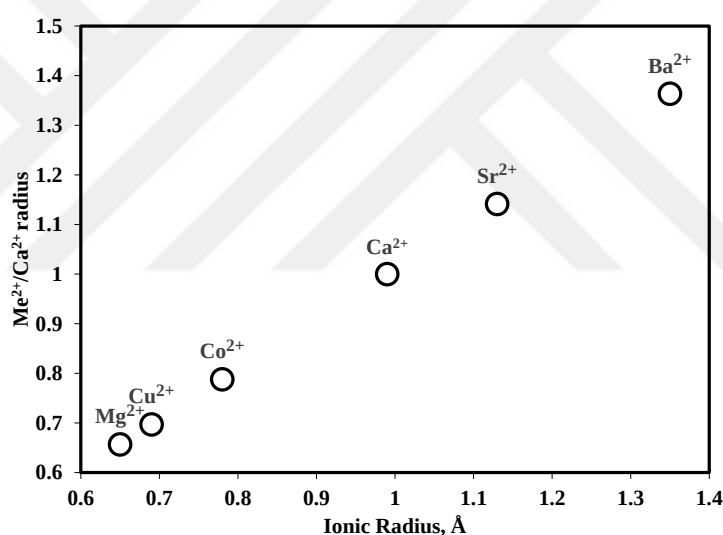
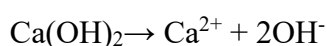
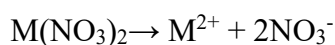


Figure 21. Ratio of the ionic radius of alkaline earth and transition metals to the ionic radius of Ca^{2+} ion.

The batch reactor contains nitrate salt of the appropriate metal ($\text{M}^{2+} = \text{Mg, Ba, Sr, Co and Ca}$) and Ca(OH)_2 solutions at different concentrations and in different experiments. $\text{M(NO}_3)_2$ and Ca(OH)_2 in the tank dissociate into ions.



The behavior of carbonate and hydroxide ions in this basic environment can be considered to lead to possible different precipitates according to the type of metal ion (M^{2+}) added.

- Considering the ionic radii of the metal ions, if the M^{2+} ion can be easily substituted into the $CaCO_3$ crystal lattice, there may be some cationic doping. In this case, $CaCO_3$ peaks are still visible in the XRD of the particles obtained based on the study, but slight shifts in peak positions can be observed and may lead to changes in the morphology of the crystal. However, M^{2+} ions may adsorb on $CaCO_3$ surfaces and show some inclusion or surface retention behavior.
- Depending on the solubility product constant (K_{sp}) values, if M^{2+} ion has a solubility product low enough to precipitate hydroxide or carbonate, then a second phase can be observed. Especially if the ion radius is very different (e.g. Ba^{2+} is larger than Ca^{2+} and Mg^{2+} is smaller (graph given in Figure 21), this association mechanism results in either very limited substitution into the crystal lattice or the formation of another phase (carbonate, double carbonate or mixed oxide phases);
- New phase may not be visible in XRD and may not be distinguished in SEM since the ionic radius is larger than the Ca^{2+} ionic radius, M^{2+} ion cannot be fully integrated into the crystal lattice of $CaCO_3$, some of it may remain in the solution phase and either MCO_3 in nanocrystalline form or mixed carbonate phase (like double carbonate phase) may be formed.

When the $M(NO_3)_2$ concentration is increased to the same level as the $Ca(OH)_2$ concentration under the same experimental conditions, it is highly likely that a mixed carbonate phase such as a double carbonate containing M^{2+} together with $CaCO_3$ will begin to precipitate. This may suggest that with the increase of M^{2+} in the system, not only the $CaCO_3$ core grows, but also a mixed carbonate phase containing M^{2+} starts to precipitate. However, in experiments with thermodynamically unstable metal ions (like Co), even if some mixed carbonate phase is synthesized, it may be oxidized by the oxygen of the air. The resulting solid particles may exhibit variations in color and morphology or some distortion of the crystal lattice.

The ideal ratio for the formation of double carbonates is 1:1¹⁴⁸. In our opinion, this approach is considered as the average of the whole sample on a macro scale. When we consider the micro scale, different results are obtained from the macro scale. Even if the M^{2+}/Ca^{2+} ratio is not 1:1 in our experiment, the ions in the solution may have a stoichiometry of 1:1 on the micro scale.

4.2. Reaction Mechanism for Direct Mixing Method

Reaction kinetics studies the rate of a chemical reaction over time and the mechanism by which it proceeds. In precipitation reactions, the rate at which ions in solution reach saturation and form solid phase is critical. When the ions in water rise above a certain saturation level, they tend to precipitate. The closer the degree of saturation index (SI) to 0, the more prone to precipitation, and the $SI > 0$ supersaturation, the faster we see nucleation formation and growth.

pH is a critical parameter that directly affects both the form in which CaCO_3 will precipitate (calcite, vaterite and aragonite) and the chance of two different cations such as $\text{M}^{2+} / \text{Ca}^{2+}$ forming a new phase (double carbonate) together. This rate determines both the final crystallite size, crystal morphology and polymorphic structure. The higher the pH, the more carbonate (CO_3^{2-}) forms in solution, while the lower the pH, the more bicarbonate (HCO_3^-) or carbonic acid (H_2CO_3) forms dominate. If metal ions are present in the solution, they may partially enter the CaCO_3 crystal lattice or attach to the crystal surface, changing the growth rate or shape. When the surface morphology is examined, CaCO_3 forms with different formations can be seen.

When ions move out of the solution and form solid precipitate, the remaining free ions drop and so does the liquids conductivity. The net change indicates the balance between reaction rate and feed rate. If the signal settles at a steady level or creeps upward, the rate of precipitation has probably leveled off. Conversely, during a burst of fast reaction, the meter may suddenly plunge, or its sharp rise may briefly stall, revealing a fleeting moment of imbalance.

4.3 Chemical Synthesis of $\text{BaCa}(\text{CO}_3)_2$

4.3.1 Batch Reactor Experiment for $\text{BaCa}(\text{CO}_3)_2$ Synthesis

Three different concentration scenarios were tried for the synthesis of $\text{BaCa}(\text{CO}_3)_2$. In the first scenario, low $\text{Ba}(\text{NO}_3)_2$ solution results were observed. In the first part of the experiment, $\text{Ba}(\text{NO}_3)_2$ concentration was kept constant at 0.3 mM considering the solubility

constant in 1 liter of distilled water, Na_2CO_3 and CaCl_2 concentrations were kept constant at 25 mM each and $\text{Ca}(\text{OH})_2$ concentrations were varied as 0, 3, 5 and 10 mM. In the experiment without $\text{Ca}(\text{OH})_2$, the study could not be characterized because not enough particles could be obtained.

In the second scenario of the experiment, the concentrations of the stock solutions were again prepared at 25 mM each and the concentration of $\text{Ba}(\text{NO}_3)_2$ was adjusted to be equal to the concentration of $\text{Ca}(\text{OH})_2$ (5 mM each).

In the third scenario, this time the concentrations of Na_2CO_3 and CaCl_2 , were increased to 75 mM and 10mM $\text{Ba}(\text{OH})_2$ solution was used instead of nitrate solution.

4.3.2 Measured Reaction Kinetics Data from $\text{BaCa}(\text{CO}_3)_2$ Synthesis Attempt in Batch Reactor Experiment

By keeping the concentrations of $\text{Ba}(\text{NO}_3)_2$, CaCl_2 and Na_2CO_3 constant and varying the concentrations of $\text{Ca}(\text{OH})_2$ as 0, 3, 5 and 10 mM, respectively, the reaction kinetics of the effect of Ba^{2+} ion on CaCO_3 crystal structure and the formation of $\text{BaCa}(\text{CO}_3)_2$ were investigated as shown in Figure 22. Experiments developed for the chemical synthesis of $\text{BaCa}(\text{CO}_3)_2$ at pH shows how the effect of using different concentrations of $\text{Ca}(\text{OH})_2$ changes with time. In this experiment where 0 mM $\text{Ca}(\text{OH})_2$ was used, the pH value started with 5.44 at the beginning. This is due to the presence of $\text{Ba}(\text{NO}_3)_2$ solution in the reactor, which creates an acidic environment. As time progressed and CaCO_3 and other ions were added to the system, various reactions such as limiting the consumption of OH^- or decreasing the acidic species with the release of CO_3^{2-} started to increase the pH level rapidly and remained constant at 10.5 after 150 seconds.

Figure 22 (a) show the conductivity measurements of the experiment conducted. In the 0 mM $\text{Ca}(\text{OH})_2$ condition, the conductivity is relatively low at first 233.3 $\mu\text{S}/\text{cm}$ but increases over time to the highest values 1359 $\mu\text{S}/\text{cm}$. At first, when the pH is low pH= 5.44, the distribution of ionic species is different, but as the pH increases rapidly, more $\text{CO}_3^{2-}/\text{HCO}_3^-$ and Ca^{2+} can remain in solution. Thus, the ionic strength increases, and the conductivity gradually increases. Under conditions where the $\text{Ca}(\text{OH})_2$ concentration in the reactor is increased, precipitation can be faster in the early period since the initial pH is already high. As

precipitation increases, some ions are withdrawn from the medium and this causes the overall conductivity curve to remain lower than in the 0 mM experiment. The fluctuation in the first few measurements, especially in the 10 mM Ca(OH)_2 experiment, may be due to a sudden peak in the measurement due to the initially high OH^- concentration or the calibration and measurement sensitivity of the instrument. Then, as the system stabilizes, the curve takes the expected shape.

The higher the Ca(OH)_2 concentration (10mM), the higher the initial pH of the reactor. As can be seen in the Figure 22 (b), the pH starts from the lowest in the environment where Ca(OH)_2 is not used and the pH starts from the highest in the environment where it is used the highest. When Ca(OH)_2 is added to the system at different concentrations, it is seen that the pH value starts at around 11 at the beginning. The reason for this is related to OH^- ions. As the concentration increases, the pH value of the system increases. In the experiments where 3 mM, 5 mM and 10 mM Ca(OH)_2 were added, the initial pH was 10.8, 11.0 and 11.4, respectively; as time passed, the pH stabilized in the range of 10.4-11.0 without showing a great change. Since high Ca(OH)_2 concentration provides more OH^- ions to the medium, the pH is higher at the beginning and precipitation reactions are triggered faster. However, after a certain point, the pH stabilizes as the ions present in the system are depleted or reach equilibrium.

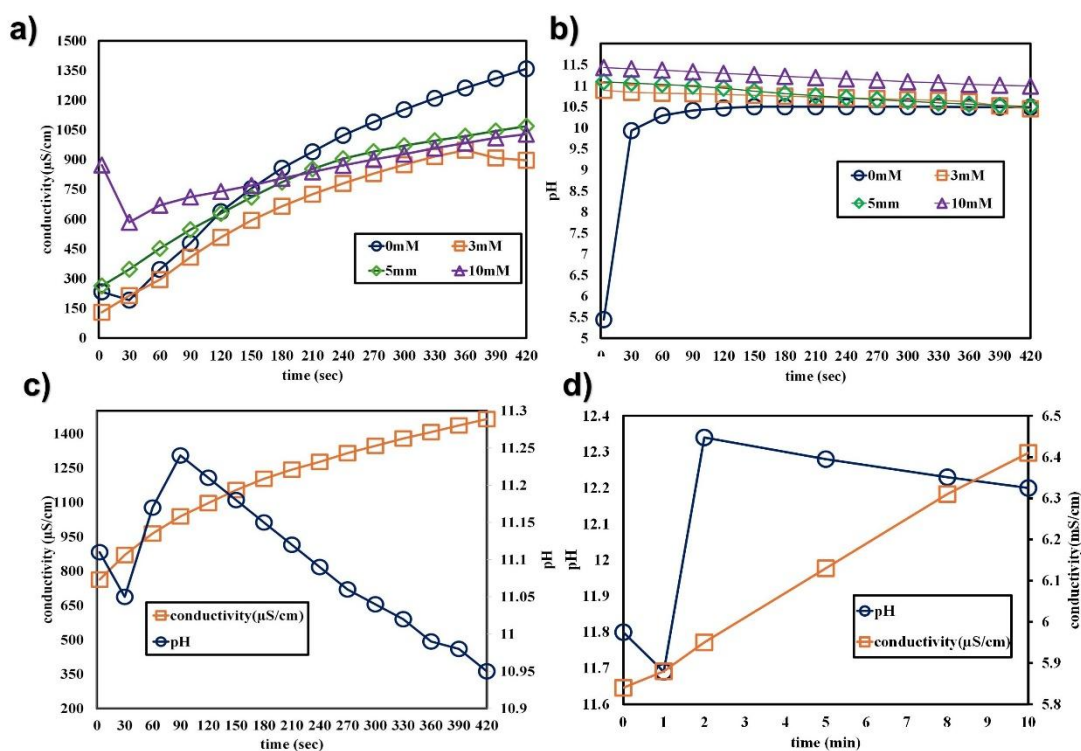


Figure 22. pH and conductivity changes of Ba experiments: a-b) conductivity and pH data for scenario 1; c) pH and conductivity results for scenario 2; d) pH and conductivity data for scenario 3.

Figure 22 (c), the pH and conductivity changes of the experiment carried out by adjusting the concentrations of the solutions in batch reactor to 5mM are shown. Initially, it starts with a rather high pH ≈ 11.11 , which is due to the strong basicity of the medium as a result of the presence of 5 mM $\text{Ca}(\text{OH})_2$ in the reactor. As time progresses, the pH first fluctuates slightly. Then it decreases to approximately $\text{pH} \approx 10.95$. This slight decrease can be explained by the ongoing precipitation of $\text{BaCa}(\text{CO}_3)_2$ and CaCO_3 in the medium consuming some of the OH^- ions. Nevertheless, the fact that the pH remains in the range 10.9-11.2 confirms that the environment is still quite basic and that the reactions proceed under these high pH conditions. The pH hovering around ≈ 11 and the presence of both Ba^{2+} , Ca^{2+} and CO_3^{2-} in the environment provide favorable conditions for the formation of $\text{BaCa}(\text{CO}_3)_2$.

In the first 3 seconds of the experiment, the conductivity is $763 \mu\text{S/cm}$, rising to $1464 \mu\text{S/cm}$ over time. This shows that the total amount of ions in the solution continues to increase. Although precipitation reactions draw some ions (Ba^{2+} , Ca^{2+} and CO_3^{2-}) into the

solid phase, factors such as solutions continuously fed into the system from the tubular reactor via a peristaltic pump and NO_3^- ions remaining in solution play a role in increasing the overall conductivity. So even if precipitation occurs, the conductivity increases over time because the net ion entry rate or the increased ion charge from nitrate is more dominant.

The result of the last parametric run attempted for the chemical synthesis of $\text{BaCa}(\text{CO}_3)_2$ is shown in Figure 22 (d). This time 10mM $\text{Ba}(\text{OH})_2$ was used in the batch reactor and the Na_2CO_3 and CaCl_2 solutions were adjusted to 75mM. Initially the pH is 11.8, decreasing slightly to 11.69 in the first minute, then rising abruptly to 12.34 in the second minute. It then decreases slightly to 12.28 at 5 minutes, 12.23 at 8 minutes and 12.20 at 10 minutes. The sudden increase in pH to 12.34 at 2 minutes indicates that a very basic environment is formed, probably as a result of the interaction of the fed Na_2CO_3 and CaCl_2 solutions with $\text{Ba}(\text{OH})_2$ in the batch reactor. The slow decrease in pH from 12.3 to 12.2 in the following minutes indicates that some of the OH^- ions in the medium were consumed in precipitation reactions with CO_3^{2-} in the presence of $\text{Ba}^{2+}/\text{Ca}^{2+}$.

Conductivity is 5.84 $\mu\text{S}/\text{cm}$ at minute 0, 5.88 at minute 1 and 5.95 at minute 2; that is, there is a very slight but continuous increase during the first 2 minutes. It then rises to 6.13 $\mu\text{S}/\text{cm}$ at 5 minutes, 6.31 $\mu\text{S}/\text{cm}$ at 8 minutes and 6.41 $\mu\text{S}/\text{cm}$ at 10 minutes. This slow but steady increase indicates that the total ionic strength created by the ions (Na^+ , Ca^{2+} , CO_3^{2-}) entering the medium continuously through the peristaltic pump is increasing over time. On the other hand, as solid phases such as $\text{BaCa}(\text{CO}_3)_2$ precipitate, some ions are withdrawn from the solution; but it is clear that the ion input from the feed or other anions remaining in the medium continue to increase the net conductivity.

Astilleros et al.¹⁴⁹ studied the incorporation of Ba^{2+} on the calcite surface in detail, with particular emphasis on the mechanisms of adsorption and incorporation of Ba^{2+} ions on calcite surface steps. It is stated that calcite grows predominantly at low to moderate Ba^{2+} concentrations, but as Ba^{2+} increases, transient or localized nucleation of Ba^{2+} -containing phases may occur. However, in most cases, due to factors such as the high ionic radius mismatch between calcite and Ba^{2+} and the pH/ion strength of the solution, a fully stable or abundant BaCO_3 phase is often not detected. They observed the formation of thick steps, two-dimensional nuclei and thus new Ba-rich phases on the surface after Ba^{2+} crosses the threshold for incorporation into calcite.

Both theoretical calculations (PHREEQC and Hydra-Medusa) and experimental analyses suggest that not only calcite but also $\text{BaCa}(\text{CO}_3)_2$ double carbonate and witherite phases become thermodynamically possible when Ba^{2+} increases in the medium. According

to PHREEQC calculations, when we change $\text{Ca}(\text{OH})_2$ concentrations in experiments with low Ba^{2+} concentrations (Figure 23, a-b), the SI values for calcite vary slightly. This can be explained by the fact that CaCO_3 added from tubular reactor to the continuous stirred system immediately dissolves and recrystallizes within seconds as soon as it is added to the system. For example, while the SI value of the calcite phase precipitated in tubular reactor was 3.13, the SI value of the calcite phase in the solution added to batch reactor and formed at the end of 1 minute started with 2.04 and became 2.76 at the end of 7 minutes.

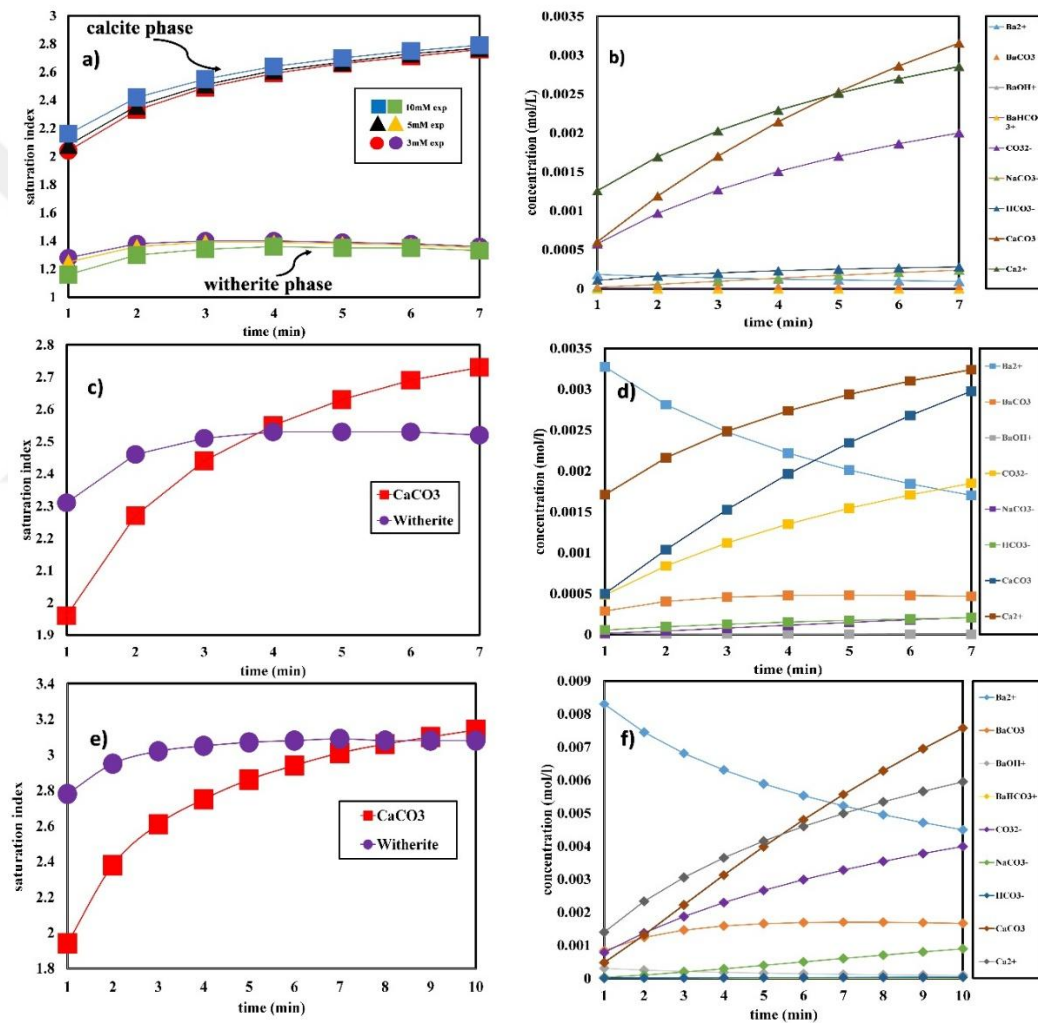


Figure 23. PHREEQC simulation of saturation indices and ion pairing for Ba systems: a-b) scenario 1, variable $\text{Ca}(\text{OH})_2$, low $\text{Ba}(\text{NO}_3)_2$; c-d) scenario 2, 5 mM $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{NO}_3)_2$ and, e-f) scenario 3.

Even though the saturation index of the witherite phase is positive ($SI = 1.28$) and thus indicates that precipitation is thermodynamically possible, the value still sits below that of calcite ($SI = 1.36$) after seven minutes of reaction. The data imply that witherite is less likely to crystallize than calcite during the early stage of the experiment. In such a case, it can be considered that the calcite phase may be more dominant in the system. Because when we examine the concentrations of the ion pairs formed in the solution over time, the fact that the concentrations of Ba^{2+} ion and the phases it forms are quite low can be considered as the inability of Ba^{2+} ion to doping the calcite crystal lattice. In such a case, Ba^{2+} may have absorbed on the calcite surface. When we consider the event from the opposite point of view, that is, when we increase the Ba^{2+} concentration this time, we theoretically calculated that the SI of the witherite phase is higher than that of calcite from 1 minute onwards ($SI_{witherite} > SI_{calcite}$) in Figure 23 (c&d). In Scenario#2, witherite $SI=2.31$ calcite $SI=1.96$ at 1 minute. The SI value of witherite remains constant from minute 4 onwards. This may indicate that witherite no longer forms a new phase in the solution or that it has reached dissolution-precipitation equilibrium. The SI value of calcite loses its rate of increase. These findings imply a decreasing precipitation rate, potentially signaling that the system is approaching equilibrium.

Since there is no thermodynamic data for $BaCa(CO_3)_2$ in the PHREEQC database or in the literature, we cannot take it into account in our theoretical calculations. Therefore, $BaCa(CO_3)_2$ phase may precipitate in a solution with high Ba^{2+} ion concentration where the witherite phase and calcite phase precipitate together. Since in XRD data, $BaCa(CO_3)_2$ peaks were detected in addition to calcite and witherite phases. Upon examining the data from Figure 23 (e&f), it is observed that increasing the Ba^{2+} concentration results in a higher saturation index for witherite compared to calcite. From the 7th to 8th minute, the SI become nearly identical, and the clear detection of the $BaCa(CO_3)_2$ phase in both XRD and SEM analyses strongly indicates that the transformation is complete from the 8th minute and ahead.

Hence, the Hydra-Medusa analysis results provide a framework which is consistent with experimental findings and data in the literature. At this point, the data we have obtained contribute to a better understanding of the formation mechanism of both $CaCO_3$, $BaCO_3$ and double carbonate phases. Figure 24 (a), shows that, in the pH~2-6 range, carbonic acid (H_2CO_3) and bicarbonate HCO_3^- are dominate in the solution. In the pH~6-9 range, $CaCO_3$ starts to precipitate in solid form. $BaCO_3$ precipitation was very limited as the Ba^{2+} level is low. We can observe that the predominant phase is calcite and Ba-containing species remain

in lower concentrations. In Figure 24, (b), higher Ba^{2+} concentrations promote the formation of solid BaCO_3 and increase the abundance of soluble species such as BaHCO_3^+ . In Figure 24 (c), the pH of the medium is at its highest value compared to the others. The possibility of the formation of the witherite phase becomes higher. In the figure, the convergence of the calcite and witherite lines is clearly seen, especially when the $\text{pH} > 6-7$ range. Due to the lack of specific database, the exact reflection of the $\text{BaCa}(\text{CO}_3)_2$ double carbonate phase is not seen in Hydra-Medusa.



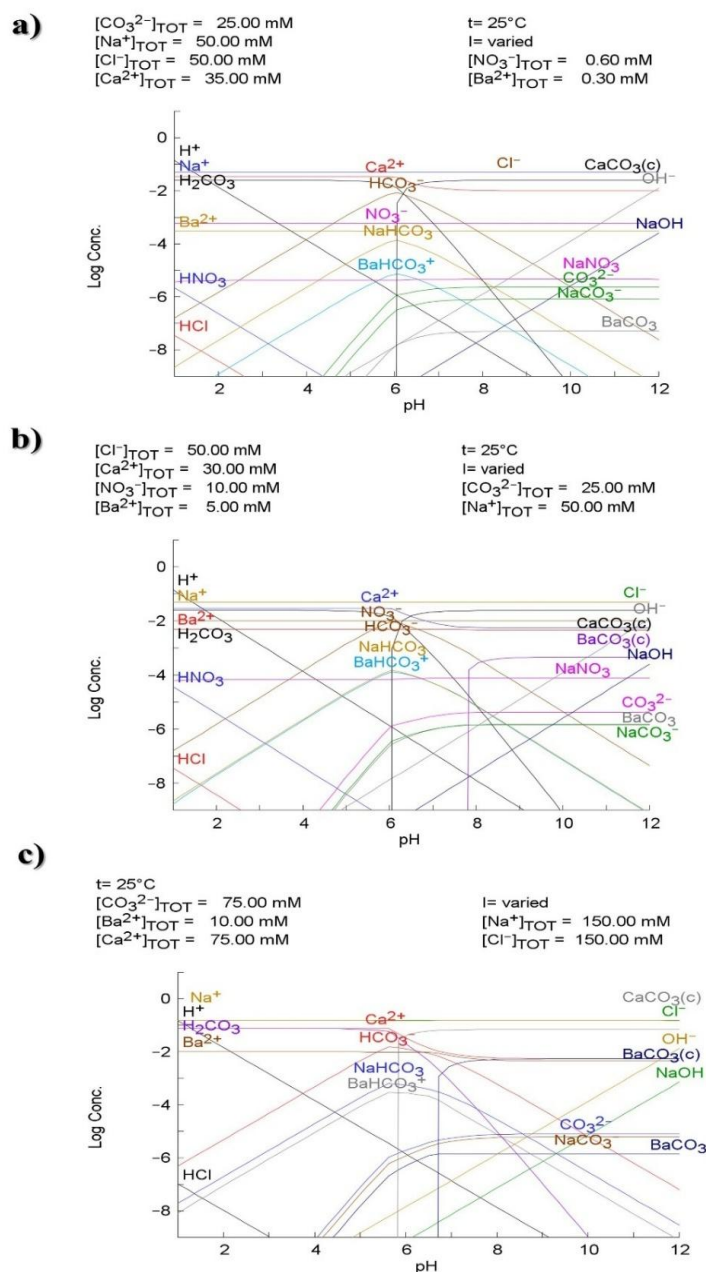


Figure 24. Speciation trends during carbonate and double carbonate precipitation under different scenarios. Data from MEDUSA–Hydra database. a) scenario #1; b) scenario #2, and c) scenario #3.

We can conclude that the amount of OH^- in the medium largely determines the initial pH and hence the precipitation reactions started. In conditions with low initial pH, precipitation delayed, while as the pH increases rapidly, the ion distribution in the solution changes and the conductivity eventually become higher. In contrast, at high

initial pH, precipitation is triggered rapidly at an early stage, so that the transition of ions to the solid phase starts sooner. However, ions that continue to enter the system due to the continuous feed flow can still lead to an increase in conductivity over the duration of the experiment. Increasing the concentration of barium ion (Ba^{2+}) facilitates the formation of double carbonate structures, $\text{BaCa}(\text{CO}_3)_2$. As observed in the experimental results, $\text{BaCa}(\text{CO}_3)_2$ starts to precipitate rapidly when the pH is high enough and Ca^{2+} and CO_3^{2-} ions are present in the solution.

4.3.3 SEM & EDX data from $\text{BaCa}(\text{CO}_3)_2$ Synthesis Attempt in Batch Reactor Experiment

Scanning Electron Microscope (SEM) images and Energy-dispersive X-ray analysis (EDX) of scenario #1 experiments by varying $\text{Ca}(\text{OH})_2$ concentration are shown in Figure 25. Figure 25 (a) depict the CaCO_3 structures obtained using a low concentration 3 mM of $\text{Ca}(\text{OH})_2$, Figure 25 (b) describe the morphology of the samples synthesized with medium 5 mM, Figure 25(c) with high 10 mM $\text{Ca}(\text{OH})_2$ concentration. In the experimental setup, CaCO_3 particles formed in tubular reactor dissolve and recrystallize when added to batch reactor. Since the low $\text{Ca}(\text{OH})_2$ concentration offers relatively more limited nucleation and growth conditions, SEM images show that calcite crystals tend to agglomerate. In the 3 mM $\text{Ca}(\text{OH})_2$ experiment, two peaks belonging to the NaCl phase were detected in the XRD data as well as calcite peaks. In parallel, the presence of Na^+ and Cl^- elements was observed in Energy-dispersive X-ray analysis (EDX) analysis, which confirms the formation of NaCl. Although no NaCl morphology is observed in SEM images, but XRD and EDX indicate that there is some NaCl in the content. NaCl crystals may be formed in much smaller size compared to CaCO_3 crystals. In this case, we think that NaCl is present between the particles. In addition to the calcite-specific basic elements C, O and Ca, a Ba signal was also detected, which appears to originate from the $\text{Ba}(\text{NO}_3)_2$ solution used but it did not appear to form a separate Ba-phase. When the concentration of $\text{Ca}(\text{OH})_2$ is increased to 5 mM, the pH and ion concentration of the medium increases, promoting more regular and homogeneous growth of the crystals. As seen in Figure 25 (b) and Figure 25 (c), calcite crystals exhibit planar surfaces with sharper edges and

rhombohedral structure. Compared to the 3 mM experiment, although aggregation persists, the edges and surfaces of the crystals are more clearly defined. EDX results also showed predominantly C, O and Ca elements in these samples, while NaCl peaks were not observed. This suggests that the NaCl phase has disappeared or is at a very low level compared to the 3 mM sample. At even higher Ca(OH)_2 concentration (10 mM) the alkalinity and ion density of the system increased. This may affect the crystal growth and morphology, favoring the transformation of calcite crystals into larger structures. SEM images show calcite crystals as larger aggregates compared to the previous samples. EDX results again confirm the predominance of the elements C, O and Ca; XRD data also confirm the formation of single-phase calcite. The conclusion drawn from these findings is that as the Ca(OH)_2 concentration increases, calcite crystals exhibit sharper, rhombohedral forms and the aggregation tendency decreases and the crystal surfaces appear more clearly. All the data obtained (SEM, XRD, and EDX) clearly showed that only calcite crystals were formed under the experimental conditions and the $\text{BaCa(CO}_3)_2$ double carbonate could not be synthesized under these conditions.

When the SEM images obtained from scenario #2 in Figure 26 are examined, the microstructural characteristics of the material at 10 μm and 5 μm scales show the presence of interconnected, irregularly shaped and agglomerated particles. Unlike the morphology in scenario #1, this time Ba^{2+} is better integrated into the crystal lattice, deviating from the typical growth pattern of calcium carbonate, reflecting the characteristics of the $\text{BaCa(CO}_3)_2$ phase in both SEM and XRD data. Considering that barium peaks are also evident in these regions in EDX analysis, it can be suggested that these areas belong to the $\text{BaCa(CO}_3)_2$ phase. While the calcite phase generally appears as round, homogeneous and interlocked aggregates, the regions belonging to the $\text{BaCa(CO}_3)_2$ phase are more distinct and can be described as crystals with layers, sharp edges and irregular morphological details.

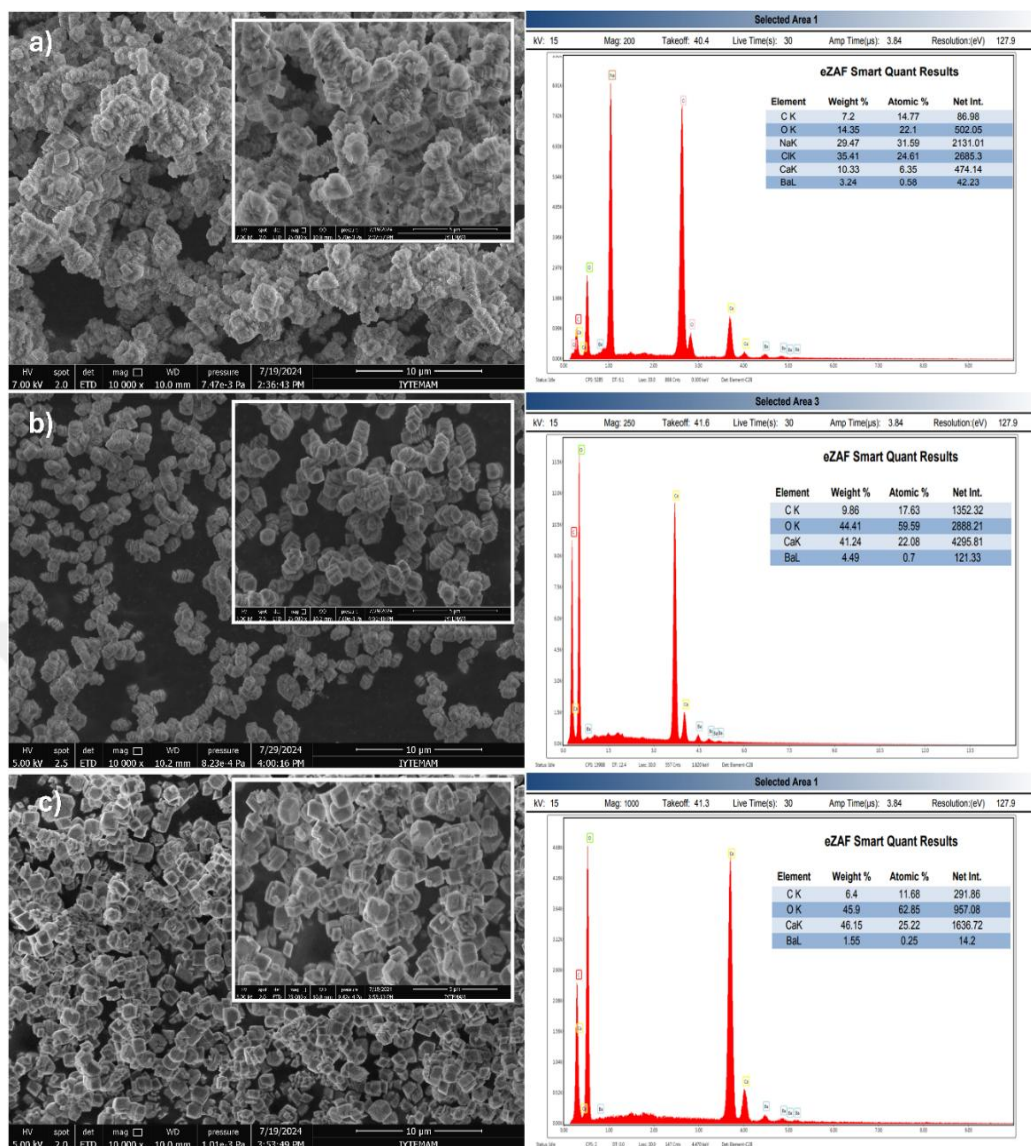


Figure 25. SEM and EDX results of scenario#1 in the Ba-related study. (a) 3mM Ca(OH)₂, (b) 5mM Ca(OH)₂ and (c) 10mM Ca(OH)₂ experiment using.

EDX analysis was performed on spectra taken from two different regions of the sample and carbon, oxygen, calcium and barium elements were detected. In the first region, 3.95 wt% C, 37.99 wt% O, 34.32 wt% Ca and 23.74 wt% Ba content was measured, while in the second region 3.84 wt% C, 39.43 wt% O, 35.06 wt% Ca and 21.67 wt% Ba were detected. These values were analyzed when in terms of atomic percentages, 8.81% C, 63.62% O, 22.94% Ca and 4.63% Ba in the first region and 8.37% C, 64.57% O, 22.92% Ca and 4.13% Ba in the second region. When the carbon and oxygen atomic ratios are analyzed, there may be deviations from the theoretical carbonate structure.

These deviations may be due to the limitations of the EDX technique in the quantification of light elements, especially carbon. However, the elemental composition and ratios support the presence of carbonate minerals. In the areas examined, the particles were seen to be micrometer-sized and porous structures were discerned. Such a morphology indicates that the material has a high surface area and may have the potential to be suitable for adsorption and catalysis.

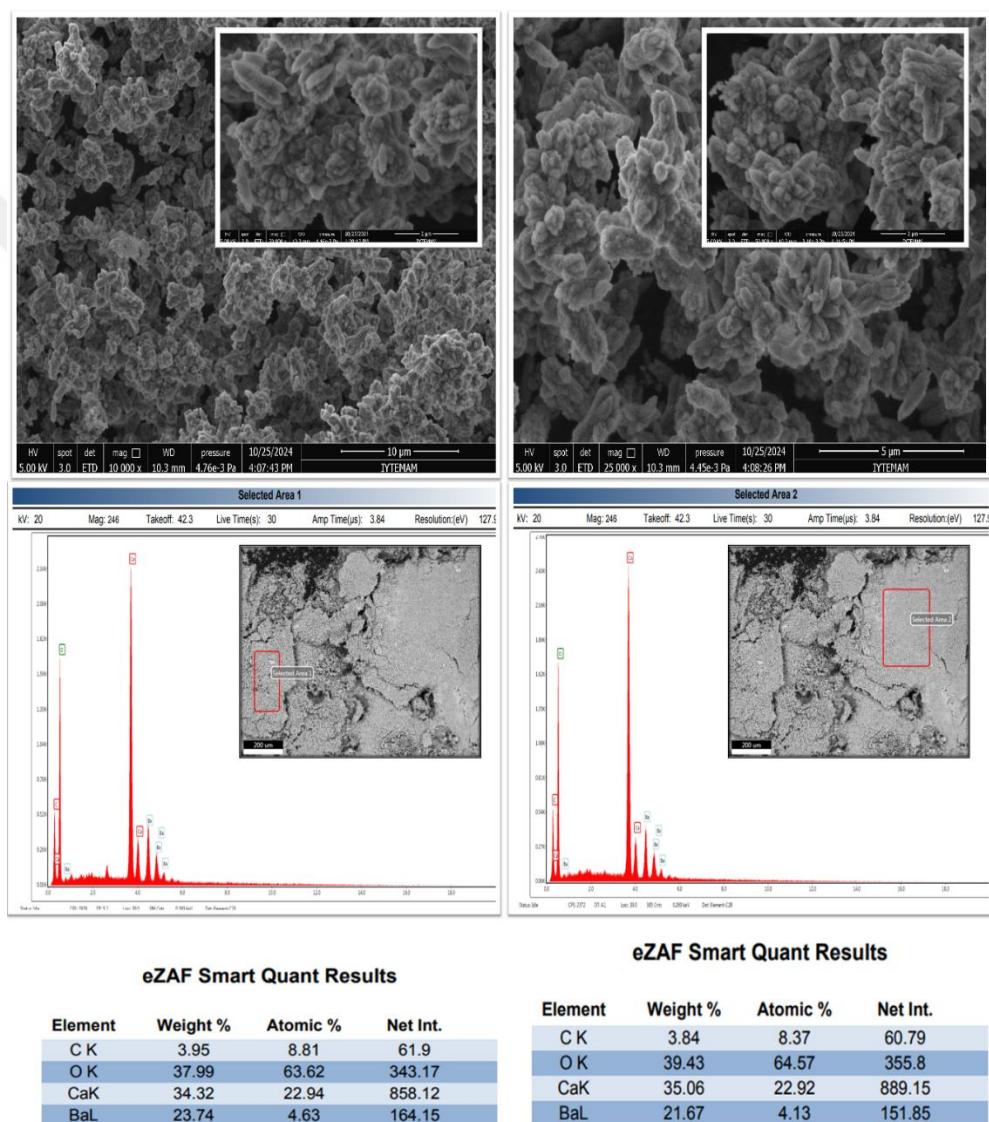


Figure 26. SEM and EDX results of scenario#2 in the Ba-related study.

The morphological changes of the products obtained at different times in the system with higher Ba^{2+} ion concentrations are shown in Figure 27. The observed particle morphology and surface structure have undergone significant changes over time. In the first 1 and 2 minutes of the experiment, amorphous-like crystalline grounds were observed. This may be due to the high degree of saturation index of witherite and calcite respectively. Although both Ba^{2+} and Ca^{2+} are present in the EDX, there is a clear difference in their contents. This can be explained by the fact that calcite, which is constantly added to the system, causes Ca^{2+} consumption due to its dissolution and recrystallisation. Since carbon (C) and oxygen (O) are classified as light elements in the periodic table, they may sometimes not be detected accurately in EDX analysis¹⁵⁰ even if they are present in the material. As the precipitation continues and time passes, an increase in the size and surface texture of the particles as well as particles towards cauliflower structures are observed after 5 minutes. For the 5-minute sample, at 10 and 10,000x magnification, cauliflower-like structures, cubic calcite formations and witherite are observed. Here, needle like particles seem to be aragonite, but they have a much thicker morphology. After 8 minutes, the growth stops, and the double carbonate phase can be easily detected. Since we observe a more balanced distribution in the $\text{Ba}^{2+}/\text{Ca}^{2+}$ ratio in the table showing the number of elements, these data support the prevalence of the alstonite phase. In addition, in EDX analysis, the fact that the regions with high Ba and Ca content correspond to different areas in the microstructure indicates that the alstonite crystals grow ‘heterogeneously’ or are in the process of partial transformation. This indicates that during the formation of the alstonite phase, the witherite and calcite phases still exist in some regions. In 10 minutes, as the formation of alstonite increases, the particle morphology becomes more regular.

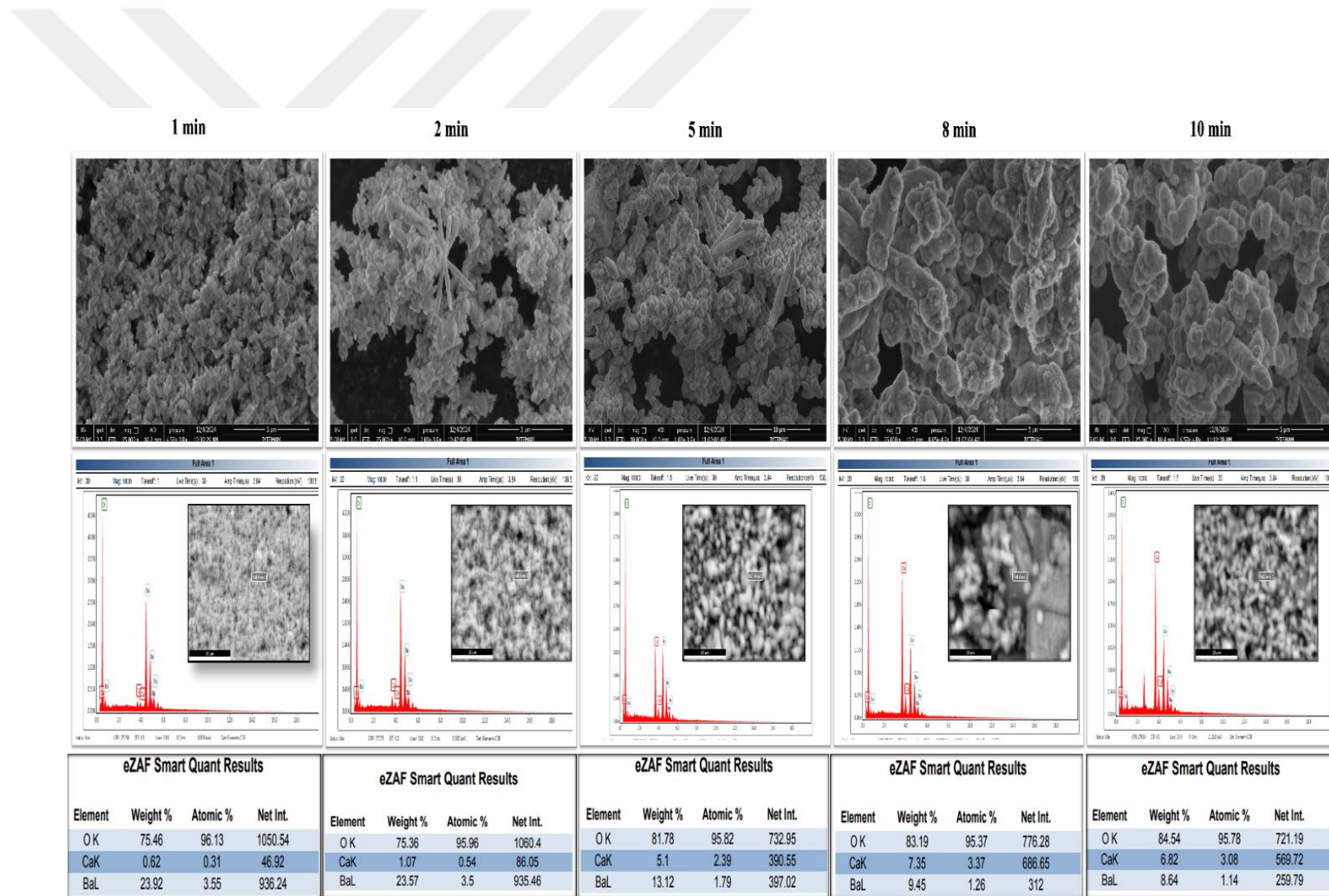


Figure 27. SEM and EDX results showing the formation of $\text{BaCa}(\text{CO}_3)_2$ at different time intervals in the scenario #3.

4.3.4 XRD data from BaCa(CO₃)₂ Synthesis Attempt in Batch Reactor Experiment

X-Ray Diffraction (XRD) data of the parametric study by varying Ca(OH)₂ concentrations are shown in Figure 28. X'Pert HighScore Plus software and International Diffraction Database (ICDD PDF-2) were used for phase identification in XRD analysis. In the studies carried out at three different concentrations, it was observed that the peak belonging to the calcite phase (PDF # 01-072-1937) was dominant.

In the study carried out at low concentration, characteristic peaks belonging to the NaCl (PDF # 01-077-2064) phase were also detected in the XRD pattern. This can be explained by the crystallization of soluble salts during drying.

In the experiment using 5 mM Ca(OH)₂, it was observed that the peaks belonging to NaCl decreased, but the calcite peaks became more prominent. This indicated that the product incorporated into the medium from tubular reactor dissolve is the presence of Ca(OH)₂ in the solution, recrystallizes and precipitates back to CaCO₃ as calcite. When 10 mM Ca(OH)₂ was used, NaCl peaks were no longer observed in the XRD pattern, while the peaks belonging to the calcite phase became more intense. The observation of only calcite phase in the solution was not prominent due to the low Ba²⁺ ion concentration since the K_{sp} value of BaCO₃ K_{sp}= 2,58*10⁻⁹ ¹⁵¹ is much lower than the K_{sp} value of CaCO₃ K_{sp}= 4.8*10⁻⁹. ¹⁵²

Crystallite size calculations were made using the data obtained from XRD analyses. In these calculations based on Scherrer equation, it was determined as 50.8 nm at 3 mM Ca(OH)₂ concentration, 41.9 nm at 5 mM Ca(OH)₂ concentration and 43.04 nm at 10 mM Ca(OH)₂ concentration.

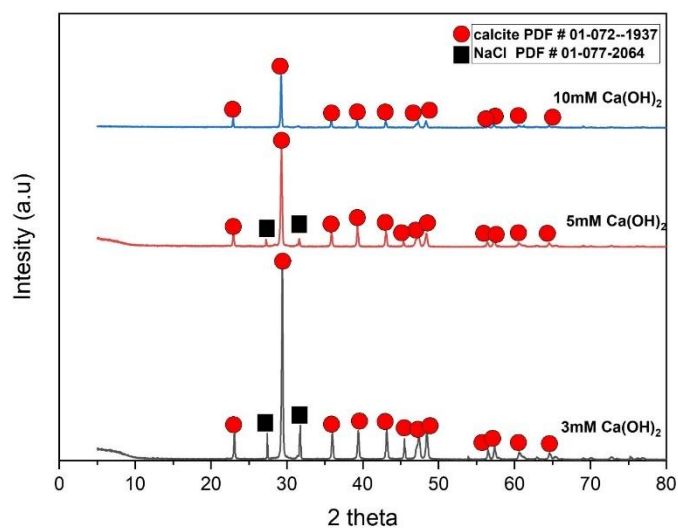


Figure 28. XRD patterns obtained from experiments using different Ca(OH)_2 concentrations in the Ba-related study.

In scenario #2, it was determined that three different phases (calcite, barytocalcite and witherite) were present in the sample in the XRD pattern of the experiment performed at equal concentrations of $\text{Ba(NO}_3)_2$ and Ca(OH)_2 (Figure 29). The peaks shown with squares in the graph belong to calcite (PDF # 01-086-2342), circles to barytocalcite (PDF # 00-015-0285) and triangles to witherite (PDF # 01-085-0720) phase.

The crystallite size of each phase of the obtained crystal was calculated by Scherrer equation. In this context, the average size of calcite was calculated as 45.96 nm, barytocalcite 62.05 nm and witherite 28.85 nm.

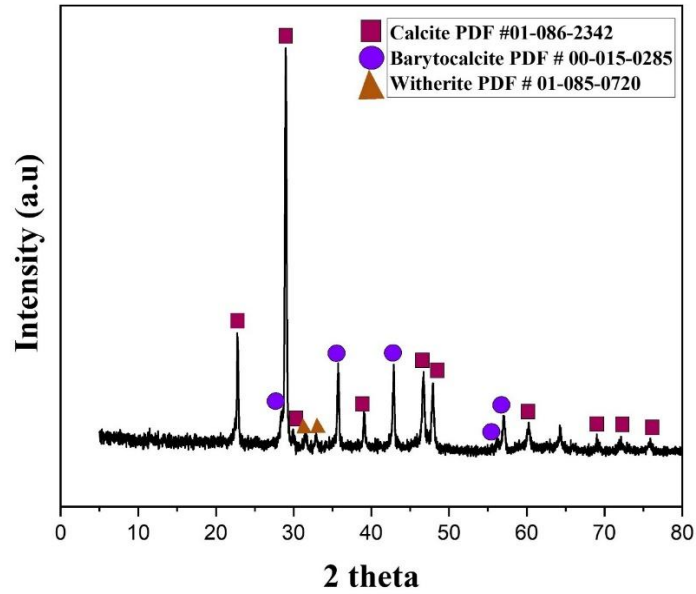


Figure 29. XRD patterns of calcite (square), barytocalcite (circle), and witherite (triangle).

In scenario #3, samples were taken at different times (2, 5, 8 and 10 minutes) of the experiment, which lasted 10 minutes in total, and examined by XRD analysis as shown in Figure 30. Circles symbolize alstonite (PDF # 00-003-0322), squares symbolize calcite (PDF # 01-086-2339), and triangles symbolize witherite (PDF # 00-041-0373).

Before the addition of crystallization medium from the tubular reactor, cubic calcite and spherical vaterite were CaCO_3 particles. When these particles were dispersed in Ba(OH)_2 solution, they dissolved and recrystallized into new crystalline forms, mostly alstonite, barium carbonate, and calcite, but not vaterite or aragonite. The XRD graph of the sample obtained in 2 minutes shows low intensity peaks. These results suggest that the crystallization process of the sample is still in the initial stage and the crystal structures were not fully developed. At 5 minutes crystallization time, a slight increase in peak intensities was observed. This indicates that the crystallization process was still in progress, and the crystal structures of the minerals were to develop. If the products from the tubular reactor continue to be added to the batch reactor, the maturation and growth of the crystal continued and a more pronounced increase in peak intensities were observed at the 8 min treatment time. These results indicated that the crystallization process reached an advanced stage, and the crystal structures became more regular. At 2 min, BaCO_3 and CaCO_3 as well

as $\text{BaCa}(\text{CO}_3)_2$ were detected, but in the 8-10 min interval the material crystallized completely as the alstonite polymorph of $\text{BaCa}(\text{CO}_3)_2$.

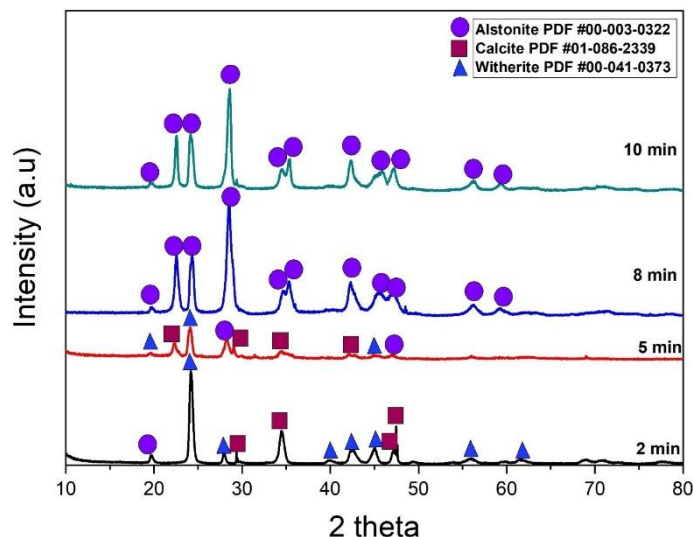


Figure 30. XRD patterns of calcite (square), alstonite (circle), and witherite (triangle).

4.4. Developed Methods for the Chemical Synthesis of $\text{CoCa}(\text{CO}_3)_2$

4.4.1 Direct Mixing Method for $\text{CoCa}(\text{CO}_3)_2$ Synthesis

Cobalt nitrate hexa-hydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and sodium carbonate (Na_2CO_3) solutions were prepared separately in 1 liter of ultrapure deionized (DI) water according to the solubility of the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. In accordance with the $\text{Co}^{2+}/\text{Ca}^{2+}$ ion ratio of 0.5, 1 and 2, each solution was added to a reactor with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2$ and then 200 ml of Na_2CO_3 solution in each of the 3 experiments unless otherwise stated.

4.4.2 Batch Reactor Experiment for $\text{CoCa}(\text{CO}_3)_2$ Synthesis

Two different concentration scenarios were tried for the synthesis of $\text{CoCa}(\text{CO}_3)_2$. In the first scenario, low $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution results were observed. In this scenario, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ concentration was kept constant at 2.75 mM considering the solubility constant in 1 liter of distilled water, Na_2CO_3 and CaCl_2 concentrations were kept constant at 25 mM and only $\text{Ca}(\text{OH})_2$ concentrations were varied as 0, 3, 5 and 10 mM respectively for 4 different experiments.

In the second scenario of the experiment, the concentrations of the stock solutions were again prepared at 25 mM each and the concentration of $\text{Co}(\text{NO}_3)_2$ was adjusted to be equal to the concentration of $\text{Ca}(\text{OH})_2$ (5 mM each).

4.4.3 Measured Reaction Kinetics Data from $\text{CoCa}(\text{CO}_3)_2$ Synthesis Attempt in Direct Mixing Experiment

The kinetics of the precipitation reactions were measured by recording pH and conductivity data. Figure 31 shows how pH and conductivity values change with time during the experiments with different initial ion mole ratios. The measurements took about 60 minutes and data were recorded at every 3 seconds. The data were subsequently categorized for every 5 minutes for a total of 60 minutes to observe pH and conductivity changes.

When the $\text{Co}^{2+}/\text{Ca}^{2+}$ ratio was 1, the initial pH value was 11.03 and decreased sharply to 10.8 in the first half hour. The metal ions in the system start to consume the CO_3^{2-} ions and in this process the release of H^+ ions or carbonate buffering lowers the pH. As a result, calcite and similar phases are formed. When we decrease the $\text{Co}^{2+}/\text{Ca}^{2+}$ ratio, it is seen that an excess of Ca^{2+} ions stabilize the chemical equilibrium of the system. Therefore, a very small change was observed in pH. In the opposite case, that is, when we increase the $\text{Co}^{2+}/\text{Ca}^{2+}$ ratio by 2 times, pH around 10.6. The resulting product oxidizes to Co_3O_4 after about 20-30 minutes in the drying process at 80°C . The reason for this could be related to O_2 in the air. When we look at the conductivity changes, the

conductivity decreased from 1494 $\mu\text{S}/\text{cm}$ to 1465 $\mu\text{S}/\text{cm}$ at the initial ratio of 1:1. This indicates that the free ions (Co^{2+} , Ca^{2+} , NO_3^- , CO_3^{2-}) in the solution decreased rapidly. In the experiment where Ca^{2+} ions are more dominant; conductivity in the solution during the precipitation stages due to the high amount of Ca^{2+} ions. Furthermore, the excess Ca^{2+} and the accompanying NO_3^- , being not yet completely precipitated, keep the conductivity high (1575 $\mu\text{S}/\text{cm}$). In the system with an excess of Co^{2+} ions (2:1), the conductivity initially remains at about 1550 $\mu\text{S}/\text{cm}$ and then decreases slightly. In general, NO_3^- and Na^+ ions remaining in the system in each experiment directly influence the total conductivity measured. Although these ions do not participate in precipitation, they can maintain the solution ionic strength ($I = \frac{1}{2} \sum C_i z_i^2$) at this high level. Especially, when there is an excess Ca^{2+} or Co^{2+} ions, NO_3^- as the counter ion also remains in solution. Consequently, even small changes in the $\text{Co}^{2+}/\text{Ca}^{2+}$ ratio can significantly alter the mechanism of the reaction, the composition of the final solid phases and the ionic environment.

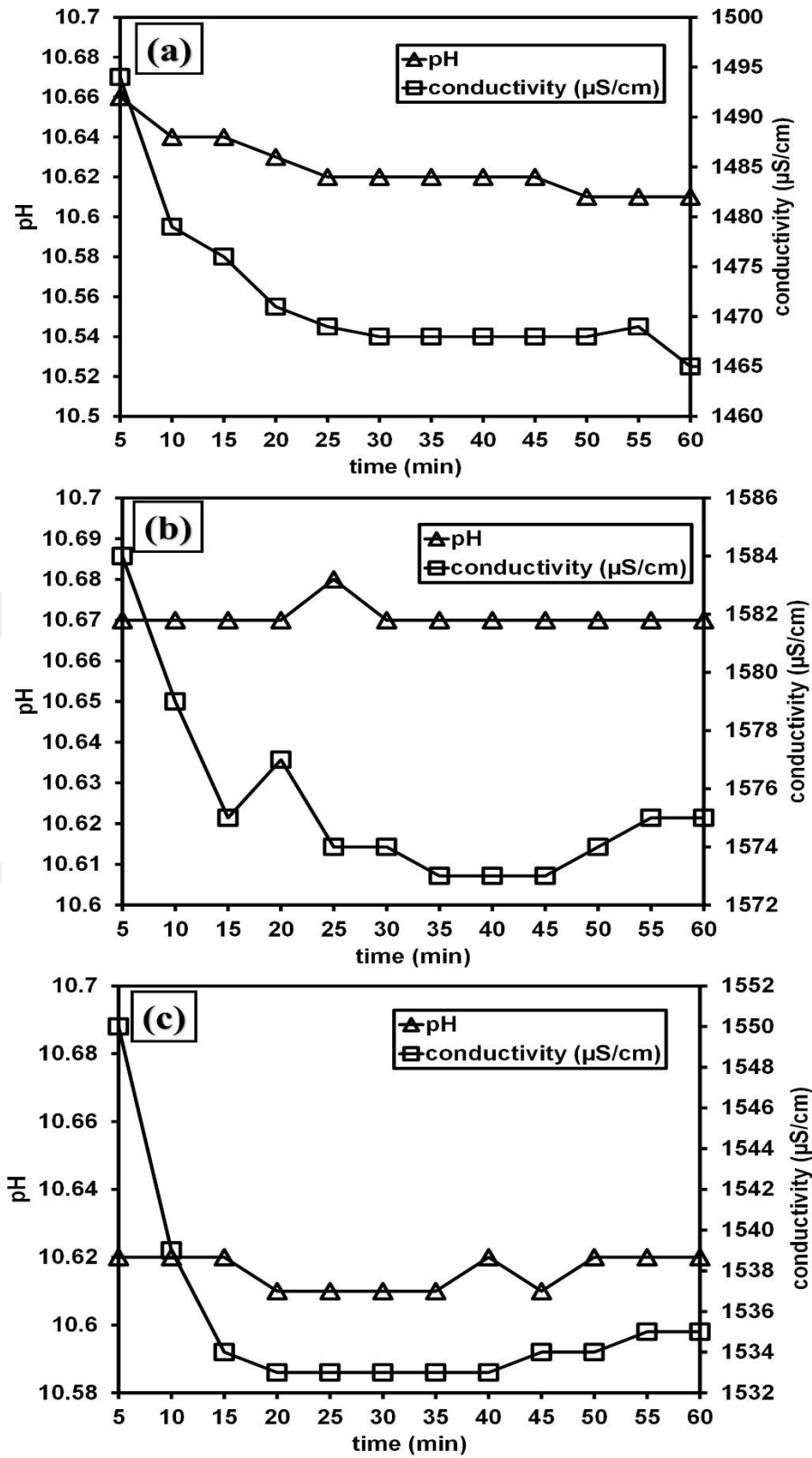


Figure 31. pH and conductivity measurements for Co-related experiments with different $\text{Co}^{2+}/\text{Ca}^{2+}$ ratios: (a) $\text{Co}^{2+}/\text{Ca}^{2+} = 0.5$, (b) $\text{Co}^{2+}/\text{Ca}^{2+} = 1$, and (c) $\text{Co}^{2+}/\text{Ca}^{2+} = 2$

4.4.4 Measured Reaction Kinetics Data from $\text{CoCa}(\text{CO}_3)_2$ Synthesis Attempt in Batch Reactor Experiment

Figure 32 shows pH and conductivity changes during the addition of CaCO_3 into $\text{Ca}(\text{OH})_2$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions. In the experiment without $\text{Ca}(\text{OH})_2$, the initial pH was around 8.3. Over the time, the pH started to gradually increase due to CO_3^{2-} ions added to the system. At the end of the 7th minute, the pH reached 9.6, showing a significant increase.

The system with $\text{Ca}(\text{OH})_2$ solutions at 3 mM and 5 mM concentrations had a higher initial pH compared to the system without $\text{Ca}(\text{OH})_2$. The pH, which started in the range of 8.5-8.7 in the first minutes, rapidly reached the values above 9.5 where it disordered. CaCO_3 , was added drop by drop to the system every second, started to recrystallize in the presence of $\text{Ca}(\text{OH})_2$ in the reactor. From the 3rd and 4th minutes, the pH started to stabilize in the range of 9.6-9.7 and slightly decreased. With 10 mM, pH was 9.7, initially. It peaked at 10.03 and then started decreasing to 9.9 over the experiment. This indicates that the high amount of OH^- ions in the medium triggered rapid precipitation; therefore, the crystallization started quite intensely in the early stages (Figure 32, a).

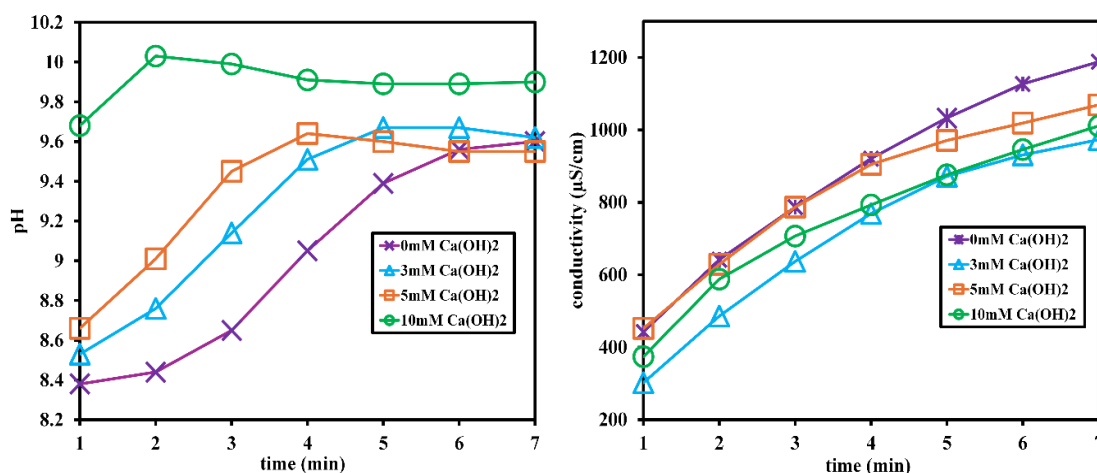


Figure 32. Time-dependent changes in pH and conductivity in the Co-related study. (a) pH changes, (b) conductivity changes.

For the conductivity measurements shown in Figure 32, (b). In the 0 mM Ca(OH)_2 experiment, Co^{2+} and Ca^{2+} were less likely to precipitate rapidly in the form of hydroxides or carbonates because no extra OH^- was added to the medium initially. This increased the conductivity over time by prolonging the residence time of free ions in solution. The Na^+ and Cl^- ions, which were fed into the reactor over time, remained in the solution, resulting in increased conductivity up to about 1118 $\mu\text{S/cm}$. When extra OH^- ions were added to the system, 973 $\mu\text{S/cm}$ in the 3 mM experiment and 1069 $\mu\text{S/cm}$ for the 5 mM experiment were obtained respectively. When we compare 3 and 5 mM Ca(OH)_2 concentration experiments, it is a point that can be considered why 5 mM shows higher conductivity although it has more precipitation potential than 3 mM. Possibly, the free ions accumulated in the solution may have increased the conductivity even more compared to the 3 mM experiment. At the highest Ca(OH)_2 concentration 10mM, a conductivity value of 374 $\mu\text{S/cm}$ was recorded at the beginning and 1011 $\mu\text{S/cm}$ at the end of 7 min. This value and the initial high pH may have triggered the precipitation of Co^{2+} and Ca^{2+} ions early and suppressed the accumulation of free ions in the medium to some extent. Therefore, very high basicity accelerates the precipitation and increases the transition to the solid phase and the amount of ions in the solution remains somewhat lower.

When we increase the Co^{2+} ion concentration up to 5 mM, we see that the pH value is clearly on the acidic side of $\text{pH}=5.85$ before the experiment starts (Figure 33). This marked difference is related to the Co^{2+} and NO_3^- ions in the solution shifting the medium to the acidic side at the first moment. When Ca(OH)_2 solution was added, the pH

rapidly increases to pH=8.39 and the conductivity to 382 $\mu\text{S}/\text{cm}$. This rapid rise was due to the OH^- ion concentration provided by the added $\text{Ca}(\text{OH})_2$.

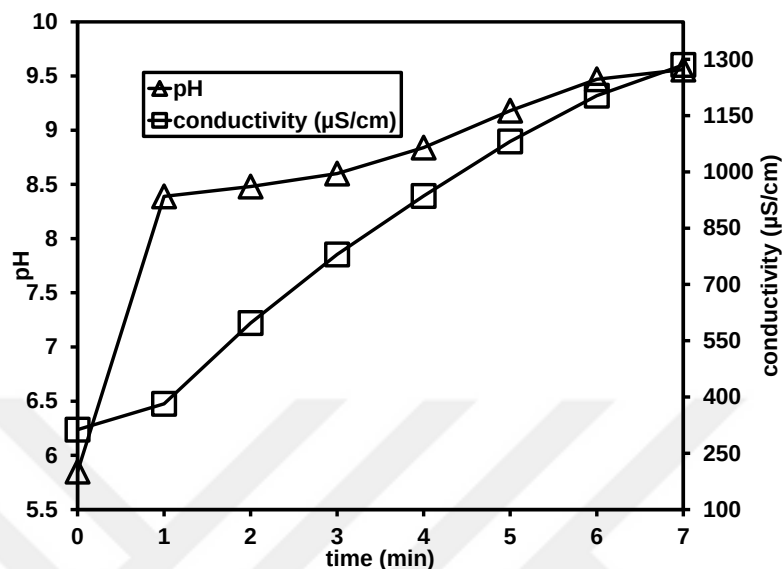


Figure 33. Time-dependent pH and conductivity behavior observed in the experiment with 5 mM $\text{Co}(\text{NO}_3)_2$ and 5 mM $\text{Ca}(\text{OH})_2$.

At the end of the 2nd minute, pH increased to steadily to 8.48, at the end of the 3rd minute to 8.60. Especially after the 5th minute, the pH rises above 9.0 and reached to a very basic value of 9.56. The presence of Co^{2+} ions and the same amount of $\text{Ca}(\text{OH})_2$ in the system caused an increase in the total ionic charge. Na^+ and Cl^- ions are also continuously fed into the system. After 7 min, the final value of 1285 $\mu\text{S}/\text{cm}$ was higher than in the previous experiment with 2.75 mM Co^{2+} . This might be explained by the approximately twofold increase in the initial Co^{2+} concentration, which results in a higher overall ionic charge in the system.

4.4.5 SEM Images from $\text{CoCa}(\text{CO}_3)_2$ Synthesis Attempt in Direct Mixing Experiment

Figure 34 shows the morphology of the obtained crystals. Especially Co_3O_4 nano particles is interested. Figure 34 (g,h and j) shows that the synthesized sample has an aggregated multi-particle morphology. These nanoparticles are aggregated in a thick layer with gaps and a porous structure between them. The formation of cobalt oxide in the sample containing dense $\text{Co}^{2+}(\text{r}=2)$, the nanospheric structure, the highly porous and hierarchical morphology of this material has an important potential for catalysis, energy storage, sensors and environmental applications.

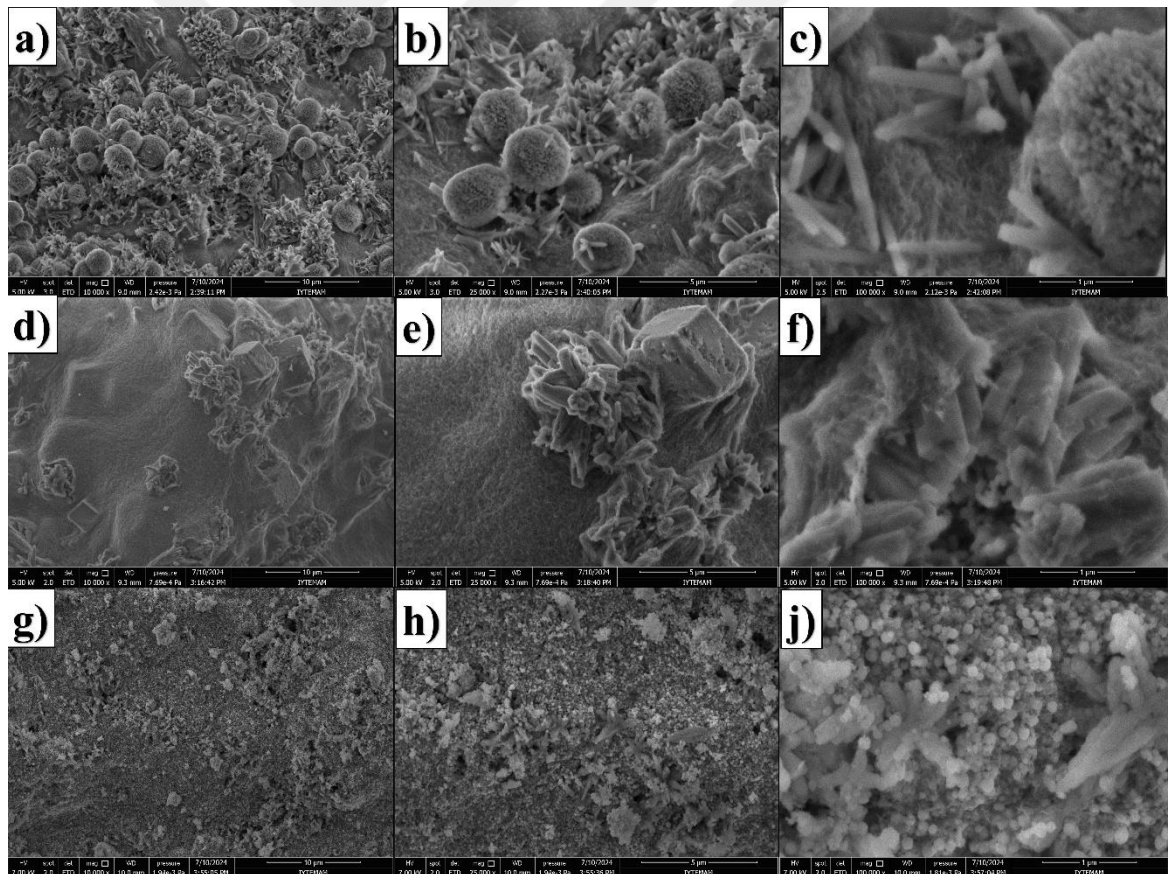


Figure 34. SEM images from the Co related study. (a-c) $\text{Co}^{2+}/\text{Ca}^{2+}=0.5$; (d-f) $\text{Co}^{2+}/\text{Ca}^{2+}=1$ and (g-j) $\text{Co}^{2+}/\text{Ca}^{2+}=2$.

Although many different shapes and sizes of Co_3O_4 are reported in the literature (spherical, polycrystalline, rod-like, even leaf-like or floral structures), particles with almost homogeneous size distribution are usually not reported. Here, a rich hierarchical organization is observed. This morphological finding stands out as the most prominent originality of this study.

Chen et al.¹⁵³ reported that nanoparticles were not suitable for photocatalytic applications because of their agglomeration into large sizes. The Co_3O_4 samples synthesized in our study exhibited a very favorable structure in terms of photocatalytic performance by maintaining high surface area for the average size of around 40 nm and limited agglomeration, thus providing advantages in terms of light absorption and reactive molecule absorption.

4.4.6 XRD data from $\text{CoCa}(\text{CO}_3)_2$ Synthesis Attempt in Direct Mixing Experiment

Figure 35 depicts the XRD patterns for particles obtained by using different $\text{Co}^{2+}/\text{Ca}^{2+}$ mole ratios. Each spectrum shows characteristic peaks belonging to the cobalt oxide (Co_3O_4) phase together with different polymorphs of calcium carbonate (calcite, aragonite and vaterite). In the sample for a $\text{Co}^{2+}/\text{Ca}^{2+}$ ratio of 0.5 (grey line), calcium carbonate is predominantly vaterite (2 theta= 24.88, 27.13, 32.66, 43, and 44), calcite (2 theta=29.4, 31.4, 36.06, 37.83, 38.59, 45.76, 50.18 and 52.34) and aragonite phases (26.13, 37.83, 38.55, 45.80, 50.18 and 52.34). In the sample for the $\text{Co}^{2+}/\text{Ca}^{2+}$ ratio of 1, the characteristic peaks for the vaterite phase significantly reduced and the calcite phase became more dominant. Characteristic peaks 2 theta= 29.4, 59.6 and 69 were measured. The fact that so little signal is evident since the material is both amorphous and the quantity is relatively small.

When the ion ratio of $\text{Co}^{2+}/\text{Ca}^{2+}=2$, a very interesting result was obtained compared to the previous. The blue line shows that both calcite and aragonite phases were observed, but the aragonite peaks are now more prominent than the calcite peaks. Also, the cobalt oxide phase is now more prominent. According to Rietveld analysis, the content is 55.7% Co_3O_4 , 43.4% aragonite and 0.9% calcite. 2 theta values were 18.83; 31.07;

36.67; 38.45; 44.62; 55.57; 59.19; 64.99 and 69 correspond to the reference patterns (PDF #01-080-1534) at (111), (220), (311), (222), (400), (422), (511), (440) and (531), respectively and confirming the cubic spinel structure of Co_3O_4 . Using the Bragg equation, cobalt oxide NP lattice constants ($\text{\AA}$) of $8.11\text{\AA}$ was recorded.

Crystallite size is estimated to range between 14.2-83.4 nm using the Debye-Scherrer's ¹⁵⁴ relation with an average size of 40.81 nm.

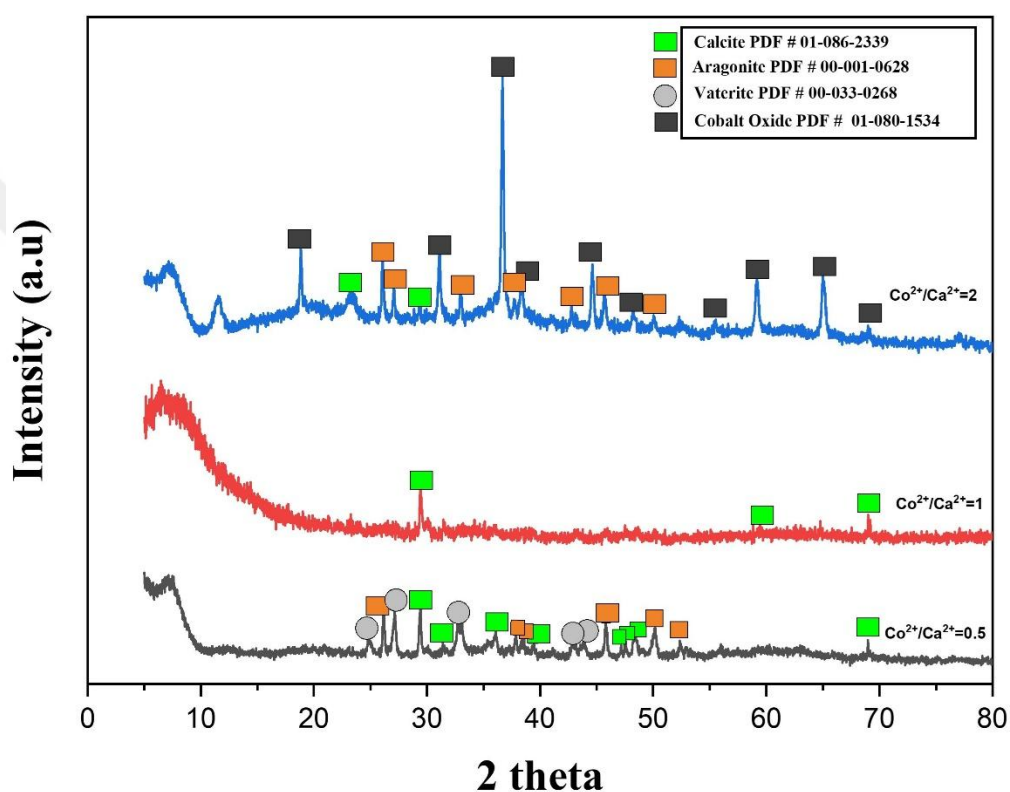


Figure 35. XRD patterns of experiments performed at different $\text{Co}^{2+}/\text{Ca}^{2+}$ mole ratios (0.5; 1 and 2). Calcite (star), aragonite (triangle), vaterite (circle) and cobalt oxide (square).

4.4.7 SEM & EDX Data from CoCa(CO₃)₂ Synthesis Attempt in Batch Reactor Experiment

The morphology of the crystals precipitated using different concentrations of Ca(OH)₂ solutions is shown in Figure 36. In the absence of Ca(OH)₂ in shown Figure 36 (a-d), distinct angular, rhombohedral or polygonal crystals are observed in some of regions, whereas in other regions more spherical and irregular structures as well as needle-like crystals are present, which is in line with the structures of calcite, vaterite and aragonite detected by XRD. Calcite has well-defined crystalline structures with rhombohedral or cubic edges. Vaterite is generally spherical, and aragonite tends to show needle-like crystal structures¹⁵⁵. These structures can be clearly observed, especially at 10,000x magnification. The reaction proceeded rapidly in the absence of the Ca(OH)₂ solution within the system. Although carbon has a significant share in the actual CaCO₃ structure, EDX sometimes has difficulty in accurately detecting light elements. The high occurrence of cobalt in the sample indicates that cobalt is present in significant quantities. However, this cobalt may be present without a distinct separate Co phase peak in the XRD pattern. This suggests that the cobalt was partially substituted during precipitation in the CaCO₃ crystal lattice or that an amorphous cobalt salt phase was dispersed in a microcrystalline form. EDX data clearly confirm the presence of cobalt (Figure 37, a). The absence of strong peaks in the XRD of cobalt's own crystal phase can be considered as partial doping into the CaCO₃ matrix or amorphous cobalt phases.

The use of 3 mM Ca(OH)₂ reveals a more distinctly needle-like or crystal morphology compared to crystallization with 0 mM Ca(OH)₂ (Figure 36, e-h). Such long and thin crystal structures are often associated with the aragonite form in the literature. The density of needle-like structures observed here suggests that calcium carbonate may have an increased tendency to aragonite. In the EDX analysis of the sample, cobalt was detected in a ratio of approximately 15.96 wt%. The presence of cobalt in this ratio indicates that Co²⁺ ions were partially incorporated into the calcium carbonate structure during precipitation (Figure 37, b).

In the case of using 5 mM Ca(OH)₂, the crystalline morphology of the precipitate exhibits a transformation into flower-like and layered structures (Figure 36, j-m). These features indicate a dual morphology; on one hand, there is evidence of needle-like or

bundle-like growth patterns that are typically associated with aragonite, while on the other hand, more angular or rhombohedral crystal characteristic of calcite can be observed in certain regions. This diversified morphology supports the multiphase distribution detected by the XRD analysis. Elemental analysis shows that calcium and oxygen are present in the highest weight percentages in the solid product, and the carbon content is within the anticipated range. Cobalt is detected at approximately 20.09%, which confirms its successful incorporation into the sample (Figure 37, c). The absence of a distinct cobalt phase in the XRD pattern suggests that cobalt may be integrated into the crystal lattice of the calcium carbonate or is accumulated in surface and amorphous regions. Additionally, trace amounts of sodium and chlorine likely originate from remnants of the precursor materials (Na_2CO_3 and CaCl_2) used during the crystallization.

In the SEM images for 10mM $\text{Ca}(\text{OH})_2$ concentration experiment (Figure 36, n-q), two distinct morphologies stand out: calcite crystals with a cubic shape and tiny structures flowers like crystallites. The presence of these varied crystal shapes can be attributed to the influence of cobalt ions on the crystal growth mechanism. However, there is no clear indication of a distinct new phase, such as $\text{CoCa}(\text{CO}_3)_2$, formed in the SEM images. According to the EDX results (Figure 37, d) the sample contains calcium, carbon, oxygen, cobalt, sodium and chlorine. Calcium (33.51%) and oxygen (39.42%) emerge as the dominant elements. The cobalt presence (21.94%) originates from the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the initial solution, which suggests that cobalt ions have partially incorporated into the crystal lattice. The lack of a new phase under these conditions could be linked to the energy barrier required for the full integration of cobalt ions into the crystal lattice not sufficiently overcome.

In scenario #2, significant differences in the crystal morphology are observed (Figure 36, r-u). Compared to the initial experiment, where large cubic crystals were predominant, increasing the Co^{2+} concentration to 5 mM while reducing $\text{Ca}(\text{OH})_2$ to 5 mM resulted in noticeable changes: the crystals became distinctly smaller, more irregular, and exhibited erosion along their edges. Additionally, the crystal surfaces generally appeared amorphous or less ordered. This suggests that the crystal growth rate and orientation are markedly influenced by the higher concentration of Co^{2+} ions. It can be inferred that introducing a greater amount of Co^{2+} ions into the medium may slow down the crystal growth, diminishing the ability of the resulting crystals to form homogeneous, ordered, and stable structures. Co^{2+} ions might play an inhibitory role in crystal growth, possibly by adsorbing onto the surfaces of CaCO_3 crystals or altering the surface energy

barriers. This could account for the observed amorphous and irregular morphologies. According to the EDX data, the sample contains carbon, oxygen, calcium, and cobalt (Figure 37, e). Notably, the atomic percentage of Co^{2+} ions (15.35%) is significantly higher. This increase aligns with the higher initial Co^{2+} concentration, indicating that Co^{2+} ions participate more actively in the crystal formation process. However, the conditions still do not appear sufficient to form a distinct phase such as $\text{CoCa}(\text{CO}_3)_2$.

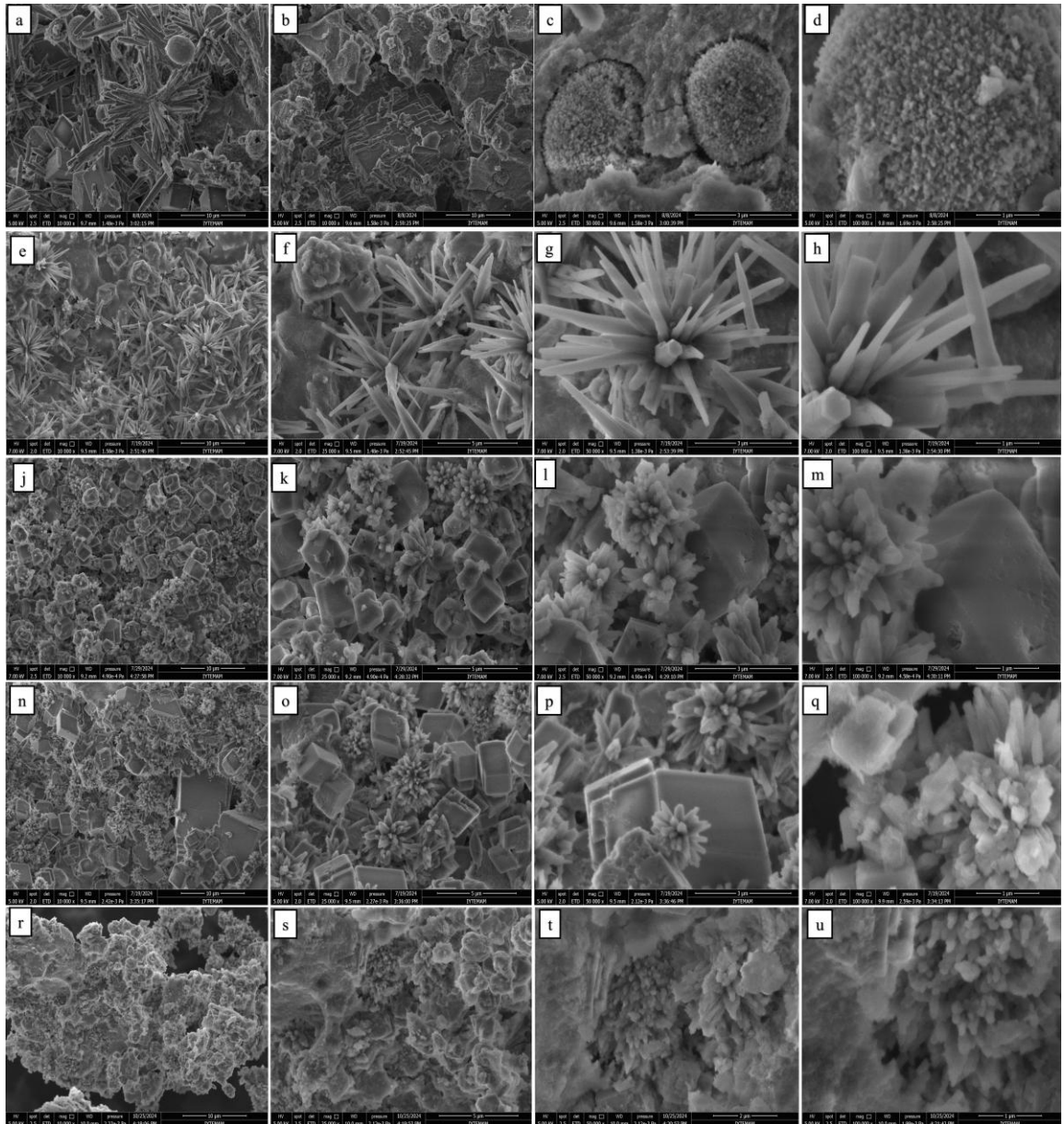


Figure 36. SEM images from the batch reactor experiment in the Co-related study. (a-d) 0 mM $\text{Ca}(\text{OH})_2$; (e-h) 3 mM $\text{Ca}(\text{OH})_2$; (i-m) 5 mM $\text{Ca}(\text{OH})_2$; (n-q) 10 mM $\text{Ca}(\text{OH})_2$ and (r-u) scenario #2.

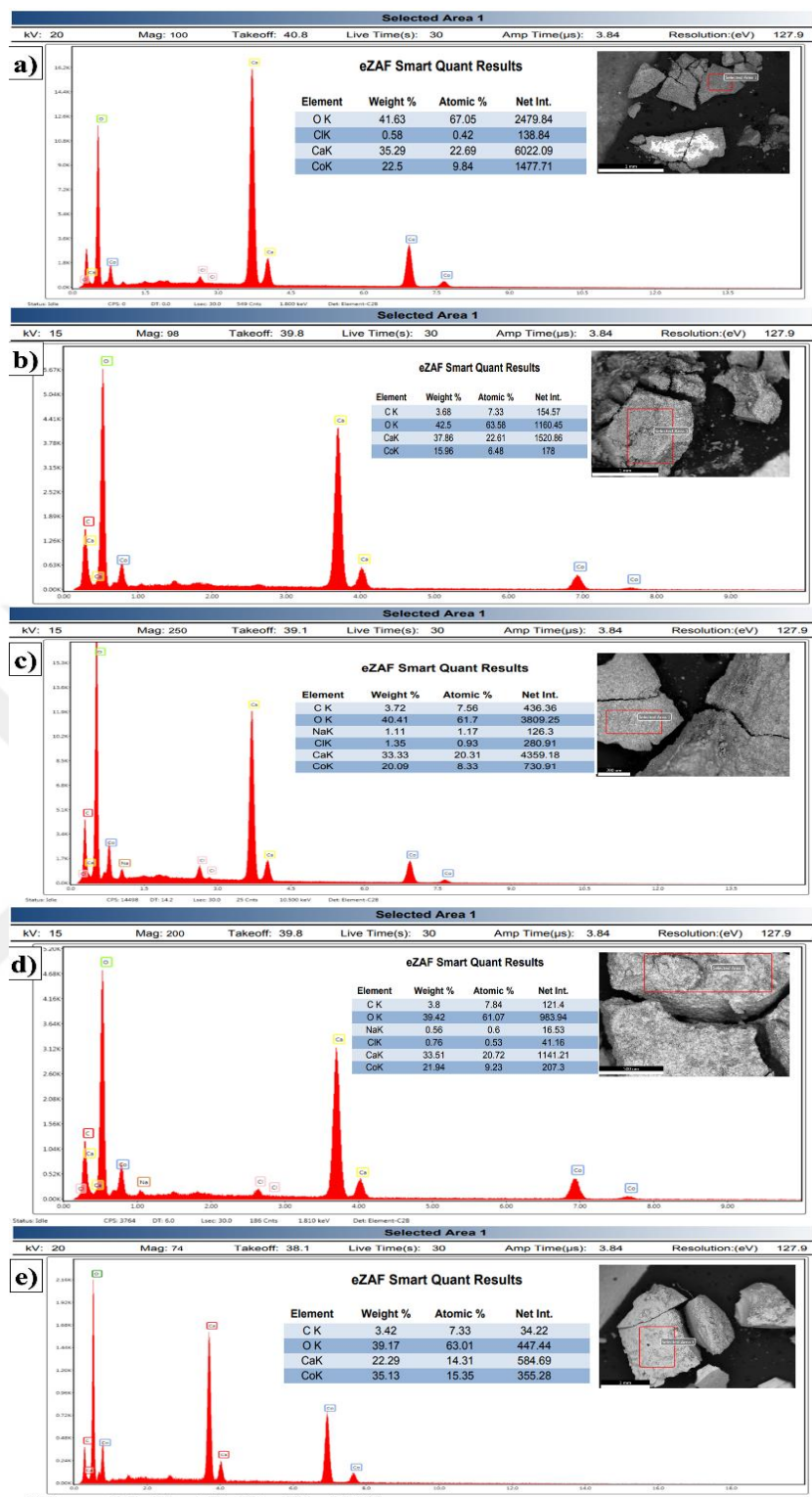


Figure 37. EDX results from the batch reactor experiment in the Co-related study. (a) 0 mM Ca(OH)_2 ; (b) 3 mM Ca(OH)_2 ; (c) 5 mM Ca(OH)_2 ; (d) 10 mM Ca(OH)_2 and (e) scenario #2.

4.4.8 XRD Data from CoCa(CO₃)₂ Synthesis Attempt in Batch Reactor Experiment

XRD analysis of the sample obtained without the use of Ca(OH)₂ as the stabilization solution revealed the presence of crystalline phases belonging primarily to the CaCO₃ structure (PDF #01-083-1762). While the characteristic peaks of the calcite phase are particularly prominent, more diffuse and low intensity peaks of other calcium carbonate polymorphs such as vaterite (PDF #01-072-0506) and aragonite (PDF #00-024-0025) are also present (Figure 38, (a)). With the addition of the calcite and vaterite mixture formed in the tubular reactor to the system, an extra aragonite phase was. The fact that no distinct peaks of a separate cobalt phase were observed in the XRD data.

When the concentration of Ca(OH)₂ is increased to 3 mM, the XRD pattern obtained in Figure 38 (b) shows a predominance of peaks belonging to the calcium carbonate as calcite structure. Although the calcium carbonate (PDF #01-085-0849) database as the record for a reference mostly refers to the peaks calcite phase, some needle-like morphologies (when evaluated with SEM data) suggest that the presence of aragonite cannot be neglected. Although the intensity of the needle-like morphology in the SEM micrographs supports the formation of aragonite, the peaks of aragonite in the XRD pattern may be weak or overlapped with calcite peaks. Another possibility is that calcite is the dominant phase, and aragonite is the secondary phase. The fact that the cobalt phase cannot be.

In the condition where Ca(OH)₂ 5 mM concentration is increased to as shown Figure 38 (c), it is seen that the peaks belonging to the calcite (PDF #01-085-1108) and aragonite (PDF #00-005-0453) phases of calcium carbonate coexist. Although the presence of cobalt content was confirmed by EDX analysis separate Co-containing crystalline phase peak was not discerned.

It is confirmed by XRD analysis that the main phase of the sample is still calcite when the Ca(OH)₂ concentration is increased to 10 mM as shown in Figure 38(d). The effect of Co²⁺ ions at different concentrations of Ca(OH)₂ using different Ca(OH)₂ concentrations performed for scenario #1 does not show any characteristic peaks of CoCa(CO₃)₂ or similar cobalt-containing secondary phases in the spectrum. Instead, CaCO₃ morphology was found to shift more towards aragonite-like needle-like structures

or flower-like structures as show in SEM images.

Unlike scenario #1, when we increase the concentration of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution up to 5 mM, calcite and aragonite phases are observed again as shown in Figure 38 (e). The role of Co^{2+} ions in the mechanism of orientation to the aragonite phase may be to change the crystallization nucleation rate or to kinetically inhibit the formation of calcite by adsorbing on the surfaces of the crystal lattice. Nevertheless, no characteristic peak of $\text{CoCa}(\text{CO}_3)_2$ was found in XRD analyses in scenario #2. This indicated that cobalt ions could not overcome the energy required for full integration into the crystal lattice or its thermodynamic stability was insufficient.



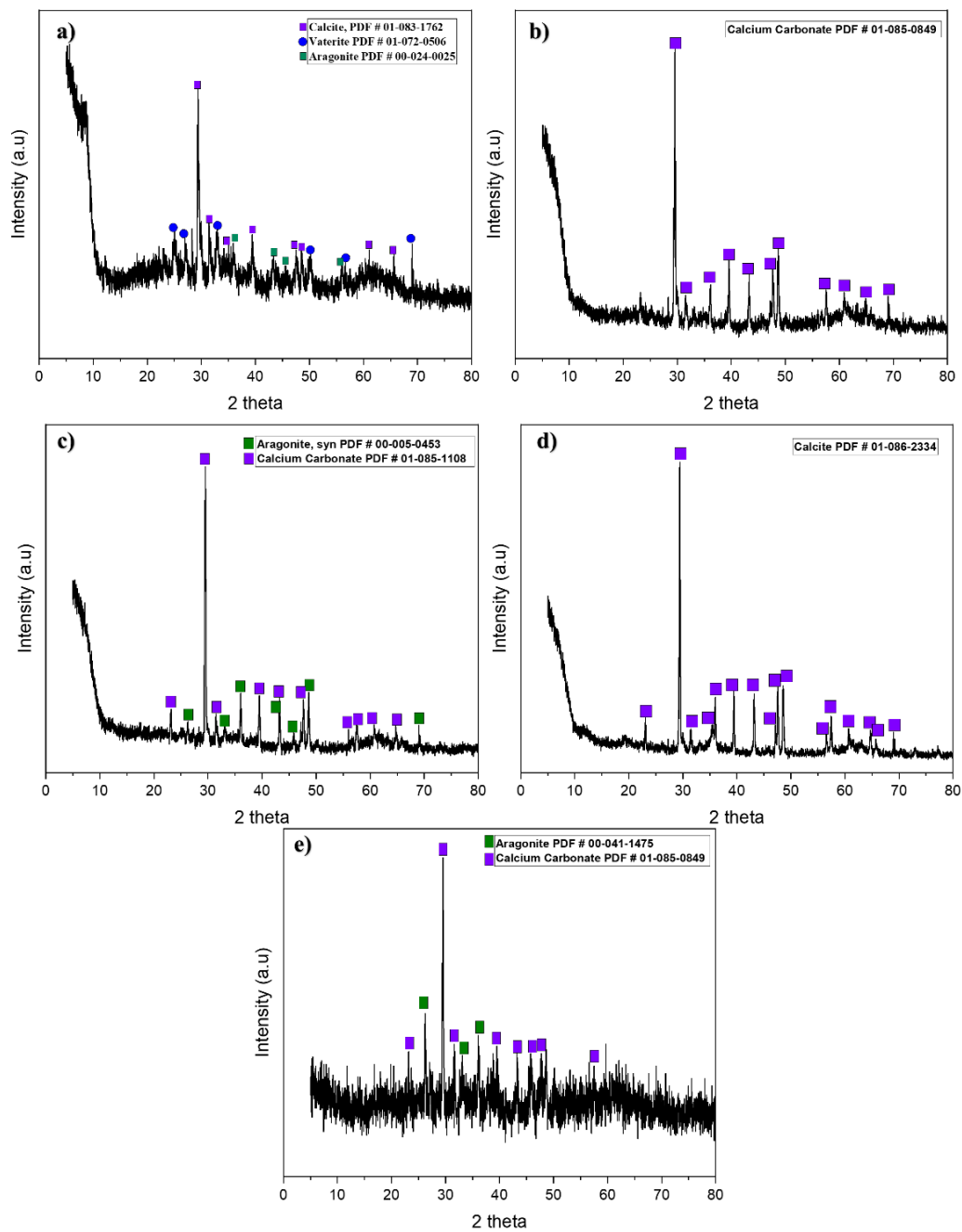


Figure 38. XRD analysis of Co-related experiments from scenario #1 and scenario #2. (a) 0mM Ca(OH)_2 , (b) 3mM Ca(OH)_2 , (c) 5mM Ca(OH)_2 , (d) Ca(OH)_2 10mM and (e) scenario #2.

4.5 Developed Methods for the Chemical Synthesis of $\text{SrCa}(\text{CO}_3)_2$

4.5.1 Direct Mixing Method for $\text{SrCa}(\text{CO}_3)_2$ Synthesis

Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and sodium carbonate (Na_2CO_3) solutions were prepared separately in 1 liter of ultrapure deionized (DI) water according to the solubility of the $\text{Sr}(\text{NO}_3)_2$ (2.85mM). In accordance with the $\text{Sr}^{2+}/\text{Ca}^{2+}$ ion ratio of 0.5, 1 and 2, each solution was added to a stirred reactor with $\text{Sr}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$ and then 200 ml of Na_2CO_3 solution for each of the 3 experiments unless otherwise stated.

4.5.2 Batch Reactor Experiment for $\text{SrCa}(\text{CO}_3)_2$ Synthesis

Two different concentration scenarios were tested for the synthesis of $\text{SrCa}(\text{CO}_3)_2$. In the first scenario, low $\text{Sr}(\text{NO}_3)_2$ concentration were used. In this scenario, $\text{Sr}(\text{NO}_3)_2$ concentration was kept constant at 2.85mM considering the solubility constant in 1 liter of distilled water, Na_2CO_3 and CaCl_2 concentrations were kept constant at 25 mM each and only $\text{Ca}(\text{OH})_2$ concentrations were varied as 0, 3, 5 and 10 mM respectively for 4 different experiments.

In the second scenario of the experiment, the concentrations of the stock solutions were of Na_2CO_3 and CaCl_2 at 25 mM each and the concentration of $\text{Sr}(\text{NO}_3)_2$ was adjusted to be equal to the concentration of $\text{Ca}(\text{OH})_2$ (5 mM each).

4.5.3 Measured Reaction Kinetics Data from $\text{SrCa}(\text{CO}_3)_2$ Synthesis Attempt in Direct Mixing Experiment

In three different $\text{Sr}^{2+}/\text{Ca}^{2+}$ ratio experiments, the pH remained alkaline, ranging from about 10.8 to 10.95 during the 60 min reaction time. This constant alkalinity indicates that the solution was strongly buffered, most likely due to the excess carbonate present in the system. This is because the final products formed were found to contain carbonate. It was observed that when the ratio was 0.5 (Figure 39, a) the pH was constant 10.84-83 up to 60 min. This leads us to conclude that at lower Sr^{2+} content relative to Ca^{2+} , the rate of carbonate consumption is moderate and leads to only small fluctuations in pH. The conductivity measurement for this system decreased from about 1644 $\mu\text{S}/\text{cm}$ for the first 5 minutes to about 1591 $\mu\text{S}/\text{cm}$ within 60 minutes. This slight decrease indicates that a number of ions were incorporated into the precipitates.

In the system with an equal ion ratio, the initial pH value was about 10.91, decreasing slightly to 10.87 in the early stages and then stabilizing around 10.90 (Figure 39, b). This pH change indicates that the carbonate ions were present and both cations were effectively incorporated into the carbonate phases formed. Indeed, the presence of $\text{Sr}_x\text{Ca}_{1-x}\text{CO}_3$ phase was detected in the final product obtained. Here the conductivity started at about 1605 $\mu\text{S}/\text{cm}$ and decrease, to 1535 $\mu\text{S}/\text{cm}$ within 60 minutes. The larger net decrease leads to the conclusion that ion removal and therefore precipitation is more extensive in the 1:1 ratio system. This suggests that the balanced presence of both cations favors a more efficient and continuous precipitation process.

The experiment containing a higher proportion of Sr^{2+} ion than Ca^{2+} ion also showed the highest initial pH value up to about 10.95, with small oscillations between 10.90 and 10.94 (Figure 39, c). The higher pH values here may be due to slower precipitation of Sr-rich carbonates, given that SrCO_3 is generally slightly more soluble than CaCO_3 . This system showed only a slight decrease in conductivity from 1599 $\mu\text{S}/\text{cm}$ at 5 min to about 1590 $\mu\text{S}/\text{cm}$ at 60 min. This minimal change can be attributed to precipitation.

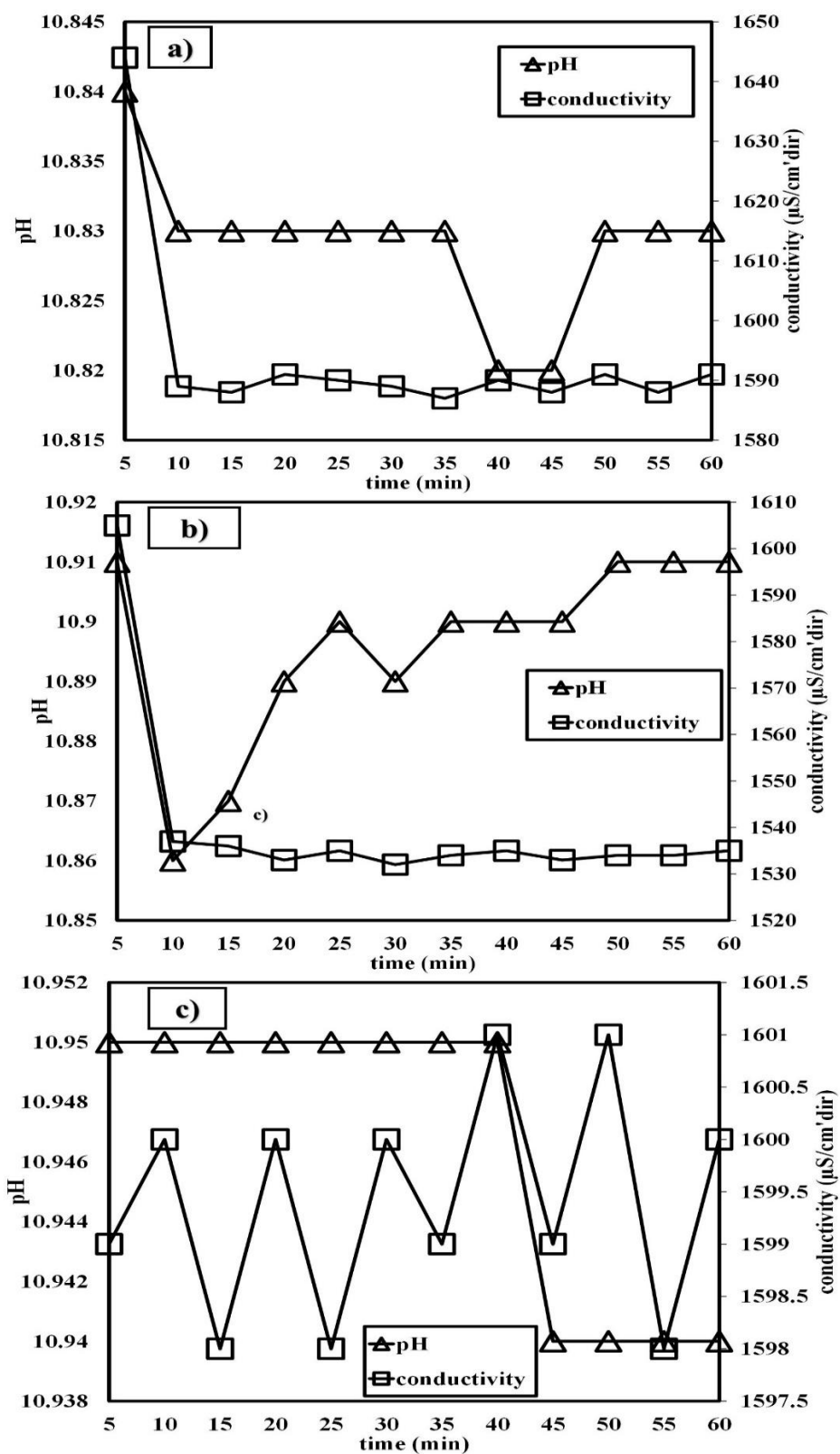


Figure 39. pH and conductivity changes over time in Sr-related direct mixing experiments. (a) $\text{Sr}^{2+}/\text{Ca}^{2+} = 0.5$, (b) $\text{Sr}^{2+}/\text{Ca}^{2+} = 1$, and (c) $\text{Sr}^{2+}/\text{Ca}^{2+} = 2$.

4.5.4 Measured Reaction Kinetics Data from $\text{SrCa}(\text{CO}_3)_2$ Synthesis

Attempt in Batch Reactor Experiment

Batch reactor was initially filled with a known concentration of $\text{Sr}(\text{NO}_3)_2$ (2.85 mM in scenario #1 and 5 mM in scenario #2). Depending on the experiment, $\text{Ca}(\text{OH})_2$ ranging from 0 to 10 mM was also added to the batch reactor. When the experiment starts, a peristaltic pump draw Na_2CO_3 and CaCl_2 solutions both at 25 mM into a tubular reactor. Inside the tubular reactor, ions in the solutions began to react and form intermediate carbonate species, which were then fed dropwise into a batch reactor containing $\text{Sr}(\text{NO}_3)_2$ and $\text{Ca}(\text{OH})_2$ if present. Overall measured pH and conductivity data were shown in Figure 40.

For the experiment without $\text{Ca}(\text{OH})_2$ as shown in Figure 40, (a), the pH was initially close to neutral 6.79, then rose sharply to above 10.3 within 1 min and continued to increase to about 10.78 in 6 min. However, by the end of 7 minutes the pH had dropped to about 9, suggesting that some of the initially formed precipitates may dissolved and carbonate/bicarbonate equilibrium established as the reaction progressed.

A pH decrease was generally observed in solutions with high $\text{Ca}(\text{OH})_2$ concentration such as 3, 5, and 10 mM. The main reason for this situation can be interpreted as dissolution and recrystallization of CaCO_3 , in the presence of OH^- ions (Figure 40, b-d, respectively).

Initially measured conductivity values were generally decreasing with increasing $\text{Ca}(\text{OH})_2$ concentrations. This can be explained by the fact that some of the Sr^{2+} , NO_3^- and Ca^{2+} , OH^- ions initially present in the medium bind to form solid particles and decrease the conductivity due to the decrease in their ionic concentrations. A steady increase in the conductivity values of all samples was recorded over time. For instance, the initial conductivity of the sample without $\text{Ca}(\text{OH})_2$ increased from 447 $\mu\text{S}/\text{cm}$ to 1368 $\mu\text{S}/\text{cm}$. This is attributed to the increased ion charge in the solution because of the continuous addition of solutions to the batch reactor through the tubular reactor. As the concentration of dissolved ions increased over time, the conductivity also increased.

Under identical experimental conditions, but with the $\text{Sr}(\text{NO}_3)_2$ concentration increased to 5 mM while maintaining $\text{Ca}(\text{OH})_2$ concentration at 5 mM, the measured pH and conductivity changes are presented in Figure 40, (e). Initially, the recorded pH was

approximately 10.18. Over time, minor fluctuations were observed, including a slight increase from 10.18 to 10.76 followed by a gradual decrease. These results indicate that, at the beginning of the reaction, the hydroxide ion concentration in the solution was sufficiently high. However, as the reaction progressed, the precipitation of CaCO_3 led to a reduction in free hydroxide ions, resulting in a downward trend in pH.

The conductivity started with $770 \mu\text{S/cm}$ and increased continuously and reached $1195 \mu\text{S/cm}$ at the end of 7 minutes. The high values can be explained by the high total ion concentrations of $\text{Sr}(\text{NO}_3)_2$ and $\text{Ca}(\text{OH})_2$ solutions used in the crystallization.

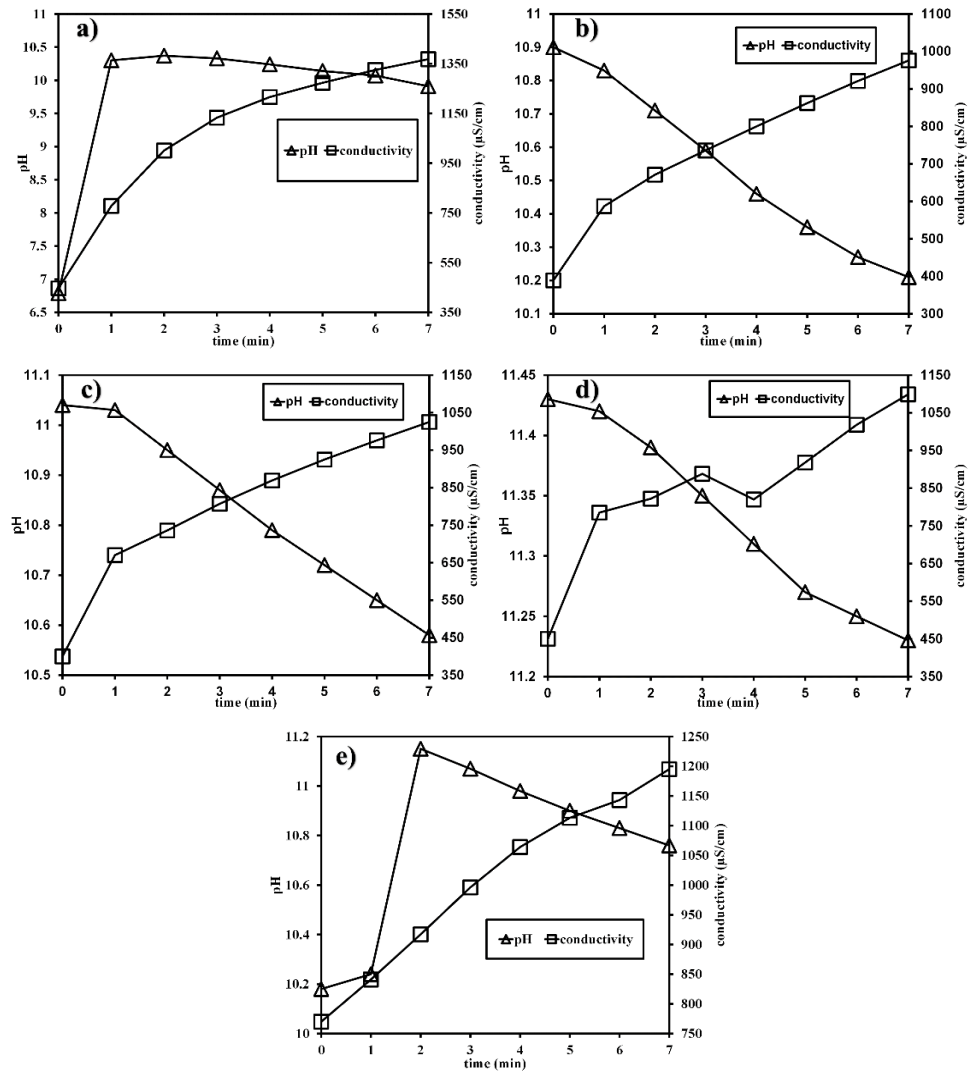


Figure 40. pH and conductivity changes over time in Sr-related batch reactor experiment.

(a) 0mM $\text{Ca}(\text{OH})_2$, (b) 3mM $\text{Ca}(\text{OH})_2$, (c) 5mM $\text{Ca}(\text{OH})_2$, (d) 10mM $\text{Ca}(\text{OH})_2$, and (e) scenario #2.

The saturation indices for calcite, aragonite and strontianite minerals calculated using PHREEQC software show that the SI values for calcite, aragonite and strontianite minerals are positive at all concentration studied (Figure 41). Positive SI values indicate that the solutions are supersaturated with respect to these minerals and their precipitation are thermodynamically favorable ¹⁵⁶. However, since thermodynamic data for $\text{SrCa}(\text{CO}_3)_2$ and $\text{Sr}_x\text{Ca}_{1-x}\text{CO}_3$ are not available in the PHREEQC database and also in the literature, the precipitation indices for double carbonates could not be calculated. Nevertheless, it can be assumed that Sr-doped CaCO_3 or double carbonate precipitated in the system through the high SI values of both calcite and strontianite.

It was observed that SI values increased during the experiment. For the solution containing 0 mM $\text{Ca}(\text{OH})_2$, the calcite SI increased from 1.77 to 2.71, while the aragonite SI increased from 1.63 to 2.56. Similar trends were also observed at other concentrations, with a significant increase in calcite and aragonite SI values as $\text{Ca}(\text{OH})_2$ concentration increased. These results clearly indicated that $\text{Ca}(\text{OH})_2$ concentration plays a promoting role in mineral precipitation. Likewise, the SI values of strontianite mineral were high positive values in all experimental conditions, confirming a high tendency of their precipitation. In all experimental conditions studied, strontianite SI values ranged from about 2.75 to 3.21.

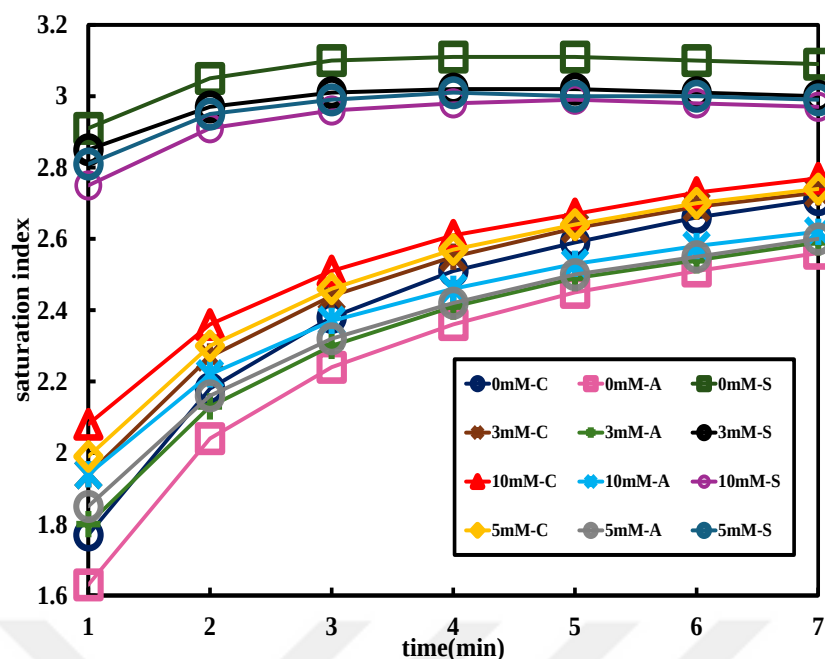


Figure 41. Saturation indices calculations using PHREEQC software in batch reactor experiment.

4.5.5 SEM Images from $\text{SrCa}(\text{CO}_3)_2$ Synthesis Attempt in Direct Mixing Experiment

The morphologies of the particles obtained at different $\text{Sr}^{2+}/\text{Ca}^{2+}$ mole ratios are given in Figure 42. When the $\text{Sr}^{2+}/\text{Ca}^{2+}$ ratio was 0.5 (Figure 42, a-c), the particles were found to have generally spherical and floral morphologies. At higher magnifications 50000x, it was clearly determined that the surface structures of the particles were complex, heterogeneous and covered with dendritic structures. Cubic structures usually indicate a typical calcite structure. Other phases indicate the Sr-doped CaCO_3 phase

Increasing the $\text{Sr}^{2+}/\text{Ca}^{2+}$ ratio to 1 (Figure 42, d-f) resulted in particles with a more defined spherical shape and clearer surface features. These compact and uniformly arranged spherical structures correspond to the $\text{Sr}_x\text{Ca}_{1-x}\text{CO}_3$ morphology previously reported by Dotta et al.¹⁵⁷.

Under the condition that the $\text{Sr}^{2+}/\text{Ca}^{2+}$ ratio is 2 (Figure 42, g-j), SEM images show more complex, flower-like structures rather than the familiar rhombohedral crystal

form of classical calcite, although calcite phase was detected in the XRD pattern. Even if these organized structures in the form of floral/spherical aggregates examined in SEM do not match the classical morphology of calcite, the morphology of calcite seems to have evolved differently in the environment where Sr^{2+} is more dominant than Ca^{2+} .

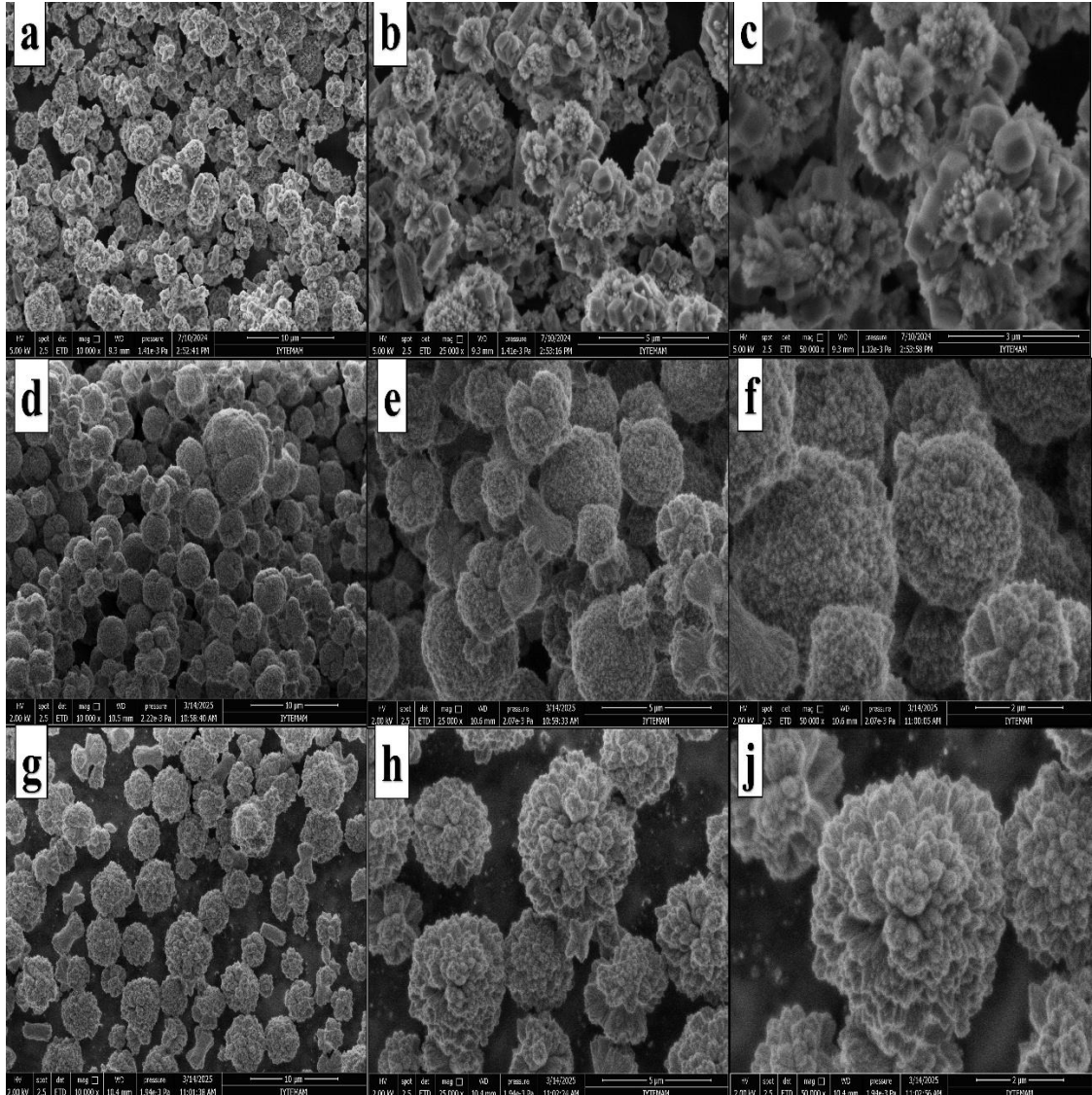


Figure 42. SEM images for Sr related Direct Mixing Experiments. (a-c) $\text{Sr}^{2+}/\text{Ca}^{2+} = 0.5$; (d-f) $\text{Sr}^{2+}/\text{Ca}^{2+} = 1$ and (g-i) $\text{Sr}^{2+}/\text{Ca}^{2+} = 2$.

4.5.6 XRD Data from $\text{SrCa}(\text{CO}_3)_2$ Synthesis Attempt in Direct Mixing Experiment

XRD analysis as shown in Figure 43, structural characterization analysis of the crystalline phases formed depending on the $\text{Sr}^{2+}/\text{Ca}^{2+}$ ratio, was performed using X'Pert HighScore Plus software and the International Diffraction Database (ICDD PDF-2).

In the experimental condition where the $\text{Sr}^{2+}/\text{Ca}^{2+}$ ratio was 0.5 Figure 43, (a), peaks belonging to calcite (CaCO_3 , PDF #01-086-2343) and strontianite calcian ($\text{Sr}_{0.5}\text{Ca}_{0.5}\text{CO}_3$, PDF # 00-044-1421) phases were detected in the XRD pattern. The simultaneous presence of calcite and strontianite calcian phases suggests that Sr^{2+} ions were partially integrated into the CaCO_3 crystal structure at this low Sr^{2+} ratio. The high intensity of the calcite peaks reflects that Ca^{2+} ions are more abundant than Sr^{2+} in the reaction mixture and precipitate due to the lower solubility product of CaCO_3 ($\text{pK}_{\text{sp}} = 8.46 \pm 0.03$) than SrCO_3 ($\text{pK}_{\text{sp}} = 9.13 \pm 0.03$)¹⁵⁸.

When the $\text{Sr}^{2+}/\text{Ca}^{2+}$ ratio was increased to 1 Figure 43, (b), it was observed that the characteristic peaks of the strontianite calcian phase became dominant in the XRD pattern, especially the intensity of the peaks belonging to the crystal planes (111), (130), (221), and (023) increased. This indicates that Sr^{2+} ions are more effectively localized in the crystal structure.

When the $\text{Sr}^{2+}/\text{Ca}^{2+}$ ratio was 2 Figure 43, (c), the peaks of the calcium carbonate (CaCO_3 , PDF #01-085-1108) phase clearly appeared. At this stage, Sr^{2+} ions were no longer effectively localized in the structure and pure CaCO_3 crystallization was observed.

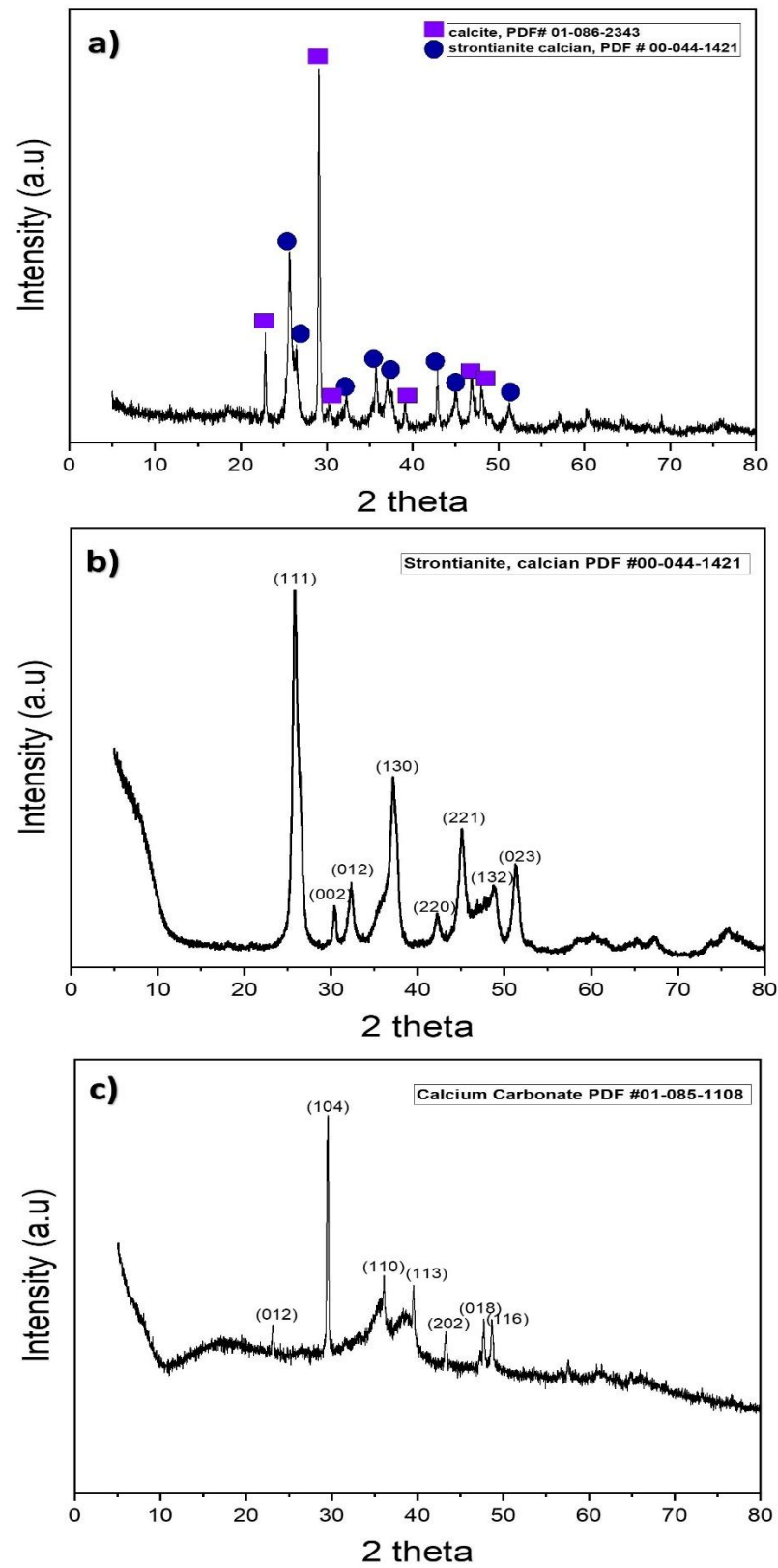


Figure 43. XRD analysis of Sr-related Direct Mixing experiments. (a) $\text{Sr}^{2+}/\text{Ca}^{2+} = 0.5$, (b) $\text{Sr}^{2+}/\text{Ca}^{2+} = 1$, and (c) $\text{Sr}^{2+}/\text{Ca}^{2+} = 2$.

4.5.7 SEM & EDX Data from SrCa(CO₃)₂ Synthesis Attempt in Batch Reactor Experiment

XRD analysis for scenario #1 in which Ca(OH)₂ concentrations were varied as 0 mM, 3 mM, 5 mM and 10 mM and Sr(NO₃)₂ concentration was kept constant at 2.85 mM are given in Figure 44.

As shown in Figure 44 (a), two distinctly different phases were observed under the experimental conditions where the Ca(OH)₂ concentration was 0 mM. XRD pattern, mainly CaCO₃ (PDF #01-071-1937) 2theta= 23.05; 29.38; 35.91; 39.35; 43.09; 47.24; 48.42; 57.5; 60.72; 64.74; 76.32; Sr_{0.5}Ca_{0.5}CO₃ (PDF #00-004-1421) contains phases with 2theta= 25.75; 26.29; 30.36; 32.19; 35.91; 37.07; 42.18; 44.93; 47.24; 48.42; 51.19; 64.70 peaks. Among these peaks, especially the peak at 29.38° shows the dominant presence of the calcite phase. It shows that Sr²⁺ substituted calcium carbonate has a similar crystal structure to the calcite phase, but due to the larger ionic radius of Sr²⁺ ions (Sr²⁺ 1.18 Å, Ca²⁺ 0.99 Å) there are slight shifts in the peak positions. This is evidence for a successful integration of strontium into the crystal lattice.

Upon adding Ca(OH)₂ to a concentration of 3 mM Figure 44, (b), the Sr_{0.5}Ca_{0.5}CO₃ phase co-existed with calcite, and the intensity of its peaks increased significantly compared to the 0 mM Ca(OH)₂ experiment.. The slight broadening observed in the peaks indicates smaller crystal sizes or micro-strains in the crystal lattice. This can be attributed to the increased pH accelerating the precipitation kinetics and the crystal defects caused by the substitution of Sr²⁺ ions into the crystal lattice.

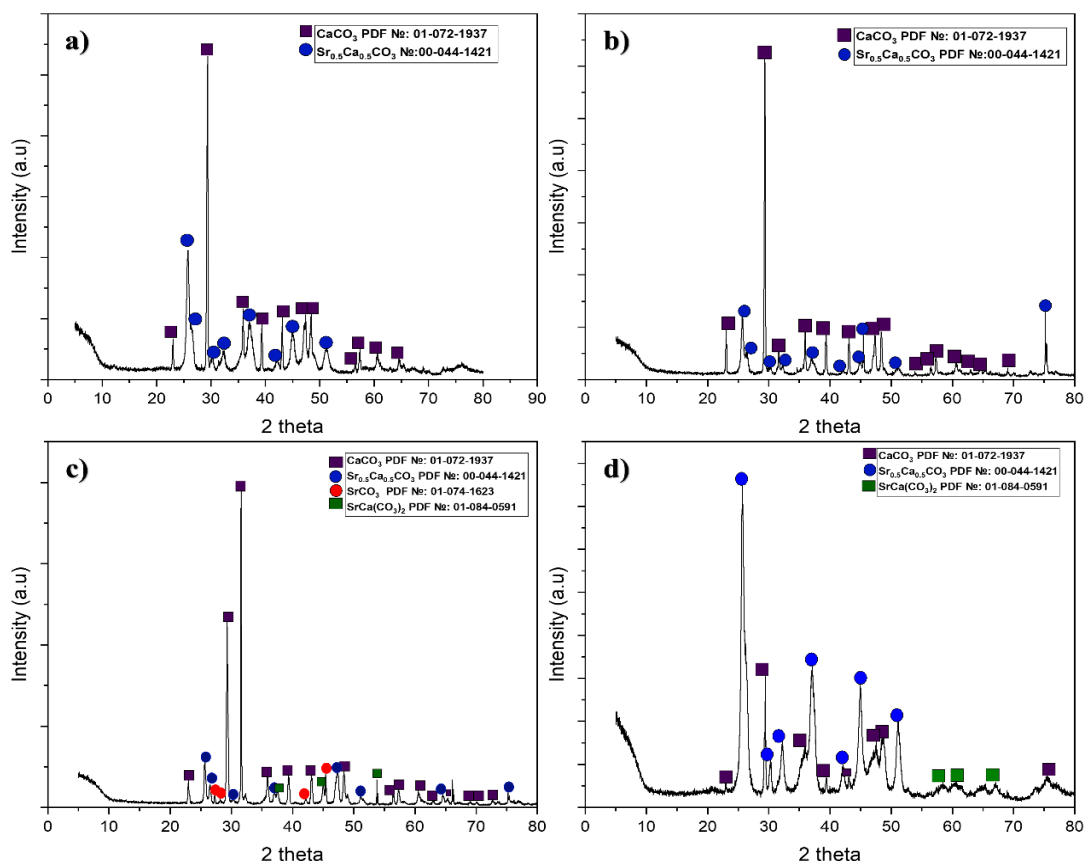


Figure 44. XRD results from the batch reactor experiment in the Sr-related study. Scenario #1. a) 0 mM Ca(OH)_2 , b) 3 mM Ca(OH)_2 , c) 5 mM Ca(OH)_2 , and d) 10 mM Ca(OH)_2 .

In Figure 44 (c), the XRD pattern shows that, in addition to CaCO_3 and $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{CO}_3$ phases, SrCO_3 (PDF No: 01-071-0528) and $\text{SrCa}(\text{CO}_3)_2$ (PDF No: 01-084-0581) phases are also partially present. In particular, the peak at $31.5^\circ 2\theta$ can be attributed to monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$)¹⁵⁹.

At the highest Ca(OH)_2 concentration of 10 mM (Figure 44, d), significant changes in phase composition were observed. The broadening of the peaks and the change in their intensities indicate a decrease in crystallite size and crystallinity according to Scherrer's equation.

The pronounced increase in Sr^{2+} ion concentration by approximately twofold facilitated enhanced integration into the calcite lattice, and in contrast to scenario #1, the $\text{SrCa}(\text{CO}_3)_2$ double carbonate phase was more prominently detected. The intensity of peaks associated with the CaCO_3 phase was notably diminished compared to all other

experiments. This phenomenon can be attributed to the dissolution of CaCO_3 in the solution through interaction with $\text{Ca}(\text{OH})_2$, which subsequently stimulated crystal growth, followed by rapid precipitation of SrCO_3 and a tendency toward $\text{SrCa}(\text{CO}_3)_2$ formation in the system. The most distinctive peaks for this double carbonate were observed at $2\theta=30.36^\circ$, 32.37° , 37.17° , 39.36° , 42.24° , 43.10° , 45° , 47.2° , and 48.43° as shown in Figure 45. Furthermore, the width and intensity of peaks in the XRD patterns suggest that the crystallinity of the precipitate varies depending on the $\text{Ca}(\text{OH})_2$ concentration. Particularly, the sharper and more intense peaks in scenario #1 indicate a higher degree of crystallinity in the precipitate. In scenario #2, the peak widths exhibited a more balanced distribution across the diffraction pattern.

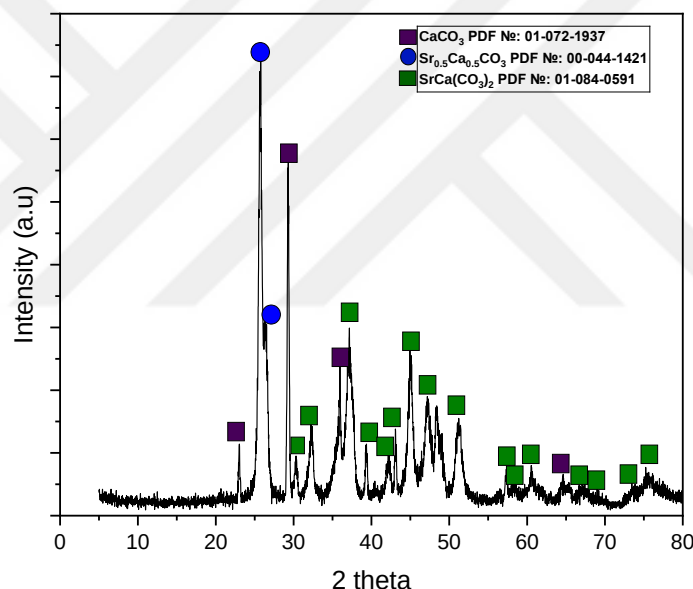


Figure 45. XRD result from the Sr-related batch reactor experiment in scenario#2.

4.5.8 XRD Data from $\text{SrCa}(\text{CO}_3)_2$ Synthesis Attempt in Batch Reactor Experiment

The SEM images and EDX results obtained in scenario #1, where the $\text{Ca}(\text{OH})_2$ concentration was varied as 0 mM, 3 mM, 5 mM, and 10 mM, were examined together (Figure 46). When SEM images obtained in the presence of 0 mM $\text{Ca}(\text{OH})_2$ are analyzed,

the presence of smaller and spherical-shaped crystals as well as cubic crystals with smooth surfaces is remarkable. While cubic crystals generally indicate pure calcite structure, spherical crystals indicate the presence of Sr-modified CaCO_3 solid particles ($\text{Sr}_x\text{Ca}_{1-x}\text{CO}_3$). The high ratio of Ca 32.28 wt% and Sr 23.57 wt% in EDX analysis confirms that Sr^{2+} ions are effectively located in the crystal structure.

When the Ca(OH)_2 concentration was increased to 3 mM, Sr-filled calcite structures with floral-like morphologies were observed in the SEM images, where the calcite crystals became smaller and the surfaces became irregular. In EDX analysis, the Sr^{2+} ratio 16.25 wt% decreased slightly while the Ca ratio increased to 21.62 wt%, indicating that the entry of Sr^{2+} ions into the crystal structure became difficult. The morphological change of $\text{Sr}_x\text{Ca}_{1-x}\text{CO}_3$ structure may be related to the increase in Ca^{2+} and OH^- concentrations in the medium.

Ca(OH)_2 concentration was further increased to 5 mM, SEM images showed the formation of distinctly elongated and needlelike crystals. This needle-like morphology is usually associated with the aragonite phase. Interestingly, no aragonite phase was observed in the XRD data, and these structures again suggest that the Sr^{2+} ion in the system shows a different effect in the process of dissolution and recrystallization of CaCO_3 added to the medium in the presence of higher Ca(OH)_2 concentration. EDX results showed a further decrease in the amount of Sr^{2+} 15.01 wt% and increase in Ca^{2+} 42.70 wt%.

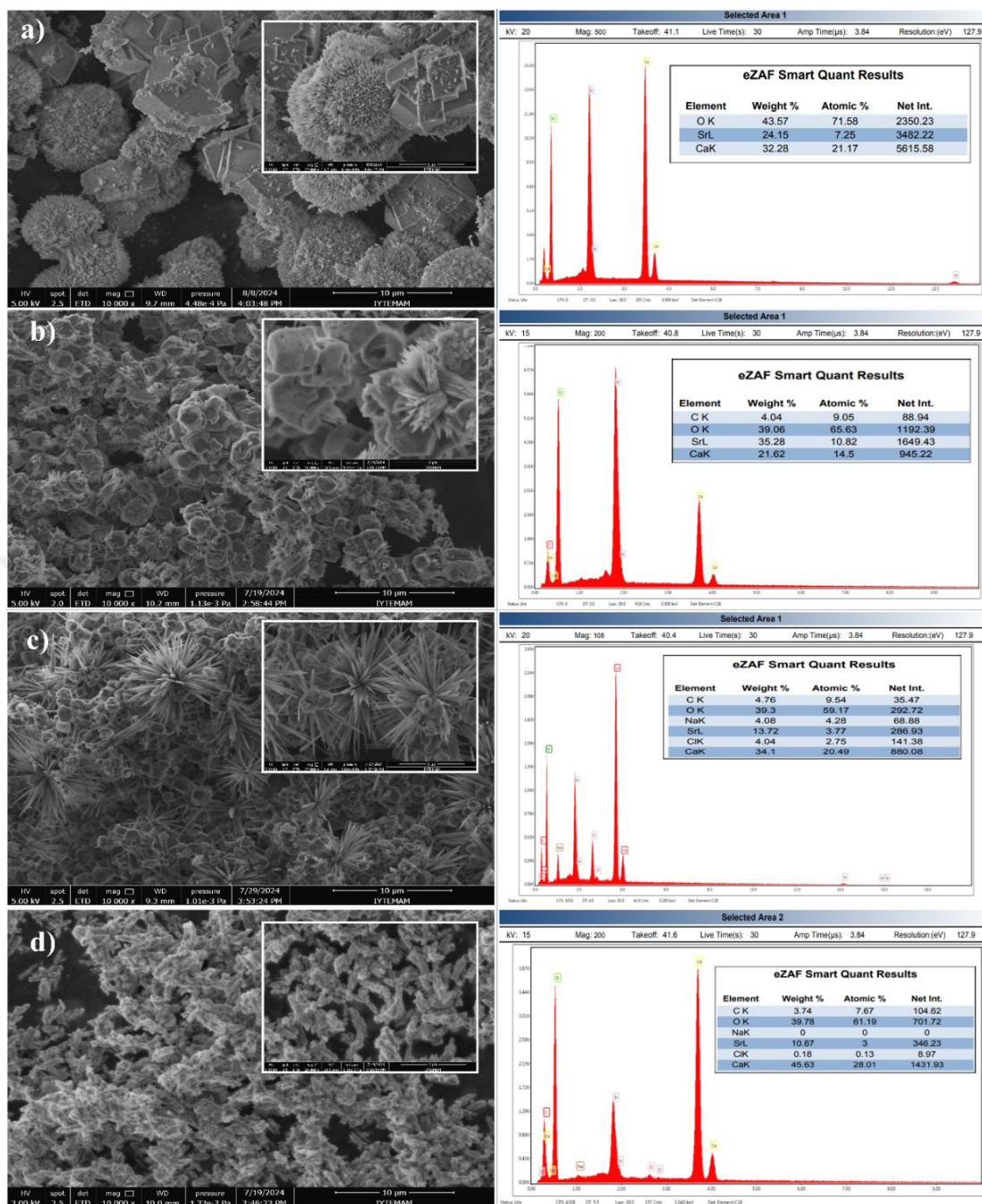


Figure 46. SEM (left) and EDX (right) results of scenario#1 for Sr-related batch reactor experiments. a) 0 mM Ca(OH)_2 , b) 3 mM Ca(OH)_2 , c) 5 mM Ca(OH)_2 , and d) 10 mM Ca(OH)_2 .

At the highest concentration of 10 mM Ca(OH)_2 , it was observed in the SEM images that the crystals transformed towards an amorphous structure and a distinct morphology was observed. This amorphization tendency may be due to complex

mechanisms occurring in the recrystallization processes resulting from the presence of excess Ca^{2+} and OH^- ions in the solution. In addition, EDX analysis showed that the amount of Ca^{2+} 45.53 wt% increased significantly while the amount of Sr^{2+} 10.67 wt% remained at a low level compared to the previous concentrations. It is understood that at high $\text{Ca}(\text{OH})_2$ concentrations, the entry of Sr^{2+} ions into the crystal structure is gradually, and therefore, morphologically irregular carbonate phases with low Sr^{2+} content are formed.

Herein, as the $\text{Ca}(\text{OH})_2$ concentration increases, the particle morphology changed from a spherical to a needle-like structure. This indicates that $\text{Ca}(\text{OH})_2$ affected the morphology of the Sr-Ca mixed phase by affecting the crystal structure. Also, it was detected that some hollow nano CaCO_3 was synthesized during the crystallization of CaCO_3 under the influence of Sr^{2+} ions.

For scenario #2 with equal concentrations (5 mM) of $\text{Ca}(\text{OH})_2$ and $\text{Sr}(\text{NO}_3)_2$ ions, three distinct morphologies are observed in the SEM images (Figure 47). As in scenario #1, the calcite phase was observed in a cubic structure. In addition, crystals with floral and dendritic spherical structures were identified as $\text{Sr}_x\text{Ca}_{1-x}\text{CO}_3$. Here, long woody structures were thought to be $\text{SrCa}(\text{CO}_3)_2$ double carbonates to the best of our knowledge. SEM morphological images of this material have not been found in the literature before. EDX analysis results revealed the presence of Ca 29 wt%, Sr 24.95 wt%, O 42.34%, and C 3.71 wt% elements. The high Sr^{2+} content and its proximity to the Ca^{2+} content for the Sr-containing mixed carbonate phases ($\text{Sr}_x\text{Ca}_{1-x}\text{CO}_3$ and $\text{SrCa}(\text{CO}_3)_2$) shows that Sr^{2+} ions are successfully localized in the crystal structure.

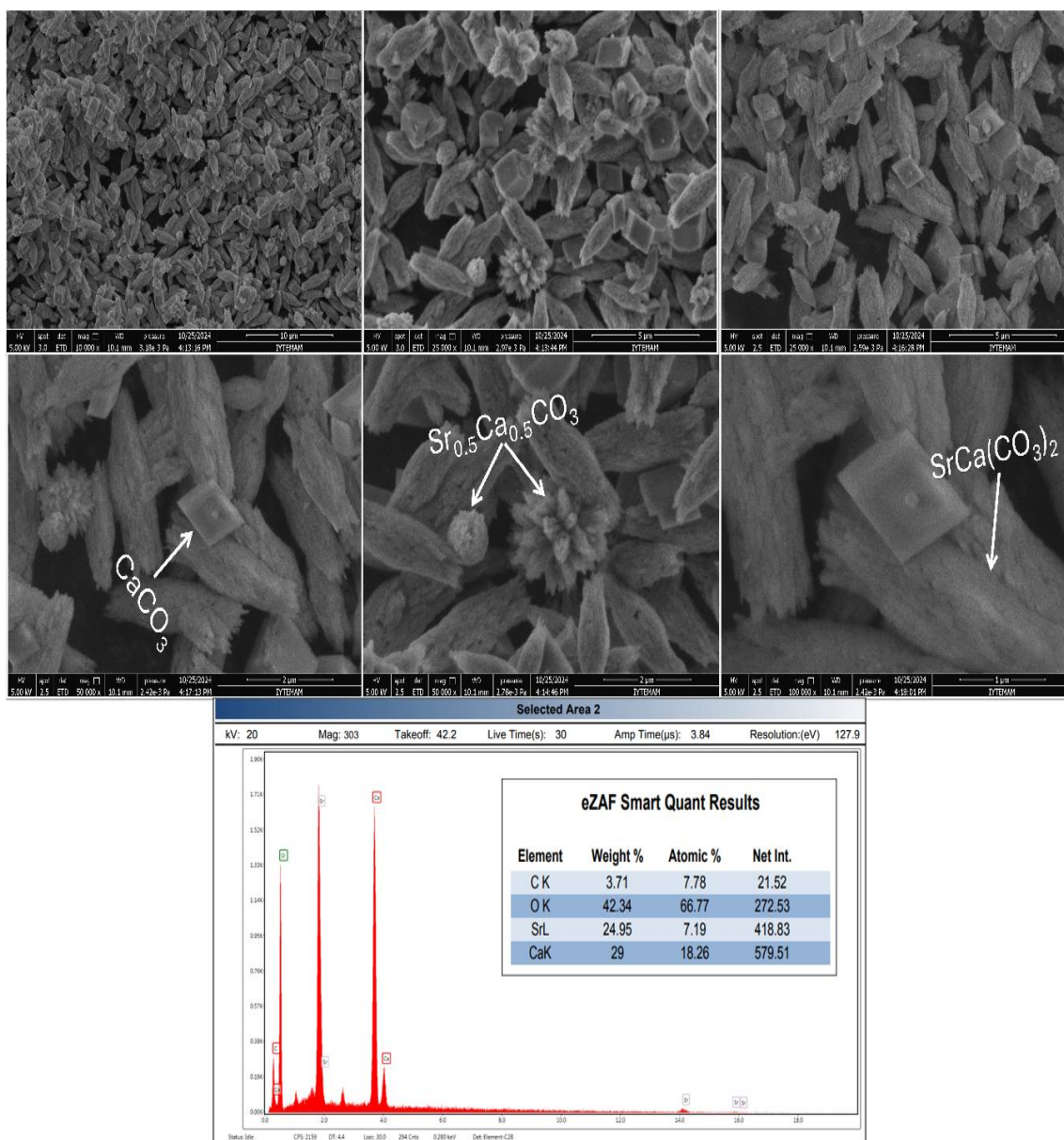


Figure 47. SEM and EDX results of CaCO_3 , $\text{Sr}_x\text{Ca}_{1-x}$ and $\text{SrCa}(\text{CO}_3)_2$.

4.6 Developed Methods for the Chemical Synthesis of $\text{MgCa}(\text{CO}_3)_2$

4.6.1 Direct Mixing Method for $\text{MgCa}(\text{CO}_3)_2$ Synthesis

Magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and sodium carbonate (Na_2CO_3) solutions were prepared separately in 1 liter of ultrapure deionized (DI) water according to the solubility of the $\text{Mg}(\text{NO}_3)_2$ (1.95 mM). In accordance with the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ion ratio of 0.5, 1 and 2, each solution was added to a reactor with $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$ and then 200 ml of Na_2CO_3 solution in each of the 3 experiments unless otherwise stated.

4.6.2 Batch Reactor Experiment for $\text{MgCa}(\text{CO}_3)_2$ Synthesis

Two different concentration scenarios were tested for the synthesis of $\text{MgCa}(\text{CO}_3)_2$. In this scenario, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ concentration was kept constant at 1.95mM considering the solubility constant in 1 liter of distilled water, Na_2CO_3 and CaCl_2 concentrations were kept constant at 25 mM and only $\text{Ca}(\text{OH})_2$ concentrations were varied as 0, 3, 5 and 10 mM respectively for 4 different experiments.

In the second scenario of the experiment, the concentrations of the stock solutions were again prepared at 25 mM each and the concentration of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was adjusted to be equal to the concentration of $\text{Ca}(\text{OH})_2$ (5 mM each).

4.6.3 Measured Reaction Kinetics Data from $\text{MgCa}(\text{CO}_3)_2$ Synthesis Attempt in Direct Mixing Experiment

pH and conductivity data measured at three different ion ratios of $\text{Mg}^{2+}/\text{Ca}^{2+}$ are shown in Figure 48. Within the scope of the experiment, measurements were made every 5 minutes for 60 minutes during the experiment in the precipitation reactions formed by mixing $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$ and Na_2CO_3 solutions. According to the results obtained from the analysis of pH data, a significant stability in pH values was observed for all three ratios. In general, in all experimental conditions, pH values stabilized rapidly at the beginning and reached equilibrium around 10.90. The relatively high pH value of 11.16 observed at the $r=1$ ratio at the beginning decreased rapidly and reached a similar level of 10.92 with the other ratios. pH values remained constant at approximately 10.91 and 10.88 for $r=0.5$ and $r=2$ conditions, respectively. This suggests that the solubilization of carbonate salts and the formation of hydroxide ions are similar in the systems, but that the presence of a higher proportion of calcium or magnesium in the initial phase may affect the concentration of hydroxide ions for a short time.

Conductivity values generally showed a slight decrease from the beginning to the end. This may be due to the separation of ionic species from the aqueous phase and transfer to the solid phase because of precipitation. In general, a decrease in conductivity was observed as the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio increased. Conductivity values, which were 1629 $\mu\text{S}/\text{cm}$ for $r = 0.5$, 1579 $\mu\text{S}/\text{cm}$ for $r=1$ and 1563 $\mu\text{S}/\text{cm}$ for $r=2$ at the beginning of the experiment, reached 1608 $\mu\text{S}/\text{cm}$, 1554 $\mu\text{S}/\text{cm}$ and 1561 $\mu\text{S}/\text{cm}$ at the end of 60 minutes, respectively. This shows that the presence of more magnesium ions than calcium ions increase the precipitation and thus reduces the ionic charge in the aqueous phase relatively more significantly.

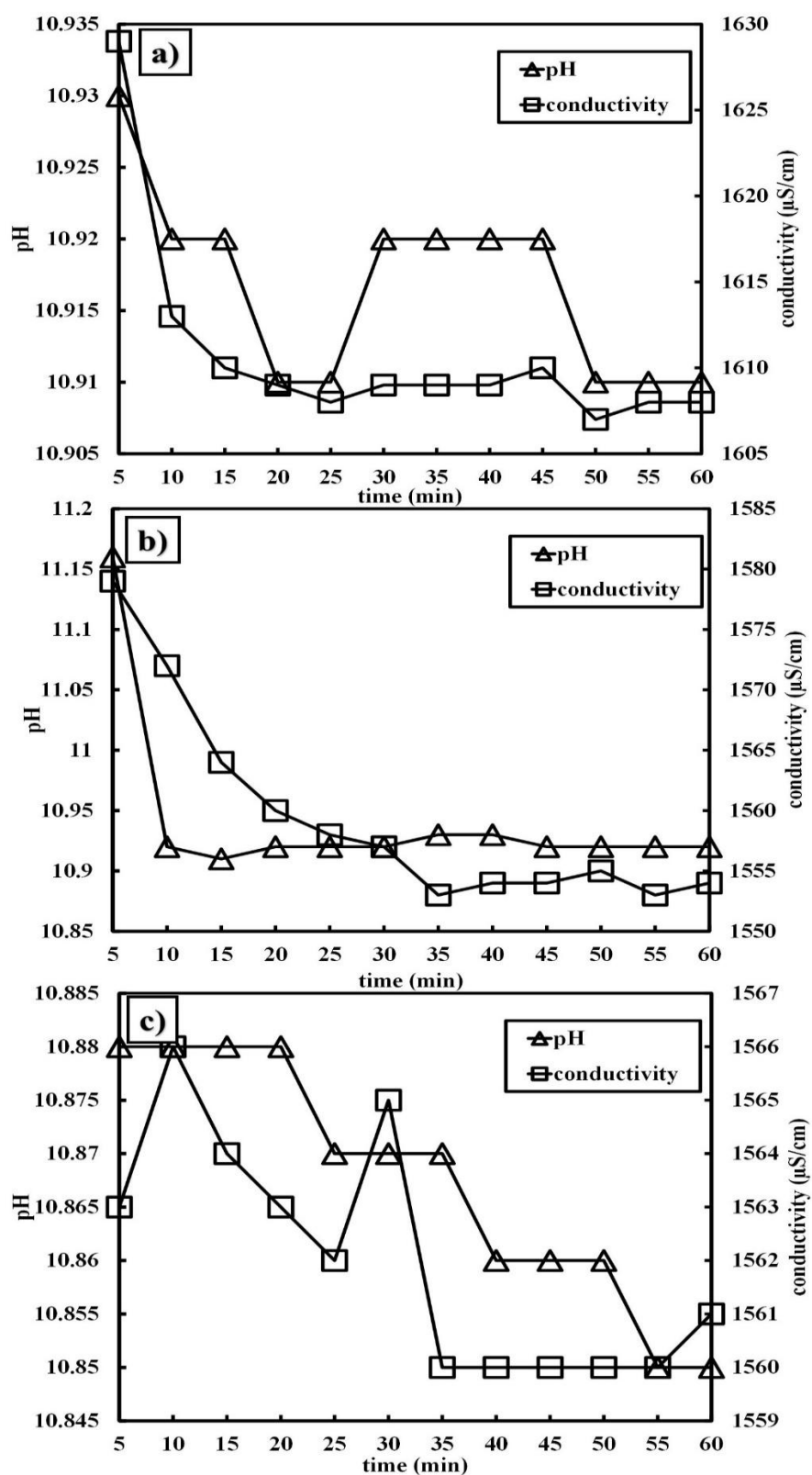


Figure 48. pH and conductivity changes over time in Mg-related direct mixing experiments. (a) $Mg^{2+}/Ca^{2+}=0.5$, (b) $Mg^{2+}/Ca^{2+}=1$ and (c) $Mg^{2+}/Ca^{2+}=2$.

4.6.4 Measured Reaction Kinetics Data from $\text{MgCa}(\text{CO}_3)_2$ Synthesis Attempt in Batch Reactor Experiment

In the experimental condition where $\text{Ca}(\text{OH})_2$ was not added initially, the pH value started quite low at 6.77 and increased as CaCO_3 was added through the tubular reactor, reaching approximately 9.88. The conductivity was initially low, 221.8 $\mu\text{S}/\text{cm}$, but increased over time to approximately 689 $\mu\text{S}/\text{cm}$. This reflects the accumulation of ions in the solution as the reaction progresses. With the increase in $\text{Ca}(\text{OH})_2$ concentration, the initial pH values increased as expected. In the experiments containing 3, 5, and 10 mM $\text{Ca}(\text{OH})_2$, the pH started at 10.76, 10.77, and 10.80, respectively, and decreased slightly with time to approximately 10.38, 10.48, and 10.56, respectively (Figure 49 a,b). This slight decrease was due to the reaction of hydroxide ions with CaCO_3 . Under these conditions, the conductivity was 246.1 $\mu\text{S}/\text{cm}$, 320 $\mu\text{S}/\text{cm}$ and 374 $\mu\text{S}/\text{cm}$ at the beginning and increased to 1004 $\mu\text{S}/\text{cm}$, 1099 $\mu\text{S}/\text{cm}$ and 999 $\mu\text{S}/\text{cm}$ at the end of the process, respectively.

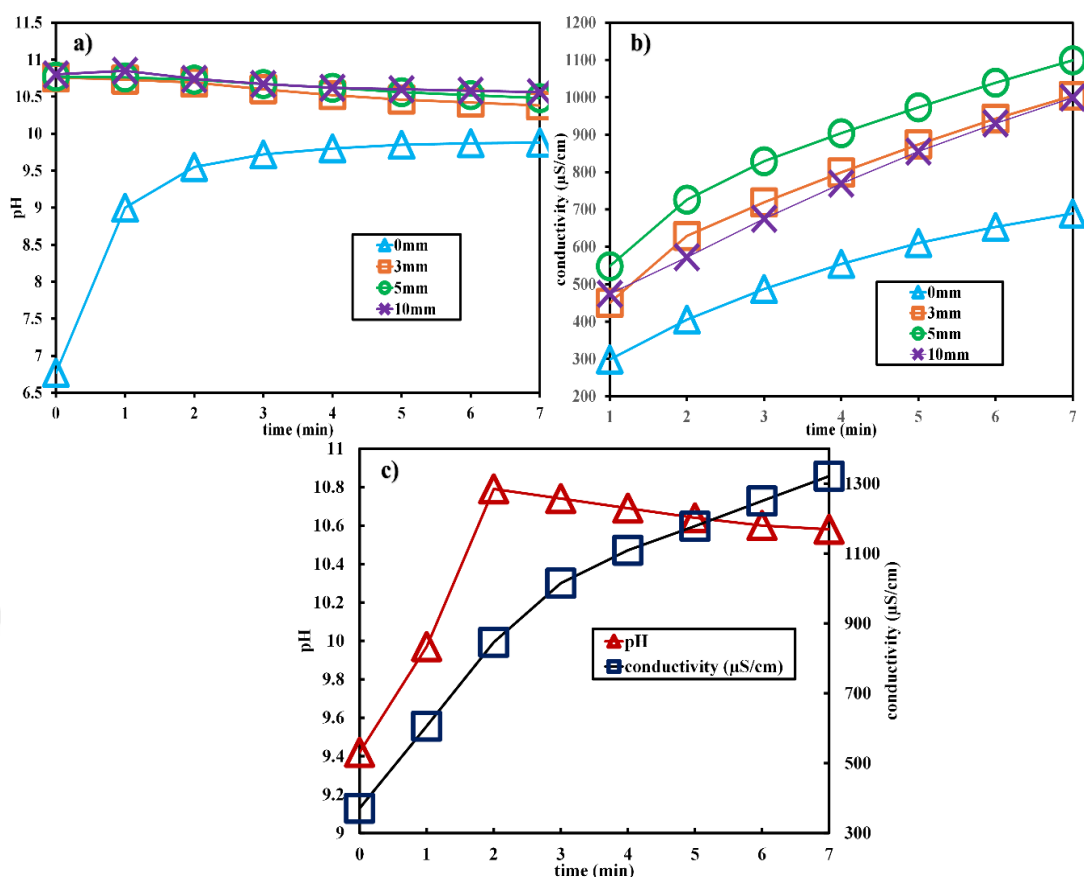


Figure 49. pH and conductivity changes over time in batch reactor experiments. (a) pH changes of scenario #1, (b) conductivity change of scenario #1 and (c) both pH and conductivity change for scenario #2.

In the second scenario, the initial pH value increased from 9.42 and reached approximately to 10.58 (Figure 49, c). This may be due to the presence of equal amounts of Ca^{2+} and Mg^{2+} ions in the medium promoted pH stabilization. While the conductivity was $371 \mu\text{S/cm}$ at the beginning, it increased $1321 \mu\text{S/cm}$ at the end of the 7th minute. This value reveals that the equal presence of both ion species in the medium increases the ionic activity and accordingly, the solution maintains its ionic charge at a high level during the precipitation process.

4.6.5 SEM Images from $\text{MgCa}(\text{CO}_3)_2$ Synthesis Attempt in Direct Mixing Experiment

SEM analyses provided important information on the crystal morphology of the samples deposited at different $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios (Figure 50). The micrographs obtained for $\text{Mg}^{2+}/\text{Ca}^{2+} = 0.5$ (Figure 50, a-d) show the presence of blocky or rhombohedral crystals with a porous texture on the surface. The edges of these crystals appear to be rough, giving the impression of being abraded or slightly rounded. Especially at 50000x magnification, the edges of these crystals appear to be rough, giving the impression of being worn or slightly rounded. In addition, thin, needle-like extensions can be seen on the surface of the blocky crystals or between them. The scarcity of these needle-like structures can be attributed to the aragonite phase, which was observed at low density in XRD analyses; however, the overall morphology suggests that calcite is predominantly dominated by magnesium calcite.

In contrast, SEM images (Figure 50, e-h) of samples precipitated at $\text{Mg}^{2+}/\text{Ca}^{2+} = 1$ show a more homogeneous structure with a large proportion of rod-like crystal clusters. Here, the crystals come together in bundles to form needle-like radially shaped aggregates. This typical morphology is consistent with the rapid and directional growth common in aragonite crystals. Although porosity is relatively low compared to the previous sample, gaps between crystals are occasionally noticeable due to the radial growth pattern.

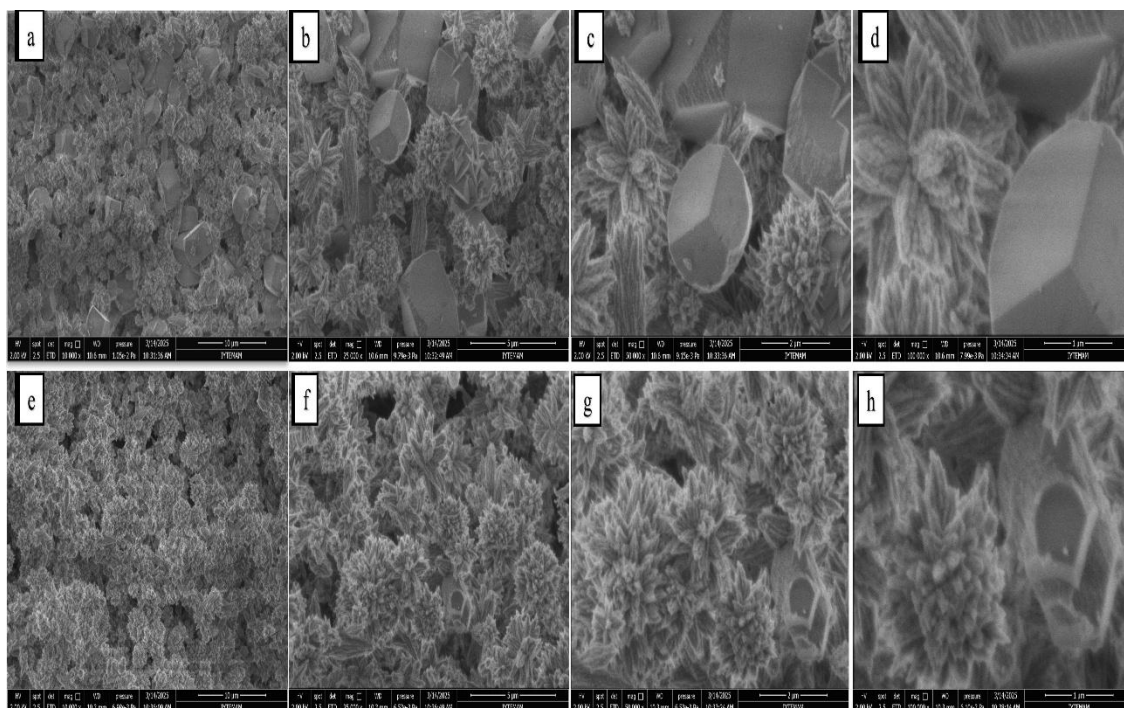


Figure 50. SEM images for Mg-related Direct Mixing Experiments. (a-d) $\text{Mg}^{2+}/\text{Ca}^{2+}=0.5$; (e-h) $\text{Mg}^{2+}/\text{Ca}^{2+}=1$ and (j-m) $\text{Mg}^{2+}/\text{Ca}^{2+}=2$.

4.6.6 XRD Data from $\text{MgCa}(\text{CO}_3)_2$ Synthesis Attempt in Direct Mixing Experiment

$\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio, XRD analyses of possible phases are given in Figure 51. The peaks marked with symbols in the XRD pattern obtained at $\text{Mg}^{2+}/\text{Ca}^{2+}=0.5$ (Figure 51, a) correspond to the Mg-containing calcite ($\text{Mg}_x\text{Ca}_{1-x}\text{CO}_3$) phase in the database (PDF #01-085-1034). Peaks characteristic of the aragonite (PDF #00-041-1475 or #01-076-0606) phase are indicated by circle symbols. Peak intensities show that at a ratio of $\text{Mg}^{2+}/\text{Ca}^{2+}=0.5$, the main phase is largely magnesium calcite, while the aragonite phase is represented by relatively low intensity peaks. This suggests that a limited amount of Mg^{2+} ions can be incorporated into the calcite lattice and that calcite-like phases are still dominantly formed. The partially observed aragonite peaks indicate that Mg^{2+} ions can also trigger the formation of aragonite instead of calcite under certain conditions.

In aqueous phase, $\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ dissolve to Mg^{2+} , Ca^{2+} and NO_3^- ions while Na_2CO_3 dissociates into Na^+ and CO_3^{2-} ions. Subsequently, Mg^{2+} and Ca^{2+} ions

react with CO_3^{2-} ions to form magnesium-calcium carbonate ($\text{Mg}_x\text{Ca}_{1-x}\text{CO}_3$) as a precipitate.

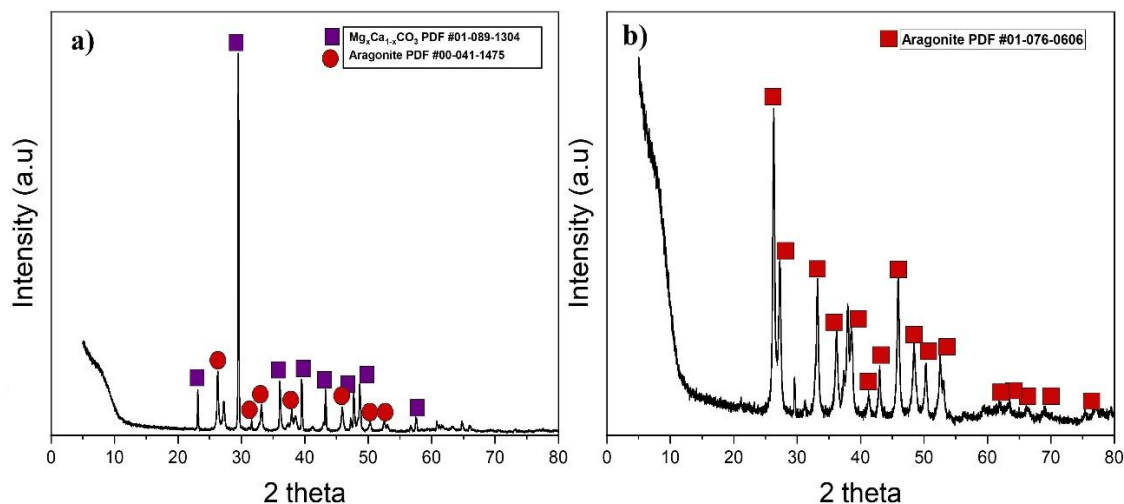


Figure 51. XRD analysis of Mg-related Direct Mixing experiments. (a) $\text{Mg}^{2+}/\text{Ca}^{2+}=0.5$; (b) $\text{Mg}^{2+}/\text{Ca}^{2+}=1$.

Figure 51, (b) shows that the intensity of aragonite peaks, indicated by red square symbols in the XRD pattern obtained in the $\text{Mg}^{2+}/\text{Ca}^{2+}=1$ condition. The peaks representing the Mg^{2+} calcite phase is still detectable; however, their relative intensity has decreased significantly.

This result indicates that the stresses and defects in the calcite lattice caused by increasing Mg^{2+} content make calcite growth kinetically and thermodynamically difficult, whereas aragonite formation becomes easier or more stable. A high $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio promotes the precipitation of calcium carbonate in the direction of the aragonite phase and this observation is in direct agreement with our experimental data^{160–167}. Due to the insufficient amount of sample obtained at the $\text{Mg}^{2+}/\text{Ca}^{2+} = 2$ ratio, XRD analysis could not be performed.

4.6.7 SEM & EDX Data from $\text{MgCa}(\text{CO}_3)_2$ Synthesis Attempt in Batch Reactor Experiment

The morphological features of synthesized CaCO_3 , $\text{Mg}_x\text{Ca}_{1-x}\text{CO}_3$ and $\text{MgCa}(\text{CO}_3)_2$ were analyzed by SEM (Figure 52). Figure 52, (a – d) shows the rhombohedral structure typical of calcite crystals¹⁶⁸ when 0 mM $\text{Ca}(\text{OH})_2$ is used. Crystals were observed as structures with sharp corners and relatively smooth edges. The relatively smooth crystal surfaces indicate a balanced precipitation mechanism rather than rapid and unidirectional growth. Layering is observed on some crystal surfaces. XRD results, it was stated that calcite is the main phase, and that the magnesium-containing calcite structure can be found at a very low level. In SEM images, it is seen that the rhombohedral morphology specific to calcite is clearly dominant. The partial substitution of magnesium into the crystal lattice is not clearly observable in the structure due to the very low amount of magnesium in the system, as can be seen from the EDX results. According to EDX analysis, the content contains 0.51% weight Mg and 51.79% Ca. Due to rapid saturation, aggregates were formed in some parts of the crystal (Figure 53, a).

Using 3 mM $\text{Ca}(\text{OH})_2$ (Figure 52, e-h), the rhombohedral forms typical of calcite crystals are still evident in the images. At 50000x magnitude zoom, more indentation marks were detected on the surface and edges of the crystals. In the center of some crystals, multidirectional elongated flower-like structures may be the result of directional growth due to Mg^{2+} incorporation. Although this type of morphology partially deviates from the flat-surfaced rhombohedral forms typical of calcite, the basic skeleton of the crystal is still the calcite lattice. EDX identified the sample containing (Figure 53, b) the weight 46.96% Ca, 1/4% Mg.

At 5 mM $\text{Ca}(\text{OH})_2$, calcite-specific rhombohedral shapes are predominantly observed (j-m). However, in some crystals, slight deviations from the rhombohedral structure are observed. Compared to the 3 mM $\text{Ca}(\text{OH})_2$ condition, it can be said that the crystal surfaces exhibit a slightly rougher or layered appearance. In some crystals, floral morphologies starting in the centre and growing outwards are present in this sample as in the previous sample. In the EDX data (Figure 53, c) the percentage of Mg weight in the content was measured as 0.96%.

In the experiment for 10mM of $\text{Ca}(\text{OH})_2$ concentration, the crystals appear to be

densely packed and form large aggregates (n-g). Compared to the 5 mM Ca(OH)_2 condition, there is tighter packing between the particles. Although the basic crystal shapes are still in calcite-like rhombohedral or blocky forms, increased roughness and thin layers are noticeable on the surface in details. Compared to the 5 mM condition, floral morphologies are relatively reduced. Instead, more dense and tightly aggregated blocky crystals appear to dominate. In some crystal clusters, extra layers may be noticeable. Compared to the 0-5 mM conditions, it is noteworthy that crystal surface roughness increased in the 10 mM Ca(OH)_2 sample. In the EDX data (Figure 53, d), the percentage of Mg weight in the content was measured as 0.65%.

In scenario 2, when the concentration of $\text{Mg(NO}_3)_2$ was increased and the concentration was equal to 5mM of Ca(OH)_2 , more regular and homogeneous aggregation was observed compared to the previous scenarios (Figure 52, r-u) . Most of the crystal structure exhibit blocky or rhombohedral forms typical of carbonate minerals such as calcite and dolomite. However, the slight shortening (truncation) or stepped structure observed on the surfaces and edges suggests that the crystal has acquired different growth habits than pure calcite. This may be a morphological indication that Mg^{2+} ions have started to enter the lattice in a regular manner. Compared to the prominent floral structures observed in previous scenarios (e.g. 5 mM and 10 mM Ca(OH)_2), it is may be important that the crystal surfaces in this sample have a flatter, layered appearance with steps on the surfaces. This is a morphological change frequently reported in the transition from calcite to dolomite-like phase^{169,170}. According to EDX analysis (Figure 53, e), this sample was found to have the highest Mg content (2.31%) compared to other samples.

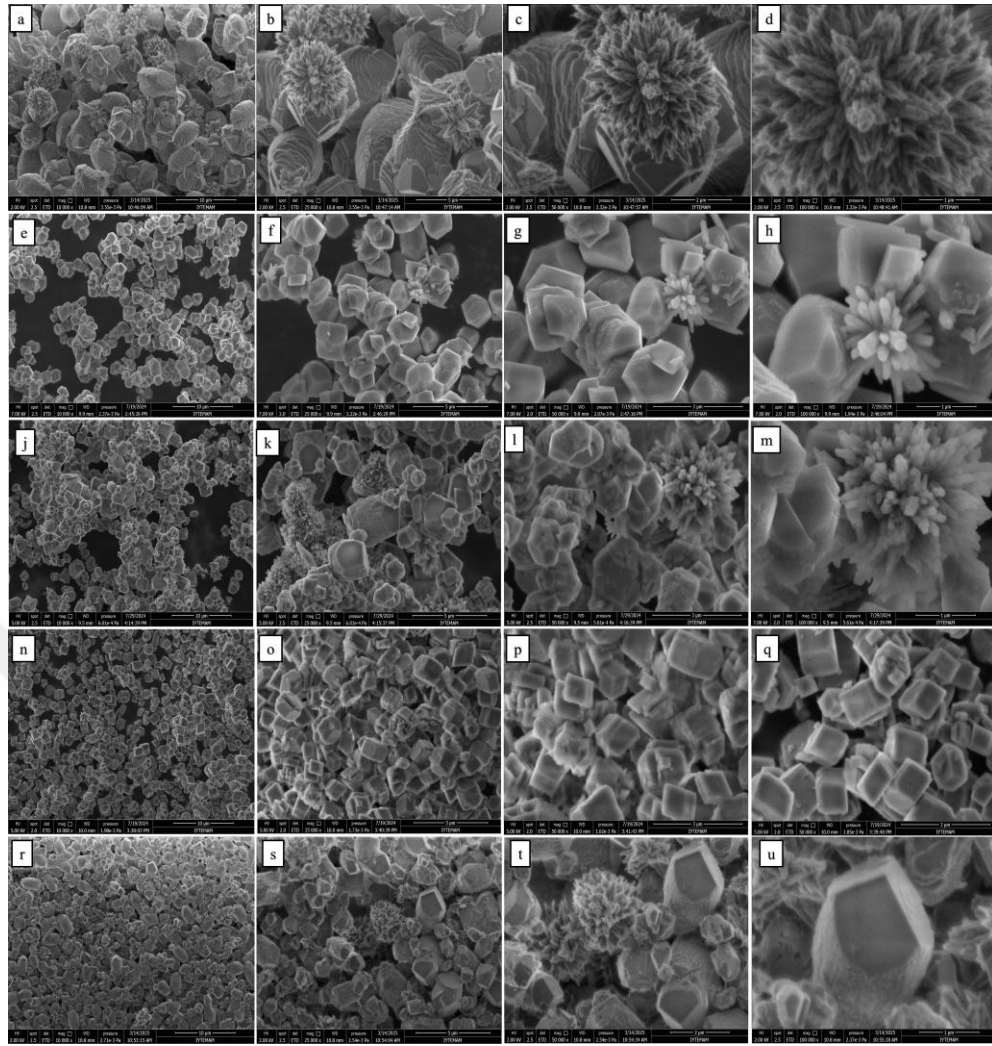


Figure 52. SEM results of Mg related experiments in direct mixing experiment. (a-d) 0mM Ca(OH)_2 ; (e-h) 3 mM Ca(OH)_2 ; (j-m) 5 mM Ca(OH)_2 ; (n-q) 10 mM Ca(OH)_2 and (r-u) scenario #2.

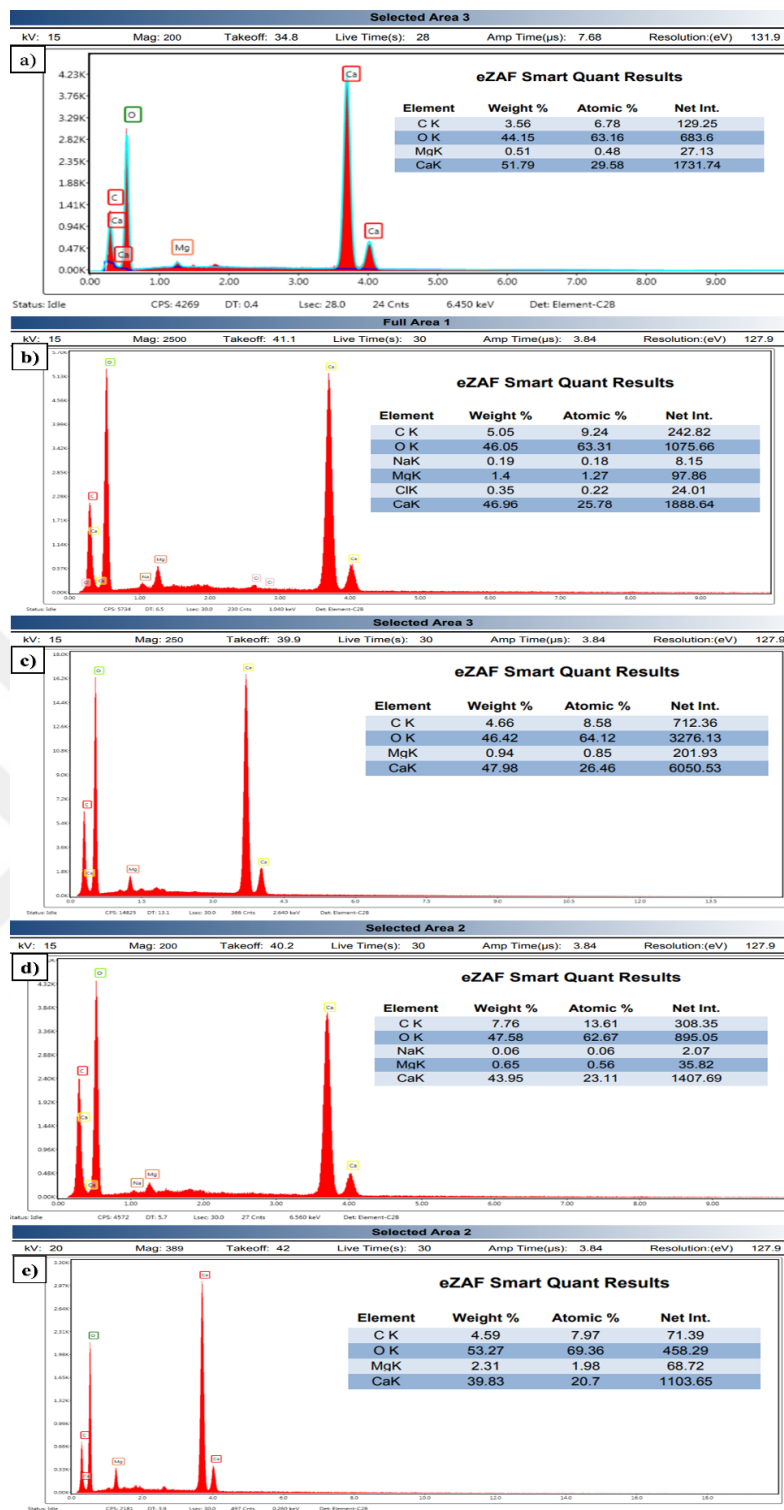


Figure 53. EDX results of Mg related experiments in direct mixing experiment. (a-d) 0mM $\text{Ca}(\text{OH})_2$; (e-h) 3 mM $\text{Ca}(\text{OH})_2$; (j-m) 5 mM $\text{Ca}(\text{OH})_2$; (n-q) 10 mM $\text{Ca}(\text{OH})_2$ and (r-u) scenario #2.

4.6.8 XRD Data from $\text{MgCa}(\text{CO}_3)_2$ Synthesis Attempt in Batch Reactor Experiment

The XRD patterns for crystals obtained in the presence of different concentrations of $\text{Ca}(\text{OH})_2$ solutions is shown in Figure 54. Firstly, in the experiment without $\text{Ca}(\text{OH})_2$ (a), the average pH was lower due to the absence of $\text{Ca}(\text{OH})_2$ in the solution. The precipitation is dominated by the calcium carbonate phase and the peak positions are consistent with the values reported for calcite in the ICDD database. Even at the relatively low concentration of 1.95 mM of Mg^{2+} ion in the solution, the increasing pH value over time helped to substitute Mg^{2+} into the calcite structure in small amounts. The XRD pattern shows the phase peaks resulting from this substitution with the reference code PDF #01-089-1305.

When the $\text{Ca}(\text{OH})_2$ concentration was increased to 3 mM, the pH of the medium increased considerably at the initial conditions with increasing OH^- ion concentration. This sharp increase in peak intensity indicates a higher degree of crystallinity Figure 54 (b). In particular, the peaks corresponding to the (104), (006) and (110) planes are sharp and high intensity¹⁷¹. The peak in the (104) plane indicates that the calcite phase is dominant. The further increase of Ca^{2+} ion concentration in the medium compared to Mg^{2+} ion concentration may have caused calcite formation to become more dominant.

Increasing the $\text{Ca}(\text{OH})_2$ concentration to 5 mM, it is understood from the characteristic peaks of calcite that the main phase is again calcite Figure 54, (c). At this stage, although weak signals were detected in the XRD pattern in addition to calcite, these may be Mg-containing phases. As can be seen from the peak intensities, there was better crystallization compared to the other 2 conditions.

Higher peak intensities are observed at the condition with the highest average pH, when 10 mM $\text{Ca}(\text{OH})_2$ is used, compared to the other experiments. Although almost all these peaks are compatible with the calcite phase, a dolomite peak was also observed Figure 54 (d). This is thought to be an irregular dolomite structure. However, too high a pH can sometimes lead to the precipitation of magnesium hydroxide phases such as $\text{Mg}(\text{OH})_2$ ¹⁷².

In parallel with these experimental conditions, increasing the concentration of $\text{Mg}(\text{NO}_3)_2$ (5 mM) and keeping the concentration of $\text{Ca}(\text{OH})_2$ constant at 5 mM increases

the amount of Mg^{2+} in the solution compared to the previous scenario and increases the pH sufficiently to promote the incorporation of magnesium into the carbonate structure. In general, under such condition, the incorporation of magnesium into the calcite crystal lattice is observed to be more successful than in the other scenarios Figure 54, (e). The peaks correspond exactly to the reference code $\text{Mg}_x\text{Ca}_{1-x}\text{CO}_3$ in the ICDD database. Such an increase in magnesium concentration showed characteristic peaks for dolomite in the crystal phase content, albeit in small amounts, despite the limited crystallization process of 7 minutes ¹⁰. Also, it is understood that this Mg-containing calcite is more dominant than dolomite. Slight shifts in the peaks were observed due to the integration of magnesium into the calcite crystal lattice.



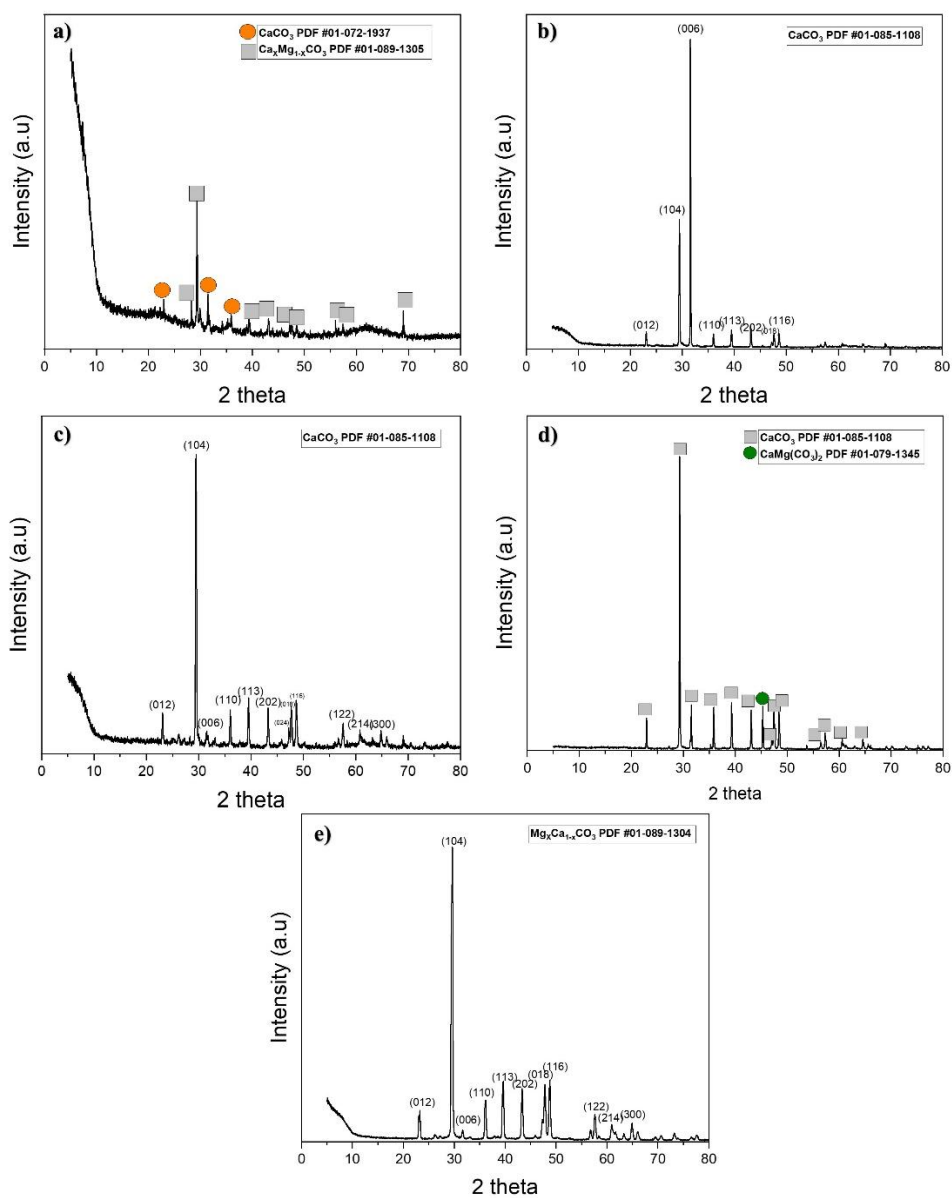


Figure 54. Calcite, Mg- substitute calcite and dolomite peaks. (a) 0 mM Ca(OH)_2 , (b) 3 mM Ca(OH)_2 , (c) 5mM Ca(OH)_2 , (d) Ca(OH)_2 10 mM, and (e) scenario #2.

CHAPTER 5

CONCLUSION

This work included extensive experimental studies on the synthesis and characterization of calcium-based double carbonates at low temperature and low-pressure conditions and the development of innovative methods for the incorporation of different ions into the calcite crystal lattice. One of the main objectives of the study was to optimize the parameters in the synthesis of double carbonates such as $\text{BaCa}(\text{CO}_3)_2$, $\text{SrCa}(\text{CO}_3)_2$, $\text{CoCa}(\text{CO}_3)_2$ and $\text{MgCa}(\text{CO}_3)_2$ using the direct mixture method and batch reactor system approach. The obtained findings showed that small changes in the synthesis conditions have decisive effects on the crystal structure, morphology and reaction kinetics.

The successful synthesis of $\text{BaCa}(\text{CO}_3)_2$ and $\text{SrCa}(\text{CO}_3)_2$ compounds reveals the methodological success. In particular, the synthesis protocol developed for $\text{SrCa}(\text{CO}_3)_2$ provided the possibility to describe in detail morphological features not yet reported in the literature to the best of our knowledge. This novel contribution allows further evaluation of the potential of $\text{SrCa}(\text{CO}_3)_2$ in terms of materials science and application technologies.

In particular, the new precipitation method developed for the synthesis of Co_3O_4 nanoparticles within the scope of the thesis has enabled to obtain products with the desired structural properties in a shorter time and with lower energy input compared to the methods previously widely used in the literature. This new approach reveals that Co_3O_4 can offer significant advantages in potential application areas such as catalysis and energy storage systems.

The data obtained by advanced techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) applied in the characterization stage revealed the dynamics of the synthesis process, structural regularities and crystal morphologies in detail. The obtained data provided important clues for optimizing the synthesis methods used and systematic control.

The targeted synthesis of $\text{MgCa}(\text{CO}_3)_2$ exhibited only partial success under the applied experimental conditions, with the desired phase forming in limited quantities. In

contrast, the synthesis attempts for $\text{CoCa}(\text{CO}_3)_2$ failed to yield the expected crystalline phase despite various methodological approaches. Nevertheless, these outcomes offer valuable insights, particularly for the design of more effective strategies for double carbonates synthesis and lay a methodological foundation for prospective studies in this field.

Future work will further demonstrate the applicability of these methods in larger systems and their potential for industrial scale-up.



REFERENCES

1. Terada, J. Rhombohedral Crystals of Ba-Ca and Sr-Ca Double Carbonates. *J Physical Soc Japan* **1952**, 7 (4), 432–434. <https://doi.org/10.1143/JPSJ.7.432>.
2. Goldsmith, J. R.; Graf, D. L. *Structural and Compositional Variations in Some Natural Dolomites*; **1958**; Vol. 66. <https://www.jstor.org/stable/30056855>.
3. Yang, Z.; Whitaker, F. F.; Liu, R.; Phillips, J. C.; Zhong, D. A New Model for Formation of Lacustrine Primary Dolomite by Subaqueous Hydrothermal Venting. *Geophys Res Lett* **2021**, 48 (6). <https://doi.org/10.1029/2020GL091335>.
4. Tucker, M. E. .; Wright, V. Paul.; DICKSON, J. A. D. . *Carbonate Sedimentology*; Blackwell Scientific Publications: Oxford, **1990**. <https://doi.org/https://doi.org/10.1002/9781444314175>.
5. Liang, W.; Peters, C.; Li, L.; Leupold, O.; Li, H.; Böttcher, M. E. BaFe[CO₃]₂, a New Double Carbonate: Synthesis, Structural Characterisation, and Geostability Implications for High and Low PT. *Geochemistry* **2021**, 81 (2), 125740. <https://doi.org/10.1016/j.chemer.2021.125740>.
6. Buasri, A.; Rochanakit, K.; Wongvitvichot, W.; Masa-ard, U.; Loryuenyong, V. The Application of Calcium Oxide and Magnesium Oxide from Natural Dolomitic Rock for Biodiesel Synthesis. *Energy Procedia* **2015**, 79, 562–566. <https://doi.org/10.1016/j.egypro.2015.11.534>.
7. Mehmood, M. Dolomite and Dolomitization Model - a Short Review. *International Journal of Hydrology* **2018**, 2 (5). <https://doi.org/10.15406/ijh.2018.02.00124>.
8. David Bressan. *The Origin Of Geological Terms: Dolomite*. <https://www.forbes.com/sites/davidbressan/2016/07/30/the-origin-of-geological-terms-dolomite/> (accessed 2025-06-21).
9. Lippmann, F. *Sedimentary Carbonate Minerals*; Springer Berlin Heidelberg: Berlin, Heidelberg, **1973**. <https://doi.org/10.1007/978-3-642-65474-9>.
10. Gregg, J. M.; Bish, D. L.; Kaczmarek, S. E.; Machel, H. G. Mineralogy, Nucleation and Growth of Dolomite in the Laboratory and Sedimentary Environment: A Review. *Sedimentology* **2015**, 62 (6), 1749–1769. <https://doi.org/10.1111/sed.12202>.
11. McKenzie Judith, A. *The dolomite problem; an outstanding controversy*.

- EurekaMag. <https://eurekamag.com/research/020/324/020324383.php> (accessed 2025-06-21).
12. Arvidson, R. S.; Mackenzie, F. T. Tentative Kinetic Model for Dolomite Precipitation Rate and Its Application to Dolomite Distribution. *Aquat Geochem* **1996**, 2, 273–298. <https://doi.org/https://doi.org/10.1007/BF01160046>.
 13. Petrash, D. A.; Bialik, O. M.; Bontognali, T. R. R.; Vasconcelos, C.; Roberts, J. A.; McKenzie, J. A.; Konhauser, K. O. Microbially Catalyzed Dolomite Formation: From near-Surface to Burial. *Earth-Science Reviews*. Elsevier B.V. August 1, **2017**, pp 558–582. <https://doi.org/10.1016/j.earscirev.2017.06.015>.
 - 14.. Warren, J. Dolomite: Occurrence, Evolution and Economically Important Associations. *Earth Sci Rev* **2000**, 52 (1–3), 1–81. [https://doi.org/https://doi.org/10.1016/S0012-8252\(00\)00022-2](https://doi.org/https://doi.org/10.1016/S0012-8252(00)00022-2).
 15. Fang, Y.; Xu, H. A New Approach To Quantify the Ordering State of Protodolomite Using XRD, TEM, and Z-Contrast Imaging. *Journal of Sedimentary Research* **2019**, 89 (6), 537–551. <https://doi.org/10.2110/jsr.2019.29>.
 16. Pichler, T.; Humphrey, J. D. Formation of Dolomite in Recent Island-Arc Sediments Due to Gas-Seawater-Sediment Interaction. *Journal of Sedimentary Research* **2001**, 71 (3), 394–399. <https://doi.org/10.1306/2DC4094D-0E47-11D7-8643000102C1865D>.
 - 17 ALAN J. WELLS. Recent Dolomite in the Persian Gulf. *Nature* **1962**, 194, 274–275.
 18. Fang, Y.; Zhang, F.; Farfan, G. A.; Xu, H. Low-Temperature Synthesis of Disordered Dolomite and High-Magnesium Calcite in Ethanol–Water Solutions: The Solvation Effect and Implications. *ACS Omega* **2022**, 7 (1), 281–292. <https://doi.org/10.1021/acsomega.1c04624>.
 19. Machel, H. G. Concepts and Models of Dolomitization: A Critical Reappraisal. *Geological Society, London, Special Publications* **2004**, 235 (1), 7–63. <https://doi.org/10.1144/GSL.SP.2004.235.01.02>.
 20. Chave, K. E. FACTORS INFLUENCING THE MINERALOGY OF CARBONATE SEDIMENTS¹. *Limnol Oceanogr* **1962**, 7 (2), 218–223. <https://doi.org/10.4319/lo.1962.7.2.0218>.
 21. Graf, D. L.; Goldsmith, J. R. Some Hydrothermal Syntheses of Dolomite and Protodolomite. *J Geol* **1956**, 64 (2), 173–186. <https://doi.org/10.1086/626332>.
 22. Johnston, J. F. W. LXXVI. On the Composition of the Right Rhombic Baryto-

- Calcite, the Bicalcareo-Carbonate of Baryta of Dr. Thomson. *Philosophical Magazine and Journal of Science* **1837**, 10 (62), 373–376. <https://doi.org/https://doi.org/10.1080/14786443708649227>.
23. Roberts, A. C. A Mineralogical Investigation of Alstonite, $\text{BaCa}(\text{CO}_3)_2$, **1976**. <https://doi.org/10.13140/RG.2.1.4988.8244>.
 24. Chuliá-Jordán, R.; Santamaria-Perez, D.; Ruiz-Fuertes, J.; Otero-De-La-Roza, A.; Popescu, C. Crystal Structure of $\text{BaCa}(\text{CO}_3)_2$ Alstonite Carbonate and Its Phase Stability upon Compression. *ACS Earth Space Chem* **2021**, 5 (5), 1130–1139. <https://doi.org/10.1021/acsearthspacechem.1c00032>.
 25. Whittaker, M. L.; Pri-Gal, E.; Schmidt, A.; Joester, D. Superlattice Ordering Transitions Driven by Short-Range Structure in Barium Calcium Carbonates. *Faraday Discuss* **2022**, 235, 416–432. <https://doi.org/10.1039/d1fd00086a>.
 26. B. Dickens; J. S. Bowen. The Crystal Structure of $\text{BaCa}(\text{CO}_3)_2$ (Barytocalcite). *Journal of Research of the National Bureau of Standards - A. Physics and Chemistry* **1971**, 75A (3), 197–203. <https://doi.org/https://doi.org/10.6028/jres.075a.020>.
 27. Effenberger H. The Crystal Structure of the Mineral Paralstonite, $\text{BaCa}(\text{CO}_3)_2$. *Neues Jahrbuch für Mineralogie, Monatshefte* **1980**, 353–363.
 28. Spahr, D.; Bayarjargal, L.; Vinograd, V.; Luchitskaia, R.; Milman, V.; Winkler, B. A New $\text{BaCa}(\text{CO}_3)_2$ Polymorph. *Acta Crystallogr B Struct Sci Cryst Eng Mater* **2019**, 75, 291–300. <https://doi.org/10.1107/S2052520619003238>.
 29. Sartori, F.; Sartori, F. New Data on Alstonite. *Lithos* **1975**, 8 (3), 199–207. [https://doi.org/https://doi.org/10.1016/0024-4937\(75\)90036-5](https://doi.org/https://doi.org/10.1016/0024-4937(75)90036-5).
 30. Frost, R. L.; Dickfos, M. J. Raman and Infrared Spectroscopic Study of the Anhydrous Carbonate Minerals Shortite and Barytocalcite. *Spectrochim Acta A Mol Biomol Spectrosc* **2008**, 71 (1), 143–146. <https://doi.org/10.1016/j.saa.2007.11.021>.
 31. Torres, A.; Luque, F. J.; Tortajada, J.; Arroyo-de Dompablo, M. E. Analysis of Minerals as Electrode Materials for Ca-Based Rechargeable Batteries. *Sci Rep* **2019**, 9 (1). <https://doi.org/10.1038/s41598-019-46002-4>.
 32. Polgári, M.; Bajnóczi, B.; Kovács Kis, V.; Götze, J.; Dobosi, G.; Tóth, M.; Vigh, T. Mineralogical and Cathodoluminescence Characteristics of Ca-Rich Kutnohorite from the Úrkút Mn-Carbonate Mineralization, Hungary. *Mineral Mag* **2007**, 71 (5), 493–508. <https://doi.org/10.1180/minmag.2007.071.5.493>.

33. Warr, L. N. IMA–CNMNC Approved Mineral Symbols. *Mineral Mag* **2021**, 85 (3), 291–320. <https://doi.org/10.1180/mgm.2021.43>.
34. Whitney, D. L.; Evans, B. W. Abbreviations for Names of Rock-Forming Minerals. *American Mineralogist* **2010**, 95 (1), 185–187. <https://doi.org/10.2138/am.2010.3371>.
35. Žák, L.; Povondra, P. TMPM Tschermaks Mineralogische Und Petrographische Mitteilungen Kutnohorite from the Chvaletice Pyrite and Manganese Deposit, East Bohemia. *TMPM Tschermaks Mineralogische und Petrographische Mitteilungen* **1981**, 28, 55–63. <https://doi.org/10.1007/BF01081850>.
36. Pucon, D. R.; Essbnn, E. J.; Qlnns, A. M. G. *Petrologic and Crystal-Chemical Implications of Cation Order-Disorder in Kutnavorite $\text{ICaMn}(\text{CO}_3)\text{Rl}^*$* ; **1987**; Vol. 72.
37. De Grave, E.; Vochten, R. An⁵⁷Fe Mössbauer Effect Study of Ankerite. *Phys Chem Minerals* **1985**, 12, 108–113. <https://doi.org/10.1007/BF01046835>.
38. Kopecskó, K.; Al Dabbas, A. Silicate Sorption on Ankerite from a Standard Silicate Solution. *Periodica Polytechnica Chemical Engineering* **2021**, 65 (3), 400–407. <https://doi.org/10.3311/PPch.16967>.
39. Wersin, P. *Svensk Kärnbränslehantering AB Impact of iron on the performance of clay barriers in waste disposal systems Report on the status of research and development*. CM Gruppen AB. https://inis.iaea.org/records/fjwa3-kvh30/preview/40042534.pdf?include_deleted=0 (accessed 2025-06-21).
40. Rosenberg, P. E.; Foit, F. F. The Stability of Transition Metal Dolomites in Carbonate Systems: A Discussion. **1979**, 43 (7), 951–955. [https://doi.org/10.1016/0016-7037\(79\)90085-1](https://doi.org/10.1016/0016-7037(79)90085-1).
41. Philip E. Rosenberg. Structural Variation in the Dolomite-Ankerite Solid-Solution Series: An X-Ray, Mössbauer, and TEM Study. *American Mineralogist* **1991**, 76, 659–660.
42. Chuliá-Jordán, R.; Santamaria-Perez, D.; Ruiz-Fuertes, J.; Otero-De-la-roza, A.; Popescu, C. Compressibility and Phase Stability of Iron-Rich Ankerite. *Minerals* **2021**, 11 (6). <https://doi.org/10.3390/min11060607>.
43. Dav, P. M.; Symmes, G. H.; Cohen, B. A.; Reeder, R. J.; I-l, D. Synthesis of the New Compound $\text{CaFe}(\text{CO}_3)_2$ and Experimental Constraints on the $(\text{Ca,Fe})\text{CO}_3$ Join. *Geochim Cosmochim Acta* **1993**, 58 (23–24), 5105–5109. [https://doi.org/https://doi.org/10.1016/0016-7037\(93\)90612-Z](https://doi.org/https://doi.org/10.1016/0016-7037(93)90612-Z).

44. Pimentel, C.; Pina, C. M. Reaction Pathways towards the Formation of Dolomite-Analogues at Ambient Conditions. **2016**, *178*, 259–267. <https://doi.org/https://doi.org/10.1016/j.gca.2015.12.040>.
45. Ivanets, A.; Kuznetsova, T. F. *MANGANESE AND COPPER OXIDE CATALYSTS DEPOSITED ON DOLOMITE SUBSTRATE FOR GROUNDWATER PURIFICATION*; **2017**. <https://www.researchgate.net/publication/315713541>.
46. Hazen, R. M.; Downs, R. T.; Jones, A. P.; Kah, L. Carbon Mineralogy and Crystal Chemistry. *Reviews in Mineralogy and Geochemistry*. **2013**, pp 7–46. <https://doi.org/10.2138/rmg.2013.75.2>.
47. Carlo G. Garavelli; Filippo Vurro; Gian Carlo Fioravanti. Minrecordite, a New Mineral from Tsumeb. *Mineralogical Record* **1982**, *13* (3), 131–136.
48. Liu, Z. T. Y.; Burton, B. P.; Khare, S. V.; Sarin, P. First-Principles Phase Diagram Calculations for the Carbonate Quasibinary Systems $\text{CaCO}_3\text{-ZnCO}_3$, $\text{CdCO}_3\text{-ZnCO}_3$, $\text{CaCO}_3\text{-CdCO}_3$ and $\text{MgCO}_3\text{-ZnCO}_3$. *Chem Geol* **2016**, *443*, 137–145. <https://doi.org/10.1016/j.chemgeo.2016.09.024>.
49. Land, L. S. Failure to Precipitate Dolomite at 25 • C from Dilute Solution Despite 1000-Fold Oversaturation after 32 Years. *Aquat Geochem* **1998**, *4*, 361–368. <https://doi.org/10.1023/A:1009688315854>.
50. Noyes, R. M. Thermodynamics of Ion Hydration as a Measure of Effective Dielectric Properties of Water. *J Am Chem Soc* **1962**, *84* (4), 513–522. <https://doi.org/10.1021/ja00863a002>.
51. Gautier, Q.; Bénézech, P.; Mavromatis, V.; Schott, J. Hydromagnesite Solubility Product and Growth Kinetics in Aqueous Solution from 25 to 75°C. *Geochim Cosmochim Acta* **2014**, *138*, 1–20. <https://doi.org/10.1016/j.gca.2014.03.044>.
52. Li, R.; Li, L.; Bai, J.; Liang, W.; Tang, H. Kutnohorite $\text{CaMn}(\text{CO}_3)_2$ Crystal Growth at High Pressure-Temperature. *High Temp High Press* **2020**, *49* (4), 343–355. <https://doi.org/10.32908/hthp.v49.831>.
53. Montes-Hernandez, G.; Findling, N.; Renard, F.; Auzende, A. L. Precipitation of Ordered Dolomite via Simultaneous Dissolution of Calcite and Magnesite: New Experimental Insights into an Old Precipitation Enigma. *Cryst Growth Des* **2014**, *14* (2), 671–677. <https://doi.org/10.1021/cg401548a>.
54. Montes-Hernandez, G.; Findling, N.; Renard, F. Dissolution-Precipitation Reactions Controlling Fast Formation of Dolomite under Hydrothermal Conditions. *Applied Geochemistry* **2016**, *73*, 169–177.

- <https://doi.org/10.1016/j.apgeochem.2016.08.011>.
55. Zhang, F.; Xu, H.; Shelobolina, E. S.; Konishi, H.; Converse, B.; Shen, Z.; Roden, E. E. The Catalytic Effect of Bound Extracellular Polymeric Substances Excreted by Anaerobic Microorganisms on Ca-Mg Carbonate Precipitation: Implications for the “Dolomite Problem.” *American Mineralogist* **2015**, *100* (2–3), 483–494. <https://doi.org/10.2138/am-2015-4999>.
 - 56.. Fang, Y.; Xu, H. Dissolved Silica-Catalyzed Disordered Dolomite Precipitation. *American Mineralogist* **2022**, *107* (3), 443–452. <https://doi.org/10.2138/am-2021-7474>.
 57. Zhang, F.; Xu, H.; Konishi, H.; Shelobolina, E. S.; Roden, E. E. Polysaccharide-Catalyzed Nucleation and Growth of Disordered Dolomite: A Potential Precursor of Sedimentary Dolomite. *American Mineralogist* **2012**, *97* (4), 556–567. <https://doi.org/10.2138/am.2012.3979>.
 58. Xu, J.; Yan, C.; Zhang, F.; Konishi, H.; Xu, H.; Teng, H. H. Testing the Cation-Hydration Effect on the Crystallization of Ca–Mg–CO₃ Systems. *Proceedings of the National Academy of Sciences* **2013**, *110* (44), 17750–17755. <https://doi.org/10.1073/pnas.1307612110>.
 59. Bruno, M.; Ghignone, S.; Pastero, L.; Aquilano, D. The Influence of Ca–Mg Disorder on the Growth of Dolomite: A Computational Study. *CrystEngComm* **2020**, *22* (29), 4853–4861. <https://doi.org/10.1039/D0CE00663G>.
 60. Matsumoto, M.; Morita, Y.; Yoshinaga, M.; Hirose, S.-I.; Onoe, K. *Reactive Crystallization of Lithium Carbonate Nanoparticles by Microwave Irradiation of Aqueous Solution Containing CO₂ Microbubbles*; **2009**; Vol. 42. <https://doi.org/10.1252/jcej.08we173>.
 61. Tsuchiya, Y.; Wada, Y.; Hiaki, T.; Onoe, K.; Matsumoto, M. Effects of CO₂ Fine Bubble Injection on Reactive Crystallization of Dolomite from Concentrated Brine. *J Cryst Growth* **2017**, *469*, 36–41. <https://doi.org/10.1016/j.jcrysgro.2016.09.037>.
 62. Matsumoto, M.; Masaoka, K.; Tsuchiya, Y.; Wada, Y.; Hiaki, T.; Onoe, K. Enhanced CaMg CO₃ 2 Production by CO₂ Microbubble Injection into Concentrated Brine. *Bull. Soc. Sea Water Sci., Jpn* **2019**, *73* (2), 65–70. https://doi.org/https://doi.org/10.11457/swsj.73.2_65.
 63. Kamei, S.; Masaoka, K.; Furukawa, S.; Matsumoto, M. Sonochemical Synthesis of Dolomite from Removed-K Bittern for Color-Tunable Phosphor Applications.

- Salt and Seawater Science & Technology* **2022**, *2*, 31–36.
https://doi.org/https://doi.org/10.11457/ssst.2.0_31.
64. Massoni, N.; Rosen, J.; Chartier, M.; Cozzika, T. Study of Barytocalcite as a Conditioning Matrix for Carbon 14: Comparison of Several Synthesis Routes. *Journal of Nuclear Materials* **2013**, *441* (1–3), 152–158.
<https://doi.org/10.1016/j.jnucmat.2013.06.003>.
 65. Win, M. S. *Scanning Electron Microscopy and Current-Voltage Characteristics of $\text{CaMn}(\text{CO}_3)_2/n\text{-Si}$ Thin Film*; **2019**; Vol. 2.
[http://www.maas.edu.mm/Research/Admin/pdf/7.%20Dr%20May%20Sandar%20Win\(75-86\).pdf](http://www.maas.edu.mm/Research/Admin/pdf/7.%20Dr%20May%20Sandar%20Win(75-86).pdf) (accessed 2025-06-21).
 66. Massoni, N.; Le Gallet, S.; Hoffmann, S.; Launeau, P.; Grin, Y.; Bernard, F. Sintering of Synthetic Barytocalcite $\text{BaCa}(\text{CO}_3)_2$, Kutnahorite $\text{CaMn}(\text{CO}_3)_2$ and Rhodochrosite MnCO_3 for Carbon-14 Sequestration. *J Eur Ceram Soc* **2015**, *35* (1), 297–308. <https://doi.org/10.1016/j.jeurceramsoc.2014.08.002>.
 67. Goldsmith, J. R.; Graf, D. L.; Witters, J.; Northrop, D. A. Studies in the System $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$: 1. Phase Relations; 2. A Method for Major-Element Spectrochemical Analysis; 3. Compositions of Some Ferroan Dolomites. *J Geol* **1962**, *70* (6). <https://doi.org/https://doi.org/10.1086/626865>.
 68. P. E. ROSENBERG. SUBSOLIDUS RELATIONS IN THE SYSTEM $\text{CaCO}_3\text{—FeCO}_3$. *Am J Sci* **1963**, *261*, 683–690.
 69. Morlidge, M.; Pawley, A.; Droop, G. Double Carbonate Breakdown Reactions at High Pressures: An Experimental Study in the System $\text{CaO-MgO-FeO-MnO-CO}_2$. *Contributions to Mineralogy and Petrology* **2006**, *152* (3), 365–373.
<https://doi.org/10.1007/s00410-006-0112-5>.
 70. Fazeli, A. R.; Tareen, J. A. K. THERMAL DECOMPOSITION OF RI-IOMBOHEDRAL DOUBLE CARBONATES OF DOLOMITE TYPE. *Journal of Thermal Analysis* **1992**, *38*, 2459–2465.
<https://doi.org/https://doi.org/10.1007/bf01974624>.
 71. Denigres Filho, R. W. N.; Rocha, G. de A.; Montes, C. R.; Vieira-Coelho, A. C. Synthesis and Characterization of Boehmites Obtained from Gibbsite in Presence of Different Environments. *Materials Research* **2016**, *19* (3), 659–668.
<https://doi.org/10.1590/1980-5373-MR-2016-0019>.
 72. Santos, H. S.; Nguyen, H.; Venâncio, F.; Ramteke, D.; Zevenhoven, R.; Kinnunen, P. Mechanisms of Mg Carbonates Precipitation and Implications for CO_2 Capture

- and Utilization/Storage. *Inorg Chem Front* **2023**, *10* (9), 2507–2546. <https://doi.org/10.1039/D2QI02482A>.
73. Spieß, L.; Teichert, G.; Schwarzer, R.; Behnken, H.; Genzel, C. *Moderne Röntgenbeugung*; Vieweg+Teubner: Wiesbaden, **2009**. <https://doi.org/10.1007/978-3-8349-9434-9>.
 74. Surdu, V. A.; György, R. X-Ray Diffraction Data Analysis by Machine Learning Methods—A Review. *Applied Sciences (Switzerland)*. Multidisciplinary Digital Publishing Institute (MDPI) September 1, **2023**. <https://doi.org/10.3390/app13179992>.
 75. Friedrich, W.; Knipping, P.; Laue, M. Interferenzerscheinungen Bei Röntgenstrahlen. *Ann Phys* **1913**, *346* (10), 971–988. <https://doi.org/10.1002/andp.19133461004>.
 76. Raliya, R.; Saran, R. P.; Choudhary, K. K. *Biosynthesis and Characterization of Nanoparticles*; **2014**. <https://www.researchgate.net/publication/262183487>.
 77. Welin, E. Notes on the Mineralogy of Sweden 6. X-Ray Powder Data for Minerals from Långban and the Related Mineral Deposits of Central Sweden. *Arkiv för Mineralogi och Geologi* **1968**, *4*, 499–541.
 78. Frondel, C.; Bauer, L. H. A Manganese Dolomite, $\text{CaMn}(\text{CO}_3)_2$. *American Mineralogist* **1955**, *40*, 748–760.
 79. Howie, R. A.; Broadhurst, F. M. X-Ray Data for Dolomite and Ankerite. *American Mineralogist* **1958**, *43*, 1210–1216.
 80. Erol, A. High-Magnification SEM Micrograph of Siloxanes. In *Atomic-force Microscopy and Its Applications*; IntechOpen, **2019**. <https://doi.org/10.5772/intechopen.82076>.
 81. Kulikova, S. A.; Belova, K. Y.; Frolova, A. V.; Vinokurov, S. E. The Use of Dolomite to Produce a Magnesium Potassium Phosphate Matrix for Radioactive Waste Conditioning. *Energies (Basel)* **2023**, *16* (14). <https://doi.org/10.3390/en16145513>.
 82. Zhang, F.; Xu, H.; Konishi, H.; Kemp, J. M.; Roden, E. E.; Shen, Z. Dissolved Sulfide-Catalyzed Precipitation of Disordered Dolomite: Implications for the Formation Mechanism of Sedimentary Dolomite. *Geochim Cosmochim Acta* **2012**, *97*, 148–165. <https://doi.org/10.1016/j.gca.2012.09.008>.
 83. Pesonen, J.; Myllymäki, P.; Tuomikoski, S.; Vervecken, G.; Hu, T.; Prokkola, H.; Tynjälä, P.; Lassi, U. Use of Calcined Dolomite as Chemical Precipitant in the

- Simultaneous Removal of Ammonium and Phosphate from Synthetic Wastewater and from Agricultural Sludge. *ChemEngineering* **2019**, 3 (2), 1–12. <https://doi.org/10.3390/chemengineering3020040>.
84. Rodriguez-Blanco, J. D.; Shaw, S.; Benning, L. G. A Route for the Direct Crystallization of Dolomite. *American Mineralogist* **2015**, 100 (5–6), 1172–1181. <https://doi.org/10.2138/am-2015-4963>.
 85. Zhu, Y.; Nong, P.; Mo, N.; Zhu, Z.; Deng, H.; Tang, S.; Yang, H.; Zhang, L.; Wang, X. Dissolution and Solubility of Calcite-Rhodochrosite Solid Solutions [(Ca1-XMnx)CO3] at 25 °C. *Geochem Trans* **2021**, 22 (1), 1. <https://doi.org/10.1186/s12932-021-00075-1>.
 86. Abeywardena, M. R.; Elkaduwe, R. K. W. H. M. K.; Karunaratne, D. G. G. P.; Pitawala, H. M. T. G. A.; Rajapakse, R. M. G.; Manipura, A.; Mantilaka, M. M. G. P. G. Surfactant Assisted Synthesis of Precipitated Calcium Carbonate Nanoparticles Using Dolomite: Effect of PH on Morphology and Particle Size. *Advanced Powder Technology* **2020**, 31 (1), 269–278. <https://doi.org/10.1016/j.appt.2019.10.018>.
 87. Mantilaka, M. M. M. G. P. G.; Karunaratne, D. G. G. P.; Rajapakse, R. M. G.; Pitawala, H. M. T. G. A. Precipitated Calcium Carbonate/Poly(Methyl Methacrylate) Nanocomposite Using Dolomite: Synthesis, Characterization and Properties. *Powder Technol* **2013**, 235, 628–632. <https://doi.org/10.1016/j.powtec.2012.10.048>.
 88. Suzuki, Y.; Morgan, P. E. D.; Ohji, T. Synthesis and Deformation Behavior of Nano-Diphasic Materials from Natural Dolomite. *Materials Science and Engineering A304* **2001**, 304–306, 780–784. [https://doi.org/https://doi.org/10.1016/S0921-5093\(00\)01566-5](https://doi.org/https://doi.org/10.1016/S0921-5093(00)01566-5).
 89. Boudchicha, M. R.; Rubio, F.; Achour, S. Synthesis of Glass Ceramics from Kaolin and Dolomite Mixture. *International Journal of Minerals, Metallurgy and Materials* **2017**, 24 (2), 194–201. <https://doi.org/10.1007/s12613-017-1395-4>.
 90. Amirthalingam, N.; Deivarajan, T.; Paramasivam, M. Mechano Chemical Synthesis of Hydroxyapatite Using Dolomite. *Mater Lett* **2019**, 254, 379–382. <https://doi.org/10.1016/j.matlet.2019.07.118>.
 91. Sendžikienė, E.; Makarevičienė, V.; Kazancev, K. Application of Dolomite as a Heterogeneous Catalyst of Biodiesel Synthesis. *Transport* **2018**, 33 (5), 1155–1161. <https://doi.org/10.3846/transport.2018.6723>.

92. Correia, L. M.; de Sousa Campelo, N.; Novaes, D. S.; Cavalcante, C. L.; Cecilia, J. A.; Rodríguez-Castellón, E.; Vieira, R. S. Characterization and Application of Dolomite as Catalytic Precursor for Canola and Sunflower Oils for Biodiesel Production. *Chemical Engineering Journal* **2015**, *269*, 35–43. <https://doi.org/10.1016/j.cej.2015.01.097>.
93. Olivia, R.; Jamarun, N.; Arif, S.; Sirin, Y. A. The Utilization of Dolomite as Catalyst in Biodiesel Production. *Rasayan Journal of Chemistry* **2017**, *10* (1), 160–164. <https://doi.org/10.7324/RJC.2017.1011555>.
94. Hafriz, R. S. R. M.; Shafizah, I. N.; Arifin, N. A.; Salmiaton, A.; Yunus, R.; Yap, Y. H. T.; Shamsuddin, A. H. Effect of Ni/Malaysian Dolomite Catalyst Synthesis Technique on Deoxygenation Reaction Activity of Waste Cooking Oil. *Renew Energy* **2021**, *178*, 128–143. <https://doi.org/10.1016/j.renene.2021.06.074>.
95. Algoufi, Y. T.; Kabir, G.; Hameed, B. H. Synthesis of Glycerol Carbonate from Biodiesel By-Product Glycerol over Calcined Dolomite. *J Taiwan Inst Chem Eng* **2017**, *70*, 179–187. <https://doi.org/10.1016/j.jtice.2016.10.039>.
96. Yang, H.; Dong, H.; Zhang, T.; Zhang, Q.; Zhang, G.; Wang, P.; Liu, Q. Calcined Dolomite: An Efficient and Recyclable Catalyst for Synthesis of α , β -Unsaturated Carbonyl Compounds. *Catal Letters* **2019**, *149* (3), 778–787. <https://doi.org/10.1007/s10562-018-2632-9>.
97. Tian, J.; Wu, Z.; Liu, Z.; Yu, C.; Yang, K.; Zhu, L.; Huang, W.; Zhou, Y. Low-Cost and Efficient Visible-Light-Driven $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ Microspheres Fabricated via an Ion Exchange Route. *Cuihua Xuebao/Chinese Journal of Catalysis* **2017**, *38* (11), 1899–1908. [https://doi.org/10.1016/S1872-2067\(17\)62924-3](https://doi.org/10.1016/S1872-2067(17)62924-3).
98. Baz, H.; Creech, M.; Chen, J.; Gong, H.; Bradford, K.; Huo, H. Water-Soluble Carbon Nanoparticles Improve Seed Germination and Post-Germination Growth of Lettuce under Salinity Stress. *Agronomy* **2020**, *10* (8). <https://doi.org/10.3390/agronomy10081192>.
99. Zhang, K.; Wang, Y.; Mao, J.; Chen, B. Effects of Biochar Nanoparticles on Seed Germination and Seedling Growth. *Environmental Pollution* **2020**, *256*, 113409. <https://doi.org/10.1016/j.envpol.2019.113409>.
100. Prażak, R.; Świąciło, A.; Krzepiło, A.; Michałek, S.; Arczewska, M. Impact of Ag Nanoparticles on Seed Germination and Seedling Growth of Green Beans in Normal and Chill Temperatures. *Agriculture* **2020**, *10* (8), 312.

<https://doi.org/10.3390/agriculture10080312>.

101. Yu, J.; Qian, J.; Wang, F.; Qin, J.; Dai, X.; You, C.; Jia, X. Study of Using Dolomite Ores as Raw Materials to Produce Magnesium Phosphate Cement. *Constr Build Mater* **2020**, *253*, 119147. <https://doi.org/10.1016/j.conbuildmat.2020.119147>.
102. Xu, J.; Lu, D.; Zhang, S.; Xu, Z.; Hooton, R. Reaction Mechanism of Dolomite Powder in Portland-Dolomite Cement. *Constr Build Mater* **2021**, *270*, 121375. <https://doi.org/10.1016/j.conbuildmat.2020.121375>.
103. Abbass, A. M.; Elrahman, M. A.; Sikora, P.; Strzałkowski, J.; Stephan, D.; Abdel-Gawwad, H. A. From Dolomite Waste to Katoite-Based Binder: Synthesis, Performance and Characterization. *Journal of Building Engineering* **2023**, *75*. <https://doi.org/10.1016/j.jobe.2023.106971>.
104. Hou, P.; Wang, X.; Zhou, X.; Cheng, X.; Shah, S. P. Regulations on the Hydration, Morphology, and Sulfate-Attack Resistivity of C3A with Micro/Nano-Silica Particles. *Constr Build Mater* **2022**, *324*, 126388. <https://doi.org/10.1016/j.conbuildmat.2022.126388>.
105. Chen, Y.; Wu, K.; Xu, L.; Wang, Z.; Zhao, Y.; Zhu, Z. Chloride Corrosion of Reinforced Calcium Aluminate Cement Mortar. *Journal of Wuhan University of Technology-Mater. Sci. Ed.* **2023**, *38* (1), 79–87. <https://doi.org/10.1007/s11595-023-2670-3>.
106. Lee, N. K.; Koh, K. T.; Park, S. H.; Ryu, G. S. Microstructural Investigation of Calcium Aluminate Cement-Based Ultra-High Performance Concrete (UHPC) Exposed to High Temperatures. *Cem Concr Res* **2017**, *102*, 109–118. <https://doi.org/10.1016/j.cemconres.2017.09.004>.
107. Filitz, R.; Kierzkowska, A. M.; Broda, M.; Müller, C. R. Highly Efficient CO₂ Sorbents: Development of Synthetic, Calcium-Rich Dolomites. *Environ Sci Technol* **2012**, *46* (1), 559–565. <https://doi.org/10.1021/es2034697>.
108. Li, K.; Sun, J.; Zhang, Y.; Zhang, X.; Liu, L.; Tong, X.; Jiang, L.; Zhou, Z.; Zhao, C. Cigarette Butt-Assisted Combustion Synthesis of Dolomite-Derived Sorbents with Enhanced Cyclic CO₂ Capturing Capability for Direct Solar-Driven Calcium Looping. *Sep Purif Technol* **2023**, *311*. <https://doi.org/10.1016/j.seppur.2023.123269>.
109. Umair Hassan, M.; Batool, M.; Hassan Farooq, T.; Saleem Arif, M.; Aamer, M.; Ahmed Waqas, M.; Albasher, G.; Sajjad, M.; Shakoor, A. How Does Dolomite

- Application Affect the Greenhouse Gases Emissions from the Terrestrial Environment? – A Global Synthesis. *Fuel* **2023**, 332. <https://doi.org/10.1016/j.fuel.2022.126048>.
110. Røsberg, I.; Frank, J.; Stuanes, A. O. Effects of Liming and Fertilization on Tree Growth and Nutrient Cycling in a Scots Pine Ecosystem in Norway. *For Ecol Manage* **2006**, 237 (1–3), 191–207. <https://doi.org/10.1016/j.foreco.2006.09.045>.
 111. Ahmad Fauzi, A. A.; Osman, A. F.; Alrashdi, A. A.; Mustafa, Z.; Abdul Halim, K. A. On the Use of Dolomite as a Mineral Filler and Co-Filler in the Field of Polymer Composites: A Review. *Polymers (Basel)* **2022**, 14 (14), 2843. <https://doi.org/10.3390/polym14142843>.
 112. Ahmad Saidi, M. A.; Mazlan, F. S.; Hassan, A.; Abd. Rashid, R.; Rahmat, A. R. Flammability, Thermal and Mechanical Properties of Polybutylene Terephthalate/Dolomite Composites. *Journal of Physical Science* **2019**, 30 (3), 175–189. <https://doi.org/10.21315/jps2019.30.3.11>.
 113. Ridhwan, J. N. M.; Noimam, N. Z.; Mohd Salleh, M. A. A.; Sam, S. T.; Musa, L.; Nik Yahya, N. Z. The Effect of Different Sizes “Batu Reput” (Dolomite) as a Filler in SMR L and ENR-50. *Adv Mat Res* **2013**, 795, 383–387. <https://doi.org/10.4028/www.scientific.net/AMR.795.383>.
 114. Osman, A. F.; Siah, L.; Alrashdi, A. A.; Ul-Hamid, A.; Ibrahim, I. Improving the Tensile and Tear Properties of Thermoplastic Starch/Dolomite Biocomposite Film through Sonication Process. *Polymers (Basel)* **2021**, 13 (2), 274. <https://doi.org/10.3390/polym13020274>.
 115. Asfa Amalia Ahmad Fauzi; Azlin Fazlina Osman; Khairul Anwar Abdul Halim; Hanafi Ismail. Ultrasonicated Dolomite as Potential Reinforcing Mineral Filler in Polymer and Copolymer-Based Composites. In *Mineral-Filled Polymer Composites: Selection, Processing, and Applications*; Ismail, H. S. S. M. ; I. R. A., Ed.; CRC Press, **2022**; p 12.
 116. Fauzi, A. A. A.; Osman, A. F.; Halim, K. A. A.; Mustafa, Z.; Alakrach, A. M.; Salleh, M. N. The Use of Ground & Ultrasonicated Dolomite (GUD) for Improving the Tensile Performance of Poly (Ethylene-Co-Vinyl Acetate) Copolymer Composite. *J Phys Conf Ser* **2021**, 2080 (1), 012029. <https://doi.org/10.1088/1742-6596/2080/1/012029>.
 117. Shahnaz Syed Bakar, S.; Shahida Zakaria, N.; Wahab, J. A.; Salleh, M. *Batu Reput Filled Recycled Polypropylene Eco-Polymer Composites*; **2013**; Vol. 7.

- <https://www.aensiweb.com/old/aeb/2013/3596-3600.pdf> (accessed 2025-06-21).
118. Manni, A.; Matadi Boumbimba, R.; Mikdam, A.; El Bouari, A.; Addiego, F.; Meziani, J.; Wary, M. Magnesite and Dolomite Micro-Particles: Preparation, Physical Properties and Application in Bio-Based Polymer Composite. *Polymer Bulletin* **2022**, 79 (4), 2149–2171. <https://doi.org/10.1007/s00289-021-03609-w>.
 119. Ghada, B.; Rachida, Z.; Ahmed, M.; Faycal, D. *Effect of Marble Powder and Dolomite on the Mechanical Properties and the Thermal Stability of Poly(Vinyl Chloride)*; **2010**; Vol. 22. https://www.researchgate.net/profile/Ahmed-Meghezzi/publication/259944025_Effect_of_Marble_Powder_and_Dolomite_on_the_Mechanical_Properties_and_the_Thermal_Stability_of_Polyvinyl_chloride/data/0a85e52ea71b347e02000000/ARTICLE-3.pdf (accessed 2025-06-21).
 120. Sönmez, M.; Jugănar, M.; Fica, A.; Fica, D.; Oprea, O.; Gurău, D.; Alexandrescu, L.; Stelescu, M. D.; Georgescu, M.; Nițuică, M.; Melinescu, A.; Marin, M. Dolomite Surface Modification with Titania and Silica Precursors and Its Morphostructural and Thermal Characterisation. In *ICAMS Proceedings of the International Conference on Advanced Materials and Systems*; Inst. Nat. Cercetare-Dezvoltare Text. Pielarie, **2020**; pp 101–106. <https://doi.org/10.24264/icams-2020.I.13>.
 121. Adesakin, A. O.; Ajayi, O. O.; Imosili, P. E.; Attahdaniel, B. E.; Olusunle, S. O. O. Characterization and Evaluation of Mechanical Properties of Dolomite as Filler in Polyester. *Chemistry and Materials Research (ISSN 2224-3224, Print; ISSN 2225-0956, Online)* **2013**, Vol. 3 (8), 36–49.
 122. Fatin Mohd Din, S.; Abd Rashid, R.; Akmal Ahmad Saidi, M.; Othman, N. Mechanical, Thermal and Flammability Properties of Dolomite Filled Polypropylene Composites. *Persintis eJournal* **2018**, 8 (2), 58–73.
 123. Ali, V.; Neelkamal; Haque, F. Z.; Zulfeqar, M.; Husain, M. Preparation and Characterization of Polyether-based Polyurethane Dolomite Composite. *J Appl Polym Sci* **2007**, 103 (4), 2337–2342. <https://doi.org/10.1002/app.24839>.
 124. Ni, L.; Mao, Y.; Liu, Y.; Cai, P.; Jiang, X.; Gao, X.; Cheng, X.; Chen, J. Synergistic Reinforcement of Waterborne Polyurethane Films Using Palygorskite and Dolomite as Micro/Nano-Fillers. *Journal of Polymer Research* **2020**, 27 (1), 23. <https://doi.org/10.1007/s10965-019-1995-y>.
 125. Shamsuri, A. A.; Mohd Zolkepli, M. N.; Mohamed Ariff, A. H.; Sudari, A. K.; Abu Zarin, M. A Preliminary Investigation on Processing, Mechanical and

- Thermal Properties of Polyethylene/Kenaf Biocomposites with Dolomite Added as Secondary Filler. *J Compos* **2015**, 2015, 1–7. <https://doi.org/10.1155/2015/760909>.
126. Verma, S. K.; Gangil, B.; Gupta, A.; Rajput, N. S.; Singh, T. Dolomite Dust Filled Glass Fiber Reinforced Epoxy Composite: Influence of Fabrication Techniques on Physicomechanical and Erosion Wear Properties. *Polym Compos* **2022**, 43 (1), 551–565. <https://doi.org/10.1002/pc.26398>.
 127. Verma, S. K.; Gupta, A.; Singh, T.; Gangil, B.; János, E.; Fekete, G. Influence of Dolomite on Mechanical, Physical and Erosive Wear Properties of Natural-Synthetic Fiber Reinforced Epoxy Composites. *Mater Res Express* **2019**, 6 (12), 125704. <https://doi.org/10.1088/2053-1591/ab5abb>.
 128. Saleh, S. S. Md.; Akil, H. Md.; Kudus, M. H. A.; Ahmad, K. R.; Bakhtiar, N. S. A. A. Effect of Different Hybrid Method on Properties of Carbon Nanotubes/Dolomite Hybrid Filled Phenolic Composites. *Procedia Chem* **2016**, 19, 45–49. <https://doi.org/10.1016/j.proche.2016.03.014>.
 129. Saleh, S. S. M.; Wei, Y. S.; Mohammad, N. F.; Abdullah, S. F. A.; Akil, H. M.; Saliu, H. R. Tensile Properties of CNTs-Dolomite Hybrid Filled Epoxy Composites; **2021**; p 020236. <https://doi.org/10.1063/5.0046070>.
 130. Humphries, T. D.; Møller, K. T.; Rickard, W. D. A.; Sofianos, M. V.; Liu, S.; Buckley, C. E.; Paskevicius, M. Dolomite: A Low Cost Thermochemical Energy Storage Material. *J Mater Chem A Mater* **2019**, 7 (3), 1206–1215. <https://doi.org/10.1039/c8ta07254j>.
 131. Srinivasan, S.; Dodson, D.; Charles, M. B. J.; Wallen, S. L.; Albarelli, G.; Kaushik, A.; Hickman, N.; Chaudhary, G. R.; Stefanakos, E.; Dhau, J. Energy Storage in Earth-Abundant Dolomite Minerals. *Applied Sciences (Switzerland)* **2020**, 10 (19). <https://doi.org/10.3390/APP10196679>.
 132. Saravanan, A.; Senthil Kumar, P.; Jeevanantham, S.; Karishma, S.; Tajsabreen, B.; Yaashikaa, P. R.; Reshma, B. Effective Water/Wastewater Treatment Methodologies for Toxic Pollutants Removal: Processes and Applications towards Sustainable Development. *Chemosphere* **2021**, 280, 130595. <https://doi.org/10.1016/j.chemosphere.2021.130595>.
 133. Ghaemi, A.; Torab-Mostaedi, M.; Shahhosseini, S.; Asadollahzadeh, M. Characterization of Ag(I), Co(II) and Cu(II) Removal Process from Aqueous Solutions Using Dolomite Powder. *Korean Journal of Chemical Engineering*

- 2013**, 30 (1), 172–180. <https://doi.org/10.1007/s11814-012-0113-1>.
134. Yan, S.; Wang, Q.; Liu, J.; Huo, W.; Yang, J.; Huang, Y. Synthesis, Characterization and Adsorption Properties of Low-Cost Porous Calcined Dolomite Microspheres for Removal of Dyes. *Journal of Wuhan University of Technology-Mater. Sci. Ed.* **2019**, 34 (3), 507–515. <https://doi.org/10.1007/s11595-019-2080-4>.
 135. Zahuri, A. A.; Abdul Patah, M. F.; Kamarulzaman, Y.; Hashim, N. H.; Thirumoorthi, T.; Wan Mohtar, W. H. M.; Mohd Hanafiah, Z.; Amir, Z.; Wan-Mohtar, W. A. A. Q. I. Decolourisation of Real Industrial and Synthetic Textile Dye Wastewater Using Activated Dolomite. *Water (Switzerland)* **2023**, 15 (6). <https://doi.org/10.3390/w15061172>.
 136. Baldauf-Sommerbauer, G.; Lux, S.; Aniser, W.; Siebenhofer, M. Synthesis of Carbon Monoxide from Hydrogen and Magnesite/Dolomite. *Chem Ing Tech* **2017**, 89 (1), 172–179. <https://doi.org/10.1002/cite.201600078>.
 137. Capodaglio, A. G.; Bolognesi, S. Ecofuel Feedstocks and Their Prospects. In *Advances in Eco-Fuels for a Sustainable Environment*; Elsevier, **2019**; pp 15–51. <https://doi.org/10.1016/B978-0-08-102728-8.00002-4>.
 138. Zakaly, H. M. H.; Rashad, M.; Tekin, H. O.; Saudi, H. A.; Issa, S. A. M.; Henaish, A. M. A. Synthesis, Optical, Structural and Physical Properties of Newly Developed Dolomite Reinforced Borate Glasses for Nuclear Radiation Shielding Utilizations: An Experimental and Simulation Study. *Opt Mater (Amst)* **2021**, 114, 110942. <https://doi.org/10.1016/j.optmat.2021.110942>.
 139. Massoni, N.; Marcou, C.; Rosen, J.; Jollivet, P. The Use of Barytocalcite for Carbon 14 Immobilization: One-Year Leaching Behavior. *Journal of Nuclear Materials* **2014**, 454 (1–3), 230–237. <https://doi.org/10.1016/j.jnucmat.2014.07.077>.
 140. Chuliá-Jordán, R.; Santamaría-Pérez, D.; González-Platas, J.; Otero-de-la-Roza, A.; Ruiz-Fuertes, J.; Popescu, C. Phase Stability and Dense Polymorph of the BaCa(CO₃)₂ Barytocalcite Carbonate. *Sci Rep* **2022**, 12 (1). <https://doi.org/10.1038/s41598-022-11301-w>.
 141. Karatasios, I.; Kilikoglou, V.; Colston, B.; Theoulakis, P.; Watt, D. Setting Process of Lime-Based Conservation Mortars with Barium Hydroxide. *Cem Concr Res* **2007**, 37 (6), 886–893. <https://doi.org/10.1016/j.cemconres.2007.03.007>.
 142. Lièvremon, D.; N'negue, M. A.; Behra, P.; Lett, M. C. Biological Oxidation of

- Arsenite: Batch Reactor Experiments in Presence of Kutnahorite and Chabazite. *Chemosphere* **2003**, 51 (5), 419–428. [https://doi.org/10.1016/S0045-6535\(02\)00869-X](https://doi.org/10.1016/S0045-6535(02)00869-X).
143. Subramanian, R.; Fordsmand, H.; Paulapuro, H. PCC-Cellulose Composite Fillers. *Bioresources* 2007, 2 (1), 91–105. <https://doi.org/10.15376/biores.2.1.91-105>.
 144. Munawaroh, F.; Muharrami, L. K.; . T.; Arifin, Z. Synthesis and Characterization of Precipitated CaCO₃ from Ankerite Prepared by Bubbling Method. *KnE Engineering* **2019**, 1 (2), 98. <https://doi.org/10.18502/keg.v1i2.4435>.
 145. Al Dabbas, A.; Kopeckó, K. Corrosion of ISG by Mg-Si Precipitation in Presence of Ankerite. *Pollack Periodica* **2022**, 17 (1), 56–61. <https://doi.org/10.1556/606.2021.00410>.
 146. Ashiq, M. N.; Iqbal, M. J.; Gul, I. H. Structural, Magnetic and Dielectric Properties of Zr–Cd Substituted Strontium Hexaferrite (SrFe₁₂O₁₉) Nanoparticles. *J Alloys Compd* **2009**, 487 (1–2), 341–345. <https://doi.org/10.1016/j.jallcom.2009.07.140>.
 147. Molva, M.; Kilic, S.; Ozdemir, E. Effect of Carbonic Anhydrase on CaCO₃ Crystallization in Alkaline Solution. *Energy & Fuels* **2016**, 30 (12), 10686–10695. <https://doi.org/10.1021/acs.energyfuels.6b02475>.
 148. Kim, H.; Son, H. M.; Lee, H. K. Characterization of Bio-Adsorptive Removal Performance of Strontium through Ureolysis-Mediated Bio-Mineralization. *Chemosphere* **2022**, 288, 132586. <https://doi.org/10.1016/j.chemosphere.2021.132586>.
 149. Astilleros, J. M.; Pina, C. M.; Fernández-Díaz, L.; Putnis, A. The Effect of Barium on Calcite {104} Surfaces during Growth. *Geochim Cosmochim Acta* **2000**, 64 (17), 2965–2972. [https://doi.org/10.1016/S0016-7037\(00\)00405-1](https://doi.org/10.1016/S0016-7037(00)00405-1).
 150. Joseph I. Goldstein. *Scanning Electron Microscopy and X-Ray Microanalysis*, Latest Edition.; **2018**. <https://link.springer.com/book/10.1007/978-1-4939-6676-9> (accessed 2025-06-21).
 151. Lide, D. R. *CRC Handbook of Chemistry and Physics*, 90th Edition.; CRC Press: Florida, USA, 2010. <https://webdelprofesor.ula.ve/ciencias/isolda/libros/handbook.pdf> (accessed 2025-06-21).
 152. Frear, G. L.; Johnston, J. THE SOLUBILITY OF CALCIUM CARBONATE (CALCITE) IN CERTAIN AQUEOUS SOLUTIONS AT 25° 1. *J Am Chem Soc* 1929, 51 (7), 2082–2093. <https://doi.org/10.1021/ja01382a014>.

153. Chen, Q.-Y.; Haq, S. U.; Xing, Z.-H.; Wang, Y.-H. Temperature Effect on Green-Synthesized Co₃O₄ Nanoparticle as Photocatalyst for Overall Water Splitting. *J Photonics Energy* **2020**, *10* (04). <https://doi.org/10.1117/1.JPE.10.042006>.
154. Gaikar, P. S.; Angre, A. P.; Wadhawa, G.; Ledade, P. V.; Mahmood, S. H.; Lambat, T. L. Green Synthesis of Cobalt Oxide Thin Films as an Electrode Material for Electrochemical Capacitor Application. *Current Research in Green and Sustainable Chemistry* **2022**, *5*, 100265. <https://doi.org/10.1016/j.crgsc.2022.100265>.
155. Al Omari, M. M. H.; Rashid, I. S.; Qinna, N. A.; Jaber, A. M.; Badwan, A. A. Calcium Carbonate. In *Profiles of Drug Substances, Excipients and Related Methodology*; Academic Press Inc., **2016**; Vol. 41, pp 31–132. <https://doi.org/10.1016/bs.podrm.2015.11.003>.
156. Boch, R.; Dietzel, M.; Reichl, P.; Leis, A.; Baldermann, A.; Mittermayr, F.; Pölt, P. Rapid Ikaite (CaCO₃·6H₂O) Crystallization in a Man-Made River Bed: Hydrogeochemical Monitoring of a Rarely Documented Mineral Formation. *Applied Geochemistry* **2015**, *63*, 366–379. <https://doi.org/10.1016/j.apgeochem.2015.10.003>.
157. Dotta, T. C.; Hayann, L.; de Padua Andrade Almeida, L.; Nogueira, L. F. B.; Arnez, M. M.; Castelo, R.; Cassiano, A. F. B.; Faria, G.; Martelli-Tosi, M.; Bottini, M.; Ciancaglini, P.; Catirse, A. B. C. E. B.; Ramos, A. P. Strontium Carbonate and Strontium-Substituted Calcium Carbonate Nanoparticles Form Protective Deposits on Dentin Surface and Enhance Human Dental Pulp Stem Cells Mineralization. *J Funct Biomater* **2022**, *13* (4), 250. <https://doi.org/10.3390/jfb13040250>.
158. Millero, F. J.; Milne, P. J.; Thurmond, V. L. The Solubility of Calcite, Strontianite and Witherite in NaCl Solutions at 25°C. *Geochim Cosmochim Acta* **1984**, *48* (5), 1141–1143. [https://doi.org/10.1016/0016-7037\(84\)90205-9](https://doi.org/10.1016/0016-7037(84)90205-9).
159. Scheller, E. L.; Ingalls, M.; Eiler, J. M.; Grotzinger, J. P.; Ryb, U. The Mechanisms and Stable Isotope Effects of Transforming Hydrated Carbonate into Calcite Pseudomorphs. *Geochim Cosmochim Acta* **2023**, *354*, 146–164. <https://doi.org/10.1016/j.gca.2023.04.025>.
160. Boch, R.; Wang, X.; Kluge, T.; Leis, A.; Lin, K.; Pluch, H.; Mittermayr, F.; Baldermann, A.; Böttcher, M. E.; Dietzel, M. Aragonite–Calcite Veins of the ‘Erzberg’ Iron Ore Deposit (Austria): Environmental Implications from Young Fractures. *Sedimentology* **2019**, *66* (2), 604–635.

<https://doi.org/10.1111/sed.12500>.

161. Casella, L. A.; Griesshaber, E.; Yin, X.; Ziegler, A.; Mavromatis, V.; Müller, D.; Ritter, A.-C.; Hippler, D.; Harper, E. M.; Dietzel, M.; Immenhauser, A.; Schöne, B. R.; Angiolini, L.; Schmahl, W. W. Experimental Diagenesis: Insights into Aragonite to Calcite Transformation of *Arctica Islandica* Shells by Hydrothermal Treatment. *Biogeosciences* **2017**, *14* (6), 1461–1492. <https://doi.org/10.5194/bg-14-1461-2017>.
162. Rodriguez-Navarro, C.; Benning, L. G. Control of Crystal Nucleation and Growth by Additives. *Elements* **2013**, *9* (3), 203–209. <https://doi.org/10.2113/gselements.9.3.203>.
163. Purgstaller, B.; Dietzel, M.; Baldermann, A.; Mavromatis, V. Control of Temperature and Aqueous Mg²⁺/Ca²⁺ Ratio on the (Trans-)Formation of Ikaite. *Geochim Cosmochim Acta* **2017**, *217*, 128–143. <https://doi.org/10.1016/j.gca.2017.08.016>.
164. Rossi, C.; Lozano, R. P. Hydrochemical Controls on Aragonite versus Calcite Precipitation in Cave Dripwaters. *Geochim Cosmochim Acta* **2016**, *192*, 70–96. <https://doi.org/10.1016/j.gca.2016.07.021>.
165. Riechelmann, S.; Schröder-Ritzrau, A.; Wassenburg, J. A.; Schreuer, J.; Richter, D. K.; Riechelmann, D. F. C.; Terente, M.; Constantin, S.; Mangini, A.; Immenhauser, A. Physicochemical Characteristics of Drip Waters: Influence on Mineralogy and Crystal Morphology of Recent Cave Carbonate Precipitates. *Geochim Cosmochim Acta* **2014**, *145*, 13–29. <https://doi.org/10.1016/j.gca.2014.09.019>.
166. Astilleros, J. M.; Fernández-Díaz, L.; Putnis, A. The Role of Magnesium in the Growth of Calcite: An AFM Study. *Chem Geol* **2010**, *271* (1–2), 52–58. <https://doi.org/10.1016/j.chemgeo.2009.12.011>.
167. Reddy, M. M.; Wang, K. K. Crystallization of Calcium Carbonate in the Presence of Metal Ions. *J Cryst Growth* **1980**, *50* (2), 470–480. [https://doi.org/10.1016/0022-0248\(80\)90095-0](https://doi.org/10.1016/0022-0248(80)90095-0).
168. Kim, S.; Park, C. B. Mussel-Inspired Transformation of CaCO₃ to Bone Minerals. *Biomaterials* **2010**, *31* (25), 6628–6634. <https://doi.org/10.1016/j.biomaterials.2010.05.004>.
169. Folk, R. L. The Natural History of Crystalline Calcium Carbonate<Subtitle>Effect of Magnesium Content and

