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**Sustainable Valorization of Dolomitic Limestone Waste Rocks by a
Hybrid Metallurgical Process: Extraction of Alkaline Earth Metals**

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Département de génie chimique

Thèse présentée en vue de l'obtention du diplôme de *Philosophiæ Doctor*

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Sustainable Valorization of Dolomitic Limestone Waste Rocks by a Hybrid Metallurgical Process: Extraction of Alkaline Earth Metals

présentée par **Javad VAHABZADEH PASIKHANI**

en vue de l'obtention du diplôme de *Philosophiæ Doctor*

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DEDICATION

To my beloved parents, sisters, nieces, and nephews, who have taught me the true meaning of love and kindness.

To the honorable and resilient people of Iran, who have endured decades of hardship caused by both internal oppression and external conflict.

With hope for the restoration of freedom, dignity, and glory for my dear Iranian people.

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Javad Vahabzadeh Pasikhani

RÉSUMÉ

L'expansion rapide de la fabrication avancée, de l'électrification des transports et des systèmes énergétiques à faibles émissions de carbone a intensifié la demande mondiale en métaux critiques. Parmi ceux-ci, le magnésium (Mg) s'est imposé comme un matériau léger d'importance stratégique en raison de sa faible densité, de sa résistance spécifique élevée et de sa large applicabilité dans les systèmes structurels, électroniques et énergétiques. Cependant, la production actuelle de magnésium repose principalement sur des ressources primaires et sur des procédés pyrométallurgiques à forte intensité énergétique, en particulier la réduction silicothermique sous vide de la dolomie, associée à des émissions élevées de carbone, à une consommation énergétique importante et à des chaînes d'approvisionnement géographiquement concentrées. Ces limitations soulignent la nécessité de développer des voies de production alternatives à la fois durables et résilientes. En réponse à ces défis, un intérêt croissant s'est porté sur l'exploitation minière de la technosphère, qui permet de récupérer des métaux de valeur à partir de flux de déchets industriels et de produits en fin de vie. Parmi ces ressources, les roches stériles de calcaire dolomitique (DLWR) générées lors de l'extraction minière des phosphates, constituent une source prometteuse de magnésium mais encore sous-exploitée. Ce matériau contient des quantités importantes de Mg sous forme carbonatée, ainsi que du calcium et des impuretés. Sa valorisation offre une opportunité de répondre simultanément aux enjeux de gestion des déchets et de développement de chaînes d'approvisionnement circulaires pour les métaux critiques.

Néanmoins, plusieurs défis majeurs subsistent, notamment la nécessité d'étapes de prétraitement énergivores, la difficulté de séparer sélectivement le Mg et le Ca, la gestion des émissions de CO₂ au cours du procédé, ainsi que l'inefficacité des voies de réduction thermique conventionnelles. Cette thèse aborde ces enjeux en développant un procédé hybride hydrométallurgique–pyrométallurgique pour la production de magnésium à faible empreinte carbone à partir de DLWR. L'approche proposée combine une lixiviation acide inorganique et une précipitation alcaline sélective de composés de magnésium de haute pureté avec une réduction carbothermique électrifiée, permettant la production de magnésium métallique à pression atmosphérique.

L'étape hydrométallurgique a démontré que la lixiviation directe des DLWR à l'aide d'acide sulfurique dilué permet une extraction hautement sélective du magnésium sans calcination préalable. Contrairement aux hypothèses conventionnelles, il a été constaté que les phases

carbonatées améliorent la sélectivité du procédé en limitant la dissolution des impuretés. Dans des conditions optimisées (rapport solide/liquide de 10 g/L, 0.5 M H_2SO_4 et 80 °C), une extraction complète du magnésium a été obtenue, tandis que la co-lixiviation des impuretés a été significativement réduite de 87 % à 36 %. L'analyse cinétique a indiqué que la vitesse de lixiviation est contrôlée par la diffusion à travers la couche de produit solide (couche de cendres), avec une faible énergie d'activation (16 kJ/mol).

La séparation ultérieure des espèces dissoutes a été réalisée par une stratégie de précipitation alcaline séquentielle guidée thermodynamiquement. En contrôlant le pH, des produits de haute pureté, notamment $\text{Mg}(\text{OH})_2$ et des composés à base de calcium, ont été récupérés de manière sélective malgré leurs propriétés chimiques similaires. L'hydroxyde de magnésium a été obtenu avec une pureté supérieure à 99.5 % et un rendement de récupération d'environ 98 %, tandis que le calcium a été récupéré sous forme de CaCO_3 avec une pureté et un rendement comparables. De plus, l'intégration du captage du CO_2 dans le procédé a permis la conversion du CO_2 issu de l'acidolyse en NaHCO_3 et CaCO_3 , établissant ainsi un système en boucle fermée avec utilisation interne du carbone et des émissions réduites.

L'étape pyrométallurgique introduit une voie novatrice de production de magnésium via une réduction carbothermique assistée par micro-ondes (MW-CTR). Dans cette approche, le $\text{Mg}(\text{OH})_2$ récupéré a été utilisé directement comme matière première de réduction, éliminant la nécessité d'une conversion à haute température en MgO . La décomposition thermique du $\text{Mg}(\text{OH})_2$ génère de la vapeur d'eau, qui réagit avec le carbone pour former un mélange gazeux réducteur (CO et H_2), orientant ainsi le mécanisme vers une réduction assistée par phase gazeuse. Cette transition permet une réduction significative de la température opératoire, abaissant le seuil de formation du magnésium d'environ 700 °C par rapport aux procédés carbothermiques conventionnels à base de MgO . L'irradiation micro-ondes améliore davantage le procédé grâce à un apport d'énergie rapide et sélectif. Des vitesses de chauffage supérieures à 990 °C/min ont été atteintes, conduisant à une accélération des cinétiques réactionnelles, à une réduction du frittage et à une génération efficace de vapeur de magnésium. Dans des conditions optimisées, le procédé MW-CTR a atteint un rendement de réduction d'environ 87 % et produit du magnésium d'une pureté d'environ 94 % à pression atmosphérique. Parallèlement, un mélange de gaz de synthèse avec un rapport molaire $\text{CO}:\text{H}_2$ de 1.86 a été généré, constituant une source de valeur additionnelle.

L'intégration de ces étapes hydrométallurgiques et pyrométallurgiques a permis d'établir une voie complète de conversion des déchets miniers en magnésium métallique à haute valeur ajoutée et en coproduits chimiques. Le procédé développé élimine la nécessité de la calcination préalable, du fonctionnement sous vide et du chauffage à base de combustibles fossiles, répondant ainsi aux principales limitations des technologies conventionnelles de production du magnésium. En même temps, il introduit un cadre circulaire et à gestion du carbone combinant récupération des ressources, valorisation du CO₂ et intensification des procédés.

ABSTRACT

The rapid expansion of advanced manufacturing, transportation electrification, and low-carbon energy systems has intensified global demand for critical metals. Among these, magnesium (Mg) has emerged as a strategically important lightweight material due to its low density, high specific strength, and broad applicability in structural, electronic, and energy-related systems. However, current magnesium production relies predominantly on primary resources and energy-intensive pyrometallurgical routes, particularly the vacuum silicothermic reduction of dolime, which is associated with high carbon emissions, significant energy consumption, and geographically concentrated supply chains. These limitations highlight the need for alternative production pathways that are both sustainable and resilient. In response to these challenges, increasing attention has been directed toward technospheric mining, which recovers valuable metals from industrial waste streams and end-of-life products. Among these resources, dolomitic limestone waste rock (DLWR) generated during phosphate mining extraction is a promising yet underutilized magnesium source. This material contains substantial quantities of Mg in carbonate form, along with calcium and impurities. Its valorization provides an opportunity to simultaneously address waste management issues and develop circular supply chains for critical metals.

Nevertheless, several key challenges remain, including the need for energy-intensive pre-treatment steps, the difficulty of selectively separating Mg and Ca, the management of CO₂ emissions during processing, and the inefficiency of conventional thermal reduction routes. This dissertation addresses these challenges by developing a hybrid hydrometallurgical-pyrometallurgical process for the low-carbon production of magnesium from DLWR. The proposed approach combines inorganic acid leaching and selective alkaline precipitation of high-purity magnesium compounds with an electrified carbothermic reduction, enabling the production of metallic Mg at atmospheric pressure.

The hydrometallurgical step demonstrated that direct leaching of DLWR using dilute sulfuric acid can achieve highly selective magnesium extraction without prior calcination. Contrary to conventional assumptions, carbonate phases were found to enhance process selectivity by limiting impurity dissolution. Under optimized conditions (solid-to-liquid ratio of 10 g/L, 0.5 M H₂SO₄, and 80 °C), complete magnesium extraction was achieved, while impurity co-leaching was

significantly reduced from 87% to 36%. Kinetic analysis indicated that the leaching rate was controlled by diffusion through the ash product layer, with low activation energy (16 kJ/mol).

Subsequent separation of dissolved species was achieved through a thermodynamically guided, stepwise alkaline precipitation strategy. By controlling pH, high-purity products, including $\text{Mg}(\text{OH})_2$ and Ca-based compounds, were selectively recovered despite their similar chemical properties. Magnesium hydroxide was obtained with a purity exceeding 99.5% and a recovery efficiency of approximately 98%, while calcium was recovered as CaCO_3 with comparable purity and recovery. In addition, integrating CO_2 capture into the process enabled conversion of acidolysis-derived CO_2 to NaHCO_3 and CaCO_3 , establishing a closed-loop system with internal carbon utilization and reduced emissions.

The pyrometallurgical stage introduces a novel route to magnesium production via microwave-assisted carbothermic reduction (MW-CTR). In this approach, recovered $\text{Mg}(\text{OH})_2$ was directly used as the reduction feedstock, eliminating the need for high-temperature conversion to MgO . The thermal decomposition of $\text{Mg}(\text{OH})_2$ produced water vapor, which reacted with carbon to form a reducing gas mixture (CO and H_2), thereby shifting the reaction pathway to a gas-assisted reduction mechanism. This shift enabled a substantial reduction in operating temperature, lowering the onset of magnesium formation by approximately 700 °C compared with conventional MgO -based carbothermic processes. Microwave irradiation further enhanced the reduction process through rapid and selective energy deposition. Heating rates exceeding 990 °C/min were achieved, resulting in accelerated reaction kinetics, reduced sintering, and efficient magnesium vapor generation. Under optimized conditions, the MW-CTR process achieved a reduction efficiency of approximately 87% and produced magnesium with a purity of about 94% at atmospheric pressure. Simultaneously, a syngas mixture with a $\text{CO}:\text{H}_2$ molar ratio of 1.86 was generated, providing an additional value stream.

The integration of these hydrometallurgical and pyrometallurgical steps established a complete pathway for converting mining waste into high-value metallic magnesium and chemical co-products. The developed process eliminated the need for pre-calcination, vacuum operation, and fossil-fuel-based heating, thereby addressing key limitations of conventional magnesium production technologies. At the same time, it introduces a circular and carbon-managed framework that combines resource recovery, CO_2 utilization, and process intensification.

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LIST OF SYMBOLS AND ABBREVIATIONS

Acronyms

3WV	Three-way valve
BET	Brunauer-Emmett-Teller theory
CCUS	Carbon capture, utilization, and storage
CDO-700	Calcined dolomite (dolime) at 700 °C
CDO-900	Calcined dolomite (dolime) at 900 °C
CTR	Carbothermic reduction
CV	Check valve
DLWR	Dolomitic limestone waste rock
EDS	Energy dispersive X-ray spectroscopy
EPR	Electron paramagnetic resonance
ESB	Emergency safety box
FT	Particles filter
GC-MS	Gas chromatography-mass spectrometry
HRTEM	High-resolution transmission electron microscopy
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
MC	Microcontroller
MTR	Methanothermic reduction
MW	Microwave heating

MW-CTR	Microwave-assisted carbothermic reduction
MW-MTR	Microwave-assisted methanothermic reduction
NV	Needle valve
ORP	Redox (or oxidation-reduction) potential
PSD	Particle size distribution
QEMSCAN	Quantitative evaluation of minerals by scanning electron microscopy
REEs	Rare earth elements
RV	Relief valve
SAED	Selected area electron diffraction
SCM	Shrinking core model
SEM	Scanning electron microscopy
tce	A ton of coal equivalent
TGA	Thermogravimetric analysis
U.S. DOE	United States Department of Energy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

Roman symbols

A_0	Arrhenius pre-exponential factor or frequency factor [min^{-1}]
c	Speed of light [m/s]
$C_{i,\text{leach}}$	Concentration of metal i in leachate [mg/L]
$C_{i,\text{prec}}$	Concentration of metal i in leachate after precipitation [mg/L]

C_p	Specific heat capacity [J/kg.K]
C_{pq}	Specific heat capacities of the quartz container [kJ/kg.K]
C_{pw}	Specific heat capacities of water [kJ/kg.K]
D	Particle diameter [cm]
d_p	Penetration depth [cm]
E	Internal electric field amplitude [V/m]
E_a	Apparent activation energy [kJ/mol]
E_i	Leaching efficiency of metal i [%]
E_L	Excitation energy of the laser [eV]
E_{Mg}	Leaching efficiency of Mg [%]
E_{MW}	Consumed microwave heating energy [kWh]
f	Frequency [1]
$f_{i,ore}$	Mass fraction of metal i in initial ore [mg/mg]
H	Internal magnetic field amplitude [Amp/m]
I_{2D}	Intensity of the 2D band in Raman analysis [a.u.]
I_D	Intensity of the D band in Raman analysis [a.u.]
I_G	Intensity of the G band in Raman analysis [a.u.]
k	Apparent rate constant (first order [min^{-1}])
k_{AD}	Rate constants for ash product layer diffusion [min^{-1}]
K_{eq}	Precipitation reaction's equilibrium constant [-]
K_{CD}	Rate constants for mixed diffusion and reaction [min^{-1}]
K_{CR}	Rate constants for surface acidolysis [min^{-1}]

K_{LD}	Rate constants for liquid boundary film diffusion [min^{-1}]
K_{SP}	Solubility product constant [mol/L] ⁿ , where n is the sum of coefficients in the reaction
L_a	Crystallite size measured from Raman analysis [nm]
$m_{i,\text{leachate}}$	Mass of metal i in leachate [mg]
$m_{i,\text{ore}}$	Mass of metal i in initial ore [mg]
$m_{i,\text{prec}}$	Mass of metal i after precipitation at a specific pH level [mg]
m_{mg}	Produced magnesium [kg]
$m_{\text{Mg,Condens}}$	Mass of produced Mg metal [g]
$m_{\text{Mg,ore}}$	Mass of Mg in the initial ore [mg]
$m_{\text{MgO,f}}$	Mass of MgO after carbothermic reduction [g]
$m_{\text{MgO,i}}$	Mass of MgO before carbothermic reduction [g]
m_{ore}	Total mass of initial ore [mg]
$m_{t,\text{Condens}}$	Mass of condensate [g]
m_q	Mass of quartz container [kg]
m_w	Mass of water (kg)
MW_i	Molecular weight of metal i [g/mol]
MW_{Mg}	Molecular weight of Mg [mg/mol]
n	Avrami exponent (also called precipitation mechanism coefficient) [-]
P_i	Purity of precipitated products [%]
P_{Mg}	Magnesium purity after thermal reduction [%]
P_{MW}	Effective absorbed microwave power [kW]
Q_{MW}	Volumetric heat generation rate [W/m^3]

R	Universal gas constant [J/mol.K]
R^2	Coefficient of determination [-]
R_i	Precipitation recovery efficiency of metal i [%]
R_T	Thermal reduction efficiency [%]
S	Supersaturation of metal cations [-]
S_{Leaching}	Leaching selectivity [%]
SEC	Specific energy consumption [kWh/kg]
S/L	Solid-to-liquid ratio [g/L]
t	Reaction time [min]
t_{react}	Reaction time under microwave heating [h]
T	Temperature [K]
V_{leach}	Volume of leachate solution [L]
V_{prec}	Volume of solution after precipitation [L]

Greek symbols

α	Attenuation coefficient [cm^{-1}]
α_M	Activity of metal cations [-]
α_P	Activity of precipitants [-]
$\alpha(t)$	Fraction of the precipitated phase at time t [mg/mg]
γ	Activity coefficient for an ion [-]
ε^*	Complex permittivity [-]
ε'	Real part of the complex permittivity (dielectric constant) [-]
ε''	Imaginary part of the complex permittivity (dielectric loss factor) [-]

μ^*	Complex permeability [-]
μ'	Real part of the complex magnetic permeability [-]
μ''	Imaginary part of the complex magnetic permeability [-]
ρ	Material's density [kg/m ³]
σ	Electrical conductivity of the material [S/m]
$\tan\delta\epsilon$	Dielectric loss tangent

Other symbols

ΔG	Gibbs free energy change [kJ/mol]
ΔH	Enthalpy change [kJ/mol]
ΔH_r°	Standard enthalpy change [kJ/mol]
Δt	Microwave exposure time [s]
$\Delta \bar{T}$	Average temperature rises by microwave heating [K]
ΔT_q	Temperature increases in the quartz container by microwave heating [K]
ΔT_w	Temperature increases in water by microwave heating [K]

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CHAPTER 1 INTRODUCTION

1.1 Background and global context

Over the past decade, rapid industrial modernization, electrification of transportation systems, and the transition toward low-carbon energy technologies have substantially increased global demand for critical metals. These materials are essential to advanced manufacturing, renewable energy systems, and lightweight structural applications, yet their supply chains are often geographically concentrated and vulnerable to geopolitical disruption [2, 3]. Within this context, magnesium (Mg) has emerged as a strategically important lightweight metal for the 21st century.

Magnesium is 33% lighter than aluminum and 75% lighter than steel, making it one of the lightest structural metals available for engineering applications. Owing to its high specific strength, good castability, and alloying compatibility with aluminum, magnesium, and its alloys are widely used in aerospace, automotive, electronics, and defense sectors [4, 5]. In transportation, weight reduction directly translates to improved fuel efficiency and reduced greenhouse gas emissions, making Mg a critical enabler of decarbonization strategies [6]. Moreover, Mg plays an increasingly important role in emerging applications, including lightweight battery casings, hydrogen-storage materials, and structural components for electric vehicles [7-9].

Currently, industrial magnesium metal is produced predominantly through pyrometallurgical processes, primarily by the vacuum silicothermic reduction. Although technologically mature, this process is energy-intensive, labor-demanding, dependent on costly ferrosilicon reductant, and associated with significant CO₂ emissions [10]. Alternative approaches, including aluminothermic and carbothermic reduction, have been investigated to improve productivity and reduce reductant costs [11]. Among these, carbothermic reduction is particularly attractive due to the abundance and low cost of carbon. However, conventional carbothermic Mg production requires very high temperatures, high vacuum pressure, and careful condensation of magnesium vapor to achieve desirable yields [12].

Beyond thermal metallization technology, the selection of magnesium-bearing feedstock is equally critical. Despite the abundance of magnesium-bearing minerals, including magnesite, dolomite, brucite, and carnallite, and the presence of seawater, the global supply of primary magnesium metal is highly concentrated in a limited number of countries [13]. This geographical concentration,

coupled with increasing demand from electrification and advanced manufacturing sectors, has contributed to magnesium being classified as a critical raw material in multiple jurisdictions [14]. Ensuring secure, sustainable, and environmentally responsible Mg production has therefore become a strategic priority. To address this issue, Mg recycling from secondary resources, i.e., industrial and urban wastes, offers a promising solution. Among secondary resources, dolomitic limestone waste rock generated by phosphate mining is an ideal source of magnesium [15]. Phosphate extraction processes generate substantial quantities of carbonate-rich waste rock, often disposed of in large surface dumps. These materials typically contain significant Mg in the form of dolomite ($\text{MgCa}(\text{CO}_3)_2$), along with impurities such as silicates, alumina, and iron oxides [16]. Valorization of dolomitic limestone waste rock offers twofold benefits by mitigating environmental liabilities associated with mining waste and by recovering critical metals from secondary resources within a circular economy framework.

Among current recycling technologies, hydrometallurgical processing is widely regarded as an effective way to recover magnesium from low-grade waste rocks and end-of-life products. Acidic and alkaline leaching processes can efficiently extract Mg from the solid phase into solution, followed by selective separation methods such as precipitation, ion exchange, or membrane-based methods [17]. Nevertheless, hydrometallurgy typically produces magnesium in compound forms (e.g., chloride, sulfate, hydroxide, or carbonate), necessitating subsequent thermal treatment to generate metallic Mg. These additional steps increase energy demand and process complexity. Consequently, efficient thermal conversion techniques remain essential for producing high-purity magnesium metal from both primary and secondary sources.

Given the high-temperature nature of magnesium metallization, improving the energy efficiency of thermal reduction processes is of strategic importance. Electrification of pyrometallurgical reactors has therefore attracted growing interest. Technologies such as Joule heating, plasma systems, solar thermal concentration, and microwave irradiation have been investigated as alternatives to fossil-fuel-based combustion heating [18, 19]. Among these approaches, microwave heating is particularly compelling due to its ability to deliver energy volumetrically and selectively to microwave-absorbing materials [20]. Carbonaceous reductants and certain metallic or semi-metallic phases exhibit strong microwave absorption through electronic conduction losses, enabling rapid and localized heating at reaction interfaces [21, 22].

Microwave-assisted carbothermal reduction is a potential process-intensification strategy for magnesium production. By selectively heating carbon in MgO-C mixtures, microwave irradiation may enhance interfacial reaction kinetics, accelerate magnesium vapor generation, and reduce the required bulk temperature compared with conventional furnace heating. Although microwave-assisted carbothermic reduction has shown promising results with various transition-metal oxides, there is still a lack of systematic research on magnesium production using microwave-assisted carbothermic methods, especially at atmospheric pressure and with secondary feedstocks.

1.2 Problem statement and knowledge gap

Based on the background and global context presented in Section 1.1, dolomitic limestone waste rock represents a promising secondary resource for magnesium supply. Its abundance, the existing accumulation in phosphate-mining regions, and its significant Mg content make it an attractive candidate for circular resource valorization. Hydrometallurgical processing coupled with pyrometallurgy provides a viable route for selectively extracting metallic Mg from such carbonate-rich materials. However, several critical knowledge gaps remain unresolved.

Most studies on carbonate ore leaching emphasize pre-calcination of the feed to convert carbonates into oxide phases prior to acid leaching. From a thermodynamic standpoint, metal oxides often exhibit more favorable dissolution behavior compared with their corresponding carbonates. Consequently, calcination is commonly assumed to enhance leaching efficiency [23]. However, the broader implications of pre-calcination remain insufficiently evaluated. In particular, the effect of calcination on the co-leaching behavior of impurity phases has not been systematically examined. Phase transformation during thermal treatment may weaken mineral bonds and promote dissolution of silicate, alumina, iron oxide, and other impurities. Pre-calcination requires temperatures above 700 °C, significantly increasing energy consumption and greenhouse gas emissions [24, 25]. These concerns lead to the first fundamental research question: "Do we need pre-calcination for efficient magnesium recycling from dolomitic limestone waste rock, or can direct carbonate leaching achieve selective Mg recovery?"

Following dissolution, precipitation is typically employed to recover metals from the leachate. However, in dolomitic limestone waste rock systems, magnesium and calcium are often dissolved simultaneously at high concentrations. Because Mg^{2+} and Ca^{2+} share similar ionic radii, charge, and chemical behavior, their selective separation is inherently challenging [26]. The matrix of the

leachate, including pH, ionic strength, complexing species, and co-dissolved impurities, strongly influences precipitation selectivity and product purity. Therefore, the second research question arises: "How can selective magnesium leaching and high-purity Mg and Ca recovery be achieved from complex dolomitic limestone waste rock leachates?"

Additionally, direct acid leaching of carbonates inevitably releases CO_2 via acidolysis reactions [27]. While avoiding calcination reduces thermal-related greenhouse gas emissions, it may increase direct process-related CO_2 emissions. This introduces an important sustainability consideration: "How can CO_2 emissions be managed or valorized during direct carbonate leaching to ensure a low-carbon-footprint hydrometallurgical process?"

Following hydrometallurgical extraction, magnesium is typically recovered as chloride, sulfate, hydroxide, carbonate, or nitrate phases. Industrial magnesium production, however, conventionally relies on MgO as feedstock for thermal reduction [11]. Converting recovered Mg compounds into MgO requires additional high-temperature calcination (800-1200 °C), increasing both energy demand and operational cost [28]. This raises the first pyrometallurgical research question: "Can recycled magnesium compounds be directly utilized for metallic Mg production without intermediate thermal oxidation to MgO?"

Carbothermic reduction of MgO is thermodynamically feasible but operationally challenging. Under atmospheric pressure, the equilibrium temperature for complete reduction exceeds 1900 °C [29]. Lower temperatures require strong vacuum conditions to reduce magnesium partial pressure and shift the reaction equilibrium. Such vacuum operation increases capital cost, reduces throughput, and complicates scale-up. This leads to the second pyrometallurgical key question: "Is it possible to perform carbothermic reduction at atmospheric pressure by modifying magnesium feedstock phase, reaction chemistry, or heating strategy?"

Furthermore, conventional carbothermic reduction under vacuum typically requires 2-8 hours at temperatures between 1200 and 1400 °C [12, 30]. Heat transfer limitations, slow solid-solid reaction kinetics, and sintering contribute to extended processing times and high energy consumption. Thus, a third pyrometallurgical question emerges: "How can the heating process be intensified to accelerate carbothermic reduction while minimizing energy losses?"

Finally, magnesium vapor and carbon monoxide are generated simultaneously during carbothermic reduction. Upon condensation, Mg vapor may be partially reoxidized by CO_2 formed via the

Boudouard reaction ($2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$) [31]. Slow or poorly controlled condensation can therefore reduce overall magnesium yield. This introduces the final critical question: "How can rapid condensation of Mg vapor be achieved while preventing reoxidation within the reduction reactor?"

1.3 Research objectives

To address the scientific and technological gaps identified in Section 1.2, this dissertation aims to develop and evaluate an integrated magnesium recycling pathway that combines selective hydrometallurgical recovery from dolomitic limestone waste rock with non-vacuum carbothermic reduction assisted by a non-conventional heating method. Therefore, the main objective of this research is to develop a low-carbon, hybrid hydrometallurgical-pyrometallurgical process for the production of metallic magnesium from dolomitic limestone waste rock under atmospheric-pressure. To achieve this main objective, the following specific objectives are defined:

[SOP-1] To design and optimize a selective hydrometallurgical process for magnesium recovery from dolomitic limestone waste rock through diluted sulfuric acid leaching, stepwise alkaline precipitation, and integrated CO_2 carbonation.

This objective focuses on developing and optimizing a selective hydrometallurgical pathway for magnesium recovery from dolomitic limestone waste rock through direct carbonate leaching in H_2SO_4 solution without pre-calcination, followed by controlled NaOH-based stepwise precipitation to achieve effective Mg-Ca separation. The process aims to recover high-purity $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, and CaCO_3 while simultaneously capturing and reutilizing the CO_2 generated during acidolysis in order to minimize net process emissions. The originality of this work lies in the development and demonstration of an integrated leaching-precipitation strategy that combines dilute-acid extraction, controlled alkaline recovery, and CO_2 utilization into a closed-loop hydrometallurgical framework for the valorization of dolomitic limestone waste rock.

[SOP-2] To design and develop a microwave-assisted carbothermic reduction process at atmospheric pressure for directly producing metallic magnesium from recovered magnesium compounds.

This objective involves evaluating the carbothermic reduction behavior of $\text{Mg}(\text{OH})_2$ recovered in [SOP-1] and the design and development of a microwave-assisted reduction reactor tailored for atmospheric-pressure operation. It further includes investigating the reaction mechanism,

magnesium vapor generation, and condensation behavior to ensure efficient metal recovery, as well as assessing the simultaneous production of syngas (a mixture of CO and H₂) during reduction. The originality of this objective lies in integrating microwave heating with carbothermic reduction chemistry of Mg(OH)₂ to enable rapid magnesium production under atmospheric conditions while concurrently generating value-added syngas. Therefore, this specific objective addresses the limitations of vacuum-dependent processes and the slow heat-transfer rates associated with conventional thermal reduction.

CHAPTER 2 COHERENCE OF THE RESEARCH ARTICLES

2.1 Outline of the Chapters

The context of the next Chapters in this dissertation is presented below.

Chapter 3 presents a critical literature review of technologies for recycling magnesium from secondary sources, providing the scientific foundation for this PhD dissertation. It formulates a technological principle and a scientific hypothesis based on the state of the art, and discusses the limitations of existing technologies for sustainable magnesium recycling. The chapter first examines the classification of Mg as a lightweight critical metal and compares primary and secondary sources for its supply. It then reviews processes for recovering magnesium compounds from secondary resources, including hydrometallurgy, biometallurgy, electrometallurgy, and pyrometallurgy. Subsequently, the metallization of magnesium compounds through molten-salt electrolysis and thermal reduction is evaluated. Particular attention is given to thermal reduction, especially carbothermic reduction, and to the potential integration of microwave heating as a pathway toward low-carbon, non-vacuum magnesium production.

Chapter 4 introduces inherent carbonate-assisted acid leaching as a sustainable approach for the selective extraction of magnesium from dolomitic limestone waste rock. This chapter proposes a novel concept in which carbonate utilization, rather than CO₂ liberation, enhances hydrometallurgical recovery of critical metals from low-grade carbonate-based waste rocks while suppressing impurity co-leaching. Dilute H₂SO₄ is employed as a model leaching agent, representing the reuse of acidic effluent from phosphoric acid wet processing and promoting industrial symbiosis. The chapter investigates the acidolysis reaction from both thermodynamic and kinetic perspectives, examining the effects of CO₂ liberation, reaction temperature, solid-to-liquid ratio, and particle size. Based on these analyses, a mechanistic interpretation of inherent carbonate-assisted leaching is proposed, and a semi-empirical kinetic model is developed to determine the rate-limiting step and activation energy of Mg extraction.

Chapter 5 presents a carbon-neutral hydrometallurgical process for selectively recycling valuable metals, including magnesium, calcium, manganese, iron, aluminum, and titanium, from dolomitic limestone waste rocks generated by phosphate mining in Morocco. The chapter describes the development of a multi-step alkaline precipitation strategy coupled with CO₂ carbonation to

achieve high-purity metal separation without oxidants, reductants, or stabilizing agents, thereby ensuring both environmental and operational efficiency. Thermodynamic simulations are integrated with experimental investigations to establish a robust metal-separation framework. These simulations delineate the insolubility domains of metal cations across varying pH and redox potential (ORP) conditions, providing insight into Gibbs free energy changes, enthalpy variations, equilibrium constants, and supersaturation factors. Experimental work further optimizes key process parameters, including reaction temperature, leachate pH, stabilization time, and NaOH concentration. In addition, the chapter introduces a carbon-neutral valorization strategy in which CO_2 released during acid leaching is captured using NaOH-enriched effluent to form NaHCO_3 , which subsequently acts as a green precipitant for recovering calcium as CaCO_3 .

Chapter 6 presents a simplified carbon-neutral hydrometallurgical process for selectively recycling magnesium and calcium from dolomitic limestone waste rocks. Compared with Chapter 5, a more efficient multi-step process is developed, consisting of dilute-acid leaching, water leaching, alkaline precipitation, and CO_2 mineralization to produce high-purity $\text{Mg}(\text{OH})_2$ and CaCO_3 microspheres. Thermodynamic simulations are again combined with experimental studies to optimize Mg-Ca separation from dolomitic limestone waste rock and its associated impurities. Unlike Chapter 5, where CO_2 released during leaching was captured to generate NaHCO_3 , this chapter sequesters CO_2 using a mixture of alkaline precipitation leachate and water-leaching liquor, enabling calcium recovery directly as CaCO_3 . A key improvement is the elimination of strongly basic effluent ($\text{pH} \approx 11$) and the integration of Ca recovery from both the leaching residue and $\text{Mg}(\text{OH})_2$ precipitation liquor into a single CO_2 carbonation step.

Chapter 7 presents a fundamentally new electrified pyrometallurgical reactor for producing magnesium metal at atmospheric pressure via microwave-assisted carbothermic reduction (MW-CTR). By integrating waste valorization, non-conventional heating, thermodynamic simulation, and reaction engineering, this chapter addresses major limitations of conventional Mg production technologies, particularly the high energy demand, vacuum dependence, and environmental footprint of the Pidgeon process. A key innovation is the use of waste-derived $\text{Mg}(\text{OH})_2$, recovered from dolomitic limestone waste rock through the carbon-neutral hydrometallurgical process developed in earlier chapters, as the magnesium precursor. Unlike conventional MgO-based carbothermic reduction, $\text{Mg}(\text{OH})_2$ generates an in-situ syngas atmosphere (CO and H_2) during reduction, shifting the mechanism from a solid-solid reaction to a gas-solid pathway and lowering

the onset reduction temperature by approximately 700 °C under atmospheric pressure. This thermodynamically and kinetically favorable pathway enables non-vacuum Mg production and opens possibilities for continuous reactor operation and reduced operating costs. The chapter also demonstrates the electrification of carbothermic reduction via microwave heating, enabling rapid, selective, and volumetric energy transfer. This heating mode suppresses particle sintering and facilitates rapid Mg vapor quenching, thereby mitigating reoxidation under atmospheric conditions. Comprehensive thermodynamic analysis and advanced characterization techniques, including XRD, XPS, Raman spectroscopy, EPR, SEM, HRTEM, ICP-OES, and GC-MS, are employed to elucidate multiphase reaction-transport phenomena under microwave irradiation.

Chapter 8 provides a general discussion that synthesizes the findings of the dissertation and highlights the major scientific contributions generated by this work.

Chapter 9 formalizes the conclusions of the dissertation and highlights key directions for future research.

Appendix A provides supplementary information related to Chapter 5, including additional details on the mineralogy of dolomitic limestone waste rock, leachate composition, Avrami kinetic model fitting, calculated precipitation kinetic parameters and activation energy, thermodynamic simulations for CO₂ capture and utilization, and a preliminary economic analysis with its underlying assumptions and calculations.

Appendix B presents preliminary research on the microwave-assisted methanothermic reduction (MW-MTR) of recycled brucite into magnesium metal and syngas at atmospheric pressure. This work includes a thermodynamic assessment of gas-solid reduction reactions and initial experimental investigations. In this process, methane acts as a hydrogen carrier, generating in-situ H₂ and CO through high-temperature decomposition and reforming reactions with carbon, thereby creating a strongly reducing environment without external hydrogen supply. The simultaneous production of metallic magnesium and hydrogen-enriched syngas represents the main originality of this research, which is currently undergoing further optimization.

2.2 List of peer-reviewed publications and conference contributions

The results of this dissertation have been published in several peer-reviewed journals and presented at several conferences and events. The list of publications and conferences is presented as follows.

2.2.1 Peer-reviewed articles

1. **Javad Vahabzadeh Pasikhani**, Yassine Taha, Jamal Chaouki, "Rapid Non-Vacuum Magnesium and Syngas Production via Microwave-Assisted Carbothermic Reduction of Waste-Recycled Brucite", Chemical Engineering Journal, 23rd March 2026 (Under Review). *Chapter 7*
2. **Javad Vahabzadeh Pasikhani**, Yassine Taha, Jamal Chaouki, "Extraction of High-Purity Magnesium and Calcium from Phosphate Mine Waste Rocks by a Carbon-Neutral and Circular Hydrometallurgy", Canadian Metallurgical Quarterly, (2026), 1-12. <https://doi.org/10.1080/00084433.2026.2636864>. *Chapter 6*
3. **Javad Vahabzadeh Pasikhani**, Yassine Taha, Jamal Chaouki, "Selective recycling of critical metals from the dolomitic limestone waste through multi-step alkaline precipitation integrated with CO₂ carbonation", Journal of Environmental Management, 391 (2025), 126509. <https://doi.org/10.1016/j.jenvman.2025.126509>. *Chapter 5*
4. **Javad Vahabzadeh Pasikhani**, Yassine Taha, Jamal Chaouki, " Unveiling the role of carbonate in dolomitic limestone for efficient leaching of magnesium from phosphate mine wastes", Journal of Environmental Chemical Engineering, 13 (2025), 115191. <https://doi.org/10.1016/j.jece.2024.115191>. *Chapter 4*
5. **Javad Vahabzadeh Pasikhani** and Jamal Chaouki, "Decarbonizing Magnesium Pyrometallurgy through Methanothermic Reduction under Microwave Heating", In: Metallurgy and Materials Society of CIM (eds) Proceedings of the 65th Conference of Metallurgy and Materials, COM 2026, Springer, 28th February 2026 (Submitted a full paper). *Appendix B*

2.2.2 Conference presentations

1. **Javad Vahabzadeh Pasikhani** and Jamal Chaouki, "Decarbonizing Magnesium Pyrometallurgy through Methanothermic Reduction under Microwave Heating", the 65th Conference of Metallurgy and Materials (COM 2026), Calgary, Alberta, Canada, 17-20 August 2026. (Accepted for Oral presentation)

2. **Javad Vahabzadeh Pasikhani**, Yassine Taha, and Jamal Chaouki, "Extraction of High Purity Magnesium and Calcium from Phosphate Mine Waste Rocks by a Carbon-Neutral and Circular Hydrometallurgy", the 64th Annual Conference of Metallurgists (COM) and 6th International Conference on Light Materials-Science & Technology (LightMAT), Montreal, Quebec, Canada, 7-10 July 2025. (Oral presentation)
3. **Javad Vahabzadeh Pasikhani**, Mohammad Khajouei, Mohammad Latifi, and Jamal Chaouki, "Unveiling Production of Alkaline Earth Metals from Dolomite by Methanothermic Reduction", The 27th International Symposium for Chemical Reaction Engineering (ISCRE 27), Québec City, Canada, 11-14 June 2023. (Poster presentation)
4. **Javad Vahabzadeh Pasikhani** and Jamal Chaouki, "Selective Recovery of Magnesium as a Model of Critical Metals from Secondary Mineral Resources", Chemical Engineering Research Day, Polytechnique Montréal, Montréal, Canada, 17 March 2023. (Oral presentation)

2.3 Other contributions

Furthermore, in parallel with the research conducted in the context of this PhD dissertation, I have had a contributing role in the research projects outlined in the following US patents, book chapters, review articles, and conferences:

2.3.1 Patents

1. **Javad Vahabzadeh Pasikhani**, Mohammad Latifi, Gholamreza Roohollahi, Mohammad Khajouei, Samira Aghaee Sarbarze, Jamal Chaouki, "Process for Recycling and Extraction of Rare Earth Elements (REEs) from NdFeB magnet", File No. US 63/735,656, December 2024, (Submitted to US Patent).
2. **Javad Vahabzadeh Pasikhani**, Mohammad Latifi, Mohammad Khajouei, Gholamreza Roohollahi, Samira Aghaee Sarbarze, Jamal Chaouki, "Process for Producing Rare Earth Metals", [WO2024254705A1](#), 14 June 2024, (US Patent - Published PCT).

2.3.2 Peer-reviewed articles and book chapters

1. Pierre Sauriol, **Javad Vahabzadeh Pasikhani**, Jaber Shabanian, Jamal Chaouki, "Gas jet penetration in gas-solid fluidized and jetting-fluidized beds - A review", Powder Technology. 421 (2023) 118392. <https://doi.org/10.1016/j.powtec.2023.118392>.
2. **Javad Vahabzadeh Pasikhani**, Pierre Sauriol, Jaber Shabanian, Jamal Chaouki, "Gas Jet in a Jetting Gas-Solid Fluidized Bed: A Review of Applications, Measuring Techniques, and Design Parameters", Powder Technology, 2026 (Under preparation).
3. Henok Atile Kibret, **Javad Vahabzadeh Pasikhani**, Kazem Adavi, Jaber Shabanian, Navid Mostoufi, Jamal Chaouki, "Chapter 2 Novel thermal approaches for hydrogen production" In Hydrogen Production, Storage and Utilization: Thermochemical, Electrochemical, Sonochemical, Biological and Photocatalytic Processes edited by Slimane Merouani and Oualid Hamdaoui, 55-132. Berlin, Boston: De Gruyter, 2025.
<https://doi.org/10.1515/9783111623863-002>.

2.3.3 Conference presentations

1. Henok Atile Kibret, **Javad Vahabzadeh Pasikhani**, Abdelrahman I. Hussain, Mohammad Khodabandehloo, Fatemeh Vatankhah, Jaber Shabanian, and Jamal Chaouki, "Novel Electrified Thermal Hydrogen Production Approaches", The 23rd International Conference on Renewable Energies and Power Quality (ICREPQ'25), Tenerife, Spain, 25-27 June 2025. (Oral presentation)
2. Mohammad Khajouei, **Javad Vahabzadeh Pasikhani**, Mohammad Latifi, and Jamal Chaouki, "Develop a Sustainable Process Toward the Recovery of Hard-to-Dissolve Minerals Based on the Flash Joule Heating", The 27th International Symposium for Chemical Reaction Engineering (ISCRE 27), Québec City, Canada, 11-14 June 2023. (Poster presentation)

CHAPTER 3 LITERATURE REVIEW

3.1 Magnesium as a lightweight critical metal

The global transition toward electrification, resource efficiency, and low-carbon technologies has driven rapidly increasing demand for critical metals. According to the European Commission, critical raw materials are defined as those that are economically essential while being subject to a high risk of supply disruption due to factors such as geopolitical concentration, limited domestic reserves, or rapidly growing demand [32]. This definition highlights the dynamic nature of criticality, which is influenced not only by geological availability but also by geopolitical conditions, trade dependencies, and evolving technological requirements. Similarly, under the Energy Act of 2020, the U.S. Department of Energy defines critical materials as non-fuel substances that are indispensable for energy technologies and vulnerable to supply chain disruptions. The most recent critical materials lists published by the European Commission and the U.S. DOE are presented in Figures 3.1(a) and 3.1(b), respectively.

In both assessments, magnesium is recognized as a critical lightweight metal due to its strategic importance in transportation, energy storage, and advanced structural materials. With a density of approximately 1.74 g/cm^3 , Mg is nearly three-fifths the density of aluminum and roughly one-fifth that of steel, making it the lightest structural metal currently used at scale. This exceptionally low density positions Mg as a strong candidate for partial substitution of heavier metallic components, particularly aluminum and steel, in the automotive and transportation sectors. It has been reported that a 100 kg reduction in vehicle mass can reduce fuel consumption by approximately 0.5 L per 100 km, directly contributing to lower greenhouse gas emissions from internal combustion engine vehicles [33, 34]. Consequently, the integration of Mg-based components offers a practical pathway for vehicle lightweighting and emission mitigation.

Beyond density advantages, Mg alloys exhibit attractive specific mechanical properties, including high strength-to-weight ratios exceeding 500 MPa/kg, enabling their use in applications where mechanical performance must be maximized while minimizing mass, like aerospace [12, 35]. In addition, the relatively low melting point of Mg (650°C) facilitates energy-efficient processing routes such as high-pressure die casting, allowing the fabrication of complex, thin-walled, and dimensionally precise components [4, 36]. More recently, Mg has also attracted growing interest

in electrochemical energy storage technologies, particularly rechargeable batteries, due to its high volumetric energy density, natural abundance, and dendrite-free plating behavior [37]. As a result of this unique combination of lightweight characteristics, mechanical performance, processability, and electrochemical functionality, Mg and its alloys have found widespread application across aerospace, automotive, defense, biomedical devices, electronics, and electromagnetic shielding technologies [38, 39].

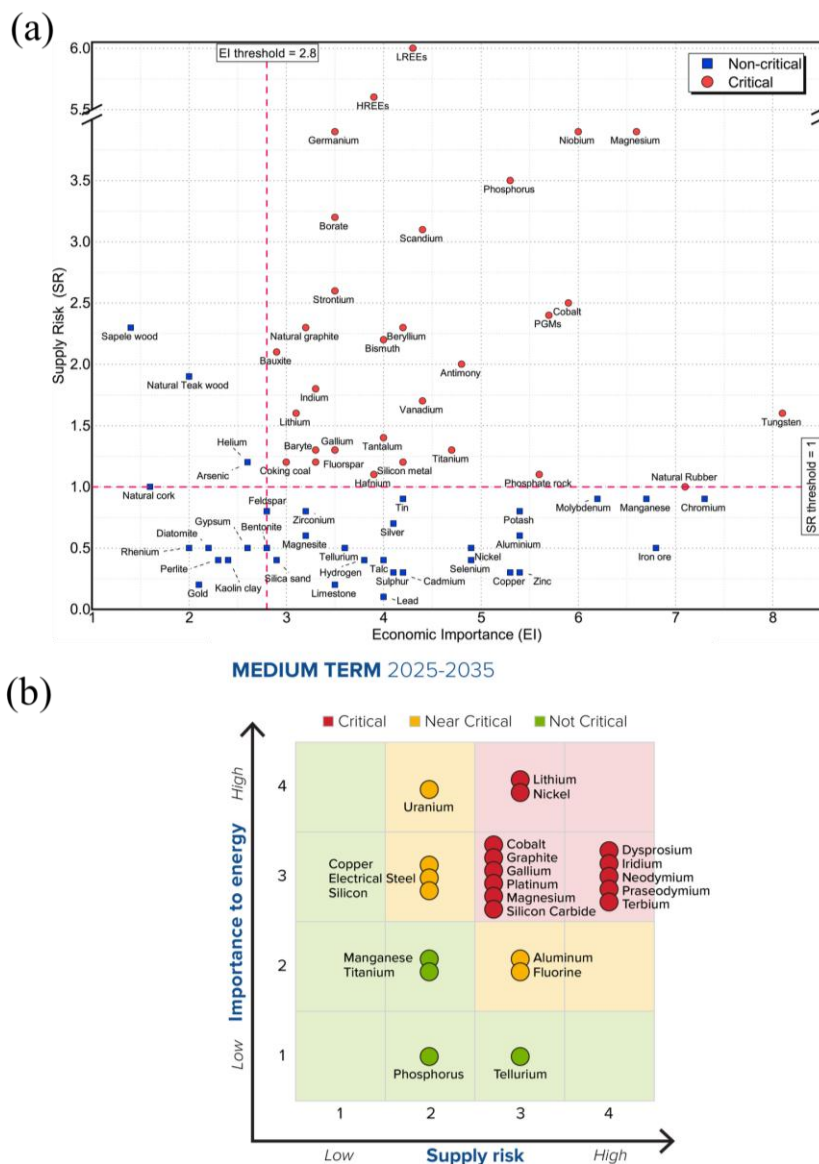


Figure 3.1 Critical metals matrix (a) reported by the European Commission in 2020, based on the supply risk-economic importance relationship, and (b) reported by the U.S. DOE for the medium term (2025-2035), based on the supply risk-energy importance relationship [40, 41].

3.2 Primary and secondary resources of magnesium supply

Magnesium is the 8th most abundant element in the Earth's crust and occurs in a wide range of mineralogical forms. To date, more than 80 minerals containing over 20 wt.% Mg in their crystal structure have been identified. However, despite this apparent abundance, only a limited number of Mg-bearing resources are economically viable for industrial exploitation due to constraints related to ore grade, mineral accessibility, processing complexity, and geographic distribution. Figure 3.2 summarizes the Mg concentrations in the principal extractable resources currently used or considered for magnesium production. Primary Mg resources include carbonate, hydroxide, chloride, and silicate minerals, as well as aqueous sources such as seawater and continental brines. Among solid minerals, magnesite (MgCO_3), dolomite ($\text{MgCa}(\text{CO}_3)_2$), brucite ($\text{Mg}(\text{OH})_2$), bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$), olivine ($(\text{Mg,Fe})_2\text{SiO}_4$) and serpentine-rich ultramafic rocks ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) have been historically exploited or investigated as feedstocks for Mg metal production. Magnesite and brucite are also widely used in the manufacture of caustic, dead-burned, and fused magnesia (MgO) for refractory and chemical applications. Other Mg-rich carbonates, such as huntite ($\text{Mg}_3\text{Ca}(\text{CO}_3)_4$) and hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), contain high Mg content, but their commercial utilization remains limited because large mineable deposits are scarce. Thus, their primary use is limited to niche applications, such as flame retardants.

Although magnesite offers a higher Mg concentration than dolomite, its industrial deployment is constrained by the geographically restricted distribution of high-grade deposits [42]. In contrast, dolomite represents one of the most abundant and widely distributed Mg-bearing carbonates, occurring on every continent [43]. Approximately 80% of carbonate reservoirs in North America and more than 50% of global carbonate reservoirs are composed of dolomitic formations, underscoring the vast availability of this resource [44]. According to international trade statistics reported by the United Nations, major exporters of dolomite include China (14.3%), Belgium (12%), Spain (8.87%), Canada (8.18%), Brazil (8.15%), Thailand (7.92%), Germany (7.6%), Netherlands (5.26%) Slovak Republic (4.8%), and Korea (4.06%), highlighting its strategic relevance in global mineral supply chains [45].

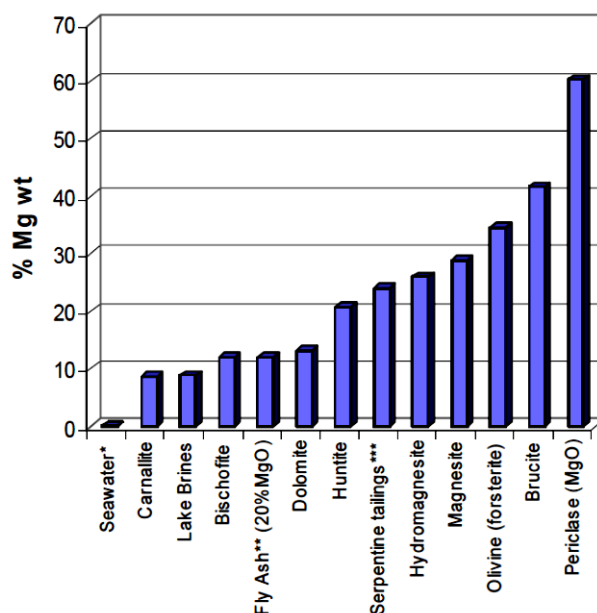


Figure 3.2 Magnesium-bearing materials used or considered for use in Mg metal production (*average, **Hazlewood Project in Australia, ***Magnola Project in Canada) [13].

Despite this broad availability, magnesium production from primary resources faces increasing limitations. These include declining ore grades, rising mining and beneficiation complexity, and growing environmental concerns associated with large-scale land disturbance, tailings generation, and chemical runoff. Traditional linear mining operations are highly energy-intensive and carbon-intensive, with the global mining sector accounting for approximately 10% of total energy-related greenhouse gas emissions in 2018 [46]. For example, when fossil fuels are used as the energy source, the carbon footprints associated with MgO production range from approximately 3.9-4.8 kgCO_{2eq}/kg for fused magnesia, 2.1-3 kgCO_{2eq}/kg for sinter magnesia, and 1.4-2.2 kgCO_{2eq}/kg for lightly calcined magnesia.

In response to these challenges, increasing attention has been directed toward secondary magnesium resources derived from industrial and urban wastes, including ferronickel slag, fly ash, red mud, asbestos tailings, and electronic waste [47, 48]. The recovery of Mg from such residues, which is referred to as technospheric mining, offers a promising pathway to reduce both production costs and environmental impacts. Secondary resources typically require only 5-10% of the energy needed for primary extraction, while simultaneously mitigating landfill disposal and legacy pollution [49]. Importantly, the valorization of Mg-rich industrial wastes enables the transformation of previously discarded materials into strategic feedstocks, contributing to supply

security, circular economy objectives, and the decarbonization of magnesium production. This model shift provides the foundation for exploring dolomitic limestone waste rock as a sustainable secondary source for Mg metal production, as investigated in this dissertation.

3.3 Dolomitic limestone waste rock: An alternative source of magnesium

Phosphate mining and processing generate large volumes of solid residues, making phosphate mine waste an attractive secondary resource for the recovery of critical metals. As illustrated in Figure 3.3, waste streams are produced at multiple stages along the phosphate value chain, including mining, comminution and beneficiation, and chemical transformation. Each waste stream is characterized by distinct chemical compositions and particle-size distributions, which strongly influence their recycling potential.

During the initial mining stage, phosphate rock is extracted using open-pit or underground methods. The overburden and non-phosphatic host rocks removed during this stage are collectively referred to as exploitation waste rock. Subsequently, the run-of-mine phosphate ore undergoes crushing, grinding, and classification, leading to the removal of coarse particles larger than 60 mm, which form the destoning waste rock. Further size classification through dry screening eliminates particles larger than 10 mm, generating the screening waste rock as a third major waste stream. These three waste rock fractions are highly heterogeneous and typically consist of mixtures of clays, limestones, marls, flintstone, sand, and residual phosphate minerals [50].

Following dry screening, the beneficiation process is applied to upgrade apatite content and remove gangue minerals such as clays, quartz, limestone, and dolomite. In Morocco, phosphate beneficiation plants generally employ three sequential unit operations: wet screening, washing, and flotation. These operations generate three additional waste streams, namely beneficiation waste rock, phosphate sludge, and flotation tailings. The chemical and mineralogical compositions of these residues vary significantly depending on the geological origin of the phosphate deposit.

Mineralogical analyses reported for beneficiation waste streams from Moroccan phosphate operations indicate that they are predominantly composed of clays, such as montmorillonite ($\text{Si}_8\text{Al}_{3.5}\text{Mg}_{0.5}\text{O}_{20}(\text{OH})_4$), illite ($((\text{K},\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})])$), and palygorskite ($((\text{Mg},\text{Al})_2\text{Si}_4\text{O}_{10}(\text{OH})_4(\text{H}_2\text{O}))$), along with quartz (SiO_2), dolomitic limestone ($\text{CaMg}(\text{CO}_3)_2$), calcite (CaCO_3), and residual phosphate minerals, primarily fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) [51-53]. In

the final processing stage, phosphoric acid is produced via sulfuric acid digestion of phosphate ore, generating phosphogypsum as a byproduct. Phosphogypsum mainly consists of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), insoluble apatite, residual acids (H_3PO_4 , H_2SO_4 , and HF), and trace elements, including rare earth elements, fluorine, and heavy metals (As, Cd, Cr, Pb, Zn, etc.) [54, 55]. It is estimated that the production of one ton of phosphoric acid generates approximately five tons of phosphogypsum [56].

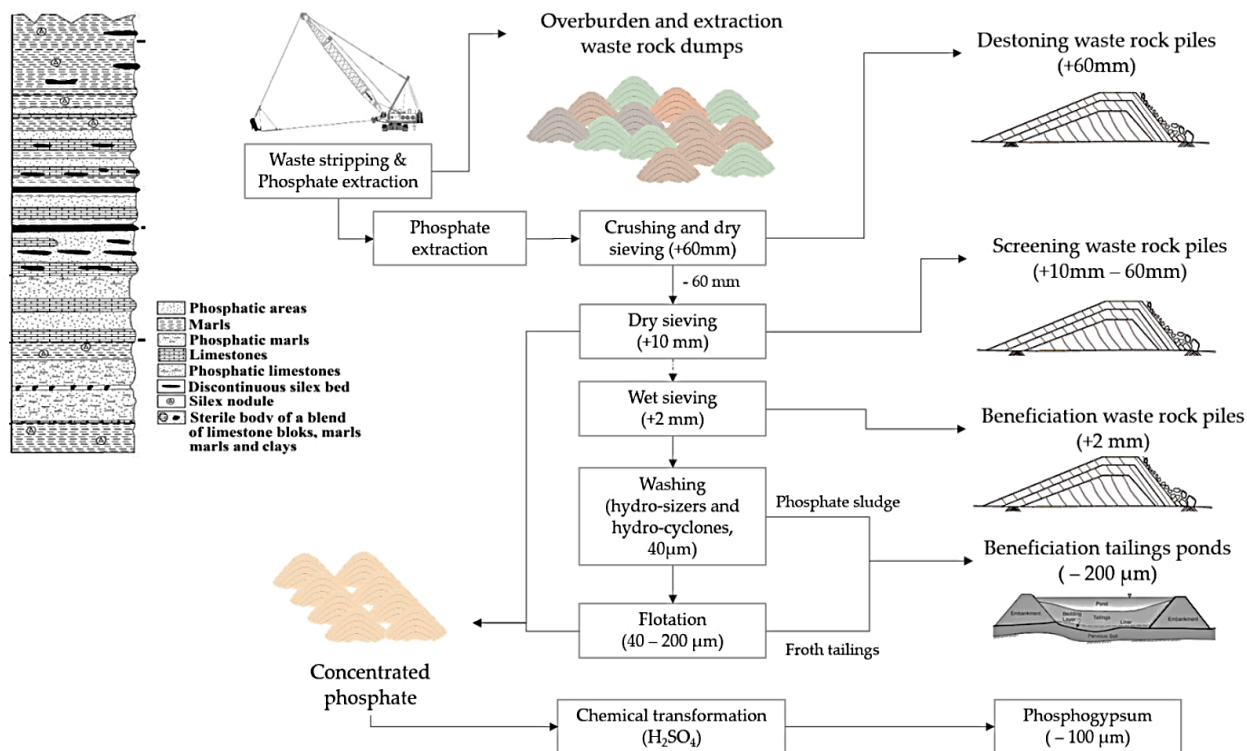


Figure 3.3 A general flowsheet of the waste streams generated by mining, beneficiation, and transformation of sedimentary phosphate ore [57].

The large-scale surface storage of these waste streams poses significant environmental risks, including land occupation, dust emissions, groundwater contamination, and long-term ecosystem degradation. In this context, technospheric mining, defined as the recovery of valuable elements from anthropogenic residues, offers a sustainable alternative to conventional disposal practices. Beyond environmental remediation, this approach enables the valorization of waste materials as secondary resources for critical metal supply.

Among the various phosphate-derived residues, dolomitic limestone waste rock exhibits exceptional potential as a source of both lightweight metal magnesium and calcium. Dolomitic

limestone is a sedimentary waste rock primarily composed of calcium magnesium carbonate ($\text{CaMg}(\text{CO}_3)_2$), with minor to moderate amounts of impurities such as SiO_2 , Al_2O_3 , P_2O_5 , TiO_2 , Fe_2O_3 , MnO , K_2O , and Na_2O [57]. According to data reported by the OCP Group and affiliated research institutions, the extraction of one ton of phosphate rock in Morocco generates approximately 3-11 tons of waste rock, of which up to 16 wt.% corresponds to dolomitic limestone [57-59]. The recycling of dolomitic limestone waste rock, rather than its disposal in landfills, offers dual benefits: mitigating environmental impacts associated with phosphate mining and recovering strategically important metals. Compared with the direct mining of primary Mg ores, the utilization of phosphate-derived dolomitic limestone represents a more economically viable and environmentally sustainable pathway for magnesium production. This abundant, underutilized secondary resource, therefore, constitutes a compelling feedstock for the development of low-carbon magnesium extraction routes, forming the basis of the research investigated in this dissertation.

3.4 Processing of magnesium from the secondary resources

The processing of magnesium from secondary resources can be classified into two approaches, depending on the targeted final product. The first approach focuses on the recovery of magnesium compounds, including magnesium oxide (MgO), magnesium hydroxide ($\text{Mg}(\text{OH})_2$), magnesium chloride (MgCl_2), magnesium carbonate (MgCO_3), magnesium sulfate (MgSO_4), and magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$), from secondary resources, like dolomitic limestone waste rock. This route primarily relies on chemical and physicochemical separation techniques and can be implemented through hydrometallurgical, biometallurgical, electrometallurgical, or pyrometallurgical processes.

The second approach involves the metallization of magnesium, in which either magnesium-rich secondary resources or recovered magnesium compounds are converted into metallic Mg. This pathway is typically achieved through molten-salt electrolysis or thermal reduction processes and represents the final step toward producing primary-grade Mg metal. Each approach presents distinct advantages and challenges, particularly when applied to complex secondary materials such as dolomitic limestone waste rock. The principles, process variants, and limitations associated with these two strategies are discussed in the following subsections.

3.4.1 Methods for recovery of magnesium compounds

3.4.1.1 Hydrometallurgical process

Hydrometallurgy is one of the most widely applied routes for the recovery of metals from low-grade ores and secondary resources, owing to its operational flexibility, relatively low processing temperature, and ability to treat chemically complex feedstocks. In the context of magnesium recovery, hydrometallurgical processing benefits from differences in mineral solubility and aqueous-phase chemistry to selectively transfer Mg from the solid phase into solution. As schematically illustrated in Figure 3.4, hydrometallurgical processing generally consists of two sequential stages: leaching and metal separation.

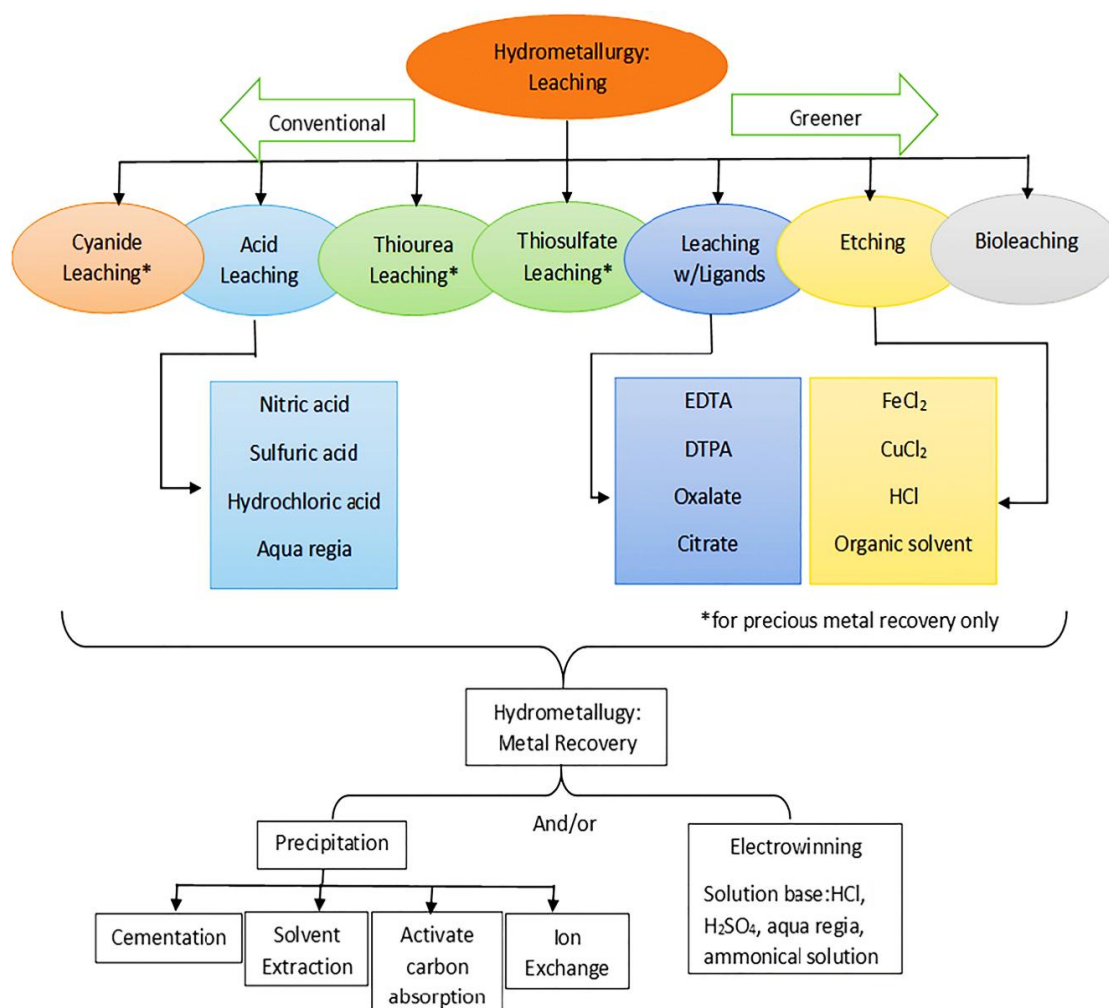


Figure 3.4 The overall flow chart illustrating the hydrometallurgical metal extraction process [60].

During the leaching stage, magnesium-bearing phases present in the solid feed are chemically dissolved and transferred into an aqueous medium, forming a leachate (or lixiviant) [61]. This step is governed by acid-base reactions, complexation equilibria, and, in some cases, redox-controlled dissolution mechanisms [17]. A wide range of leaching agents has been investigated, including inorganic acids (e.g., HCl, H₂SO₄, HNO₃, and H₃PO₄), organic acids (e.g., citric, oxalic, malic, tartaric, ascorbic acids, and glycine), alkaline salt solutions (e.g., NH₃-(NH₄)₂SO₄ or Na₂SO₃ systems), as well as water or mixed reagent systems [62, 63]. The choice of lixiviant strongly influences dissolution selectivity, impurity co-leaching, and downstream purification requirements. Leaching efficiency can be further enhanced through the addition of oxidizing agents (e.g., H₂O₂, Cl₂, NaClO, HClO) or reducing agents (e.g., Fe²⁺, SO₂), depending on the mineralogical nature of the feedstock and the targeted dissolution pathway [64, 65]. Operational parameters, including redox potential, pH, lixiviant concentration, particle size, solid-to-liquid ratio, agitation rate, temperature, and pressure, contribute to controlling both leaching kinetics and thermodynamic equilibria. Elevated temperatures and pressures are often employed to accelerate reaction rates and improve metal extraction yields [66]. However, these conditions also increase energy demand and equipment complexity.

Following leaching, dissolved magnesium is recovered from the pregnant leach solution through selective separation techniques that reduce the solubility of Mg species and transfer them back into a solid or metallic phase. Common recovery methods include precipitation, cementation, solvent extraction, adsorption, ion exchange, and electro-deposition [67-69]. Among these techniques, chemical precipitation is the most widely adopted due to its simplicity, scalability, and compatibility with large solution volumes. Magnesium precipitation can be induced using alkaline reagents such as oxides (e.g., CaO, MgO), hydroxides (e.g., NaOH, Ca(OH)₂, Mg(OH)₂, NH₄OH), sulfide-based precipitants (e.g., Na₂S, NaHS, FeS, H₂S), or carbonates (e.g., Na₂CO₃ and NaHCO₃), yielding Mg compound products such as Mg(OH)₂ or MgCO₃ [70-74].

Despite its versatility, hydrometallurgical processing of secondary Mg resources faces several limitations. These include the non-selective dissolution of calcium and impurity elements (e.g., Fe, Al, Mn, Si, and P), high reagent consumption associated with carbonate-rich feedstocks, and the generation of large volumes of saline or acidic effluents. In systems such as dolomitic limestone waste rock, where Mg and Ca coexist in comparable concentrations, achieving selective Mg recovery without excessive reagent use or complex downstream purification remains a central

challenge. Consequently, the design of hydrometallurgical routes for magnesium recovery must carefully balance extraction efficiency, selectivity, environmental footprint, and process integration with subsequent metallization steps.

3.4.1.2 Electrometallurgical process

Electrometallurgical processes employ externally applied electrical fields to drive the leaching and separation of dissolved metal species from aqueous solutions. In contrast to purely chemical hydrometallurgical routes, these methods offer improved controllability and, in some cases, reduced chemical consumption by exploiting differences in electrochemical potential, ion transport behavior, and interfacial charge-transfer mechanisms [75, 76]. Electrochemical recovery from aqueous media can be broadly categorized into electrodeposition, electrosorption, membrane-driven separation, and electrocoagulation, as illustrated in Figure 3.5.

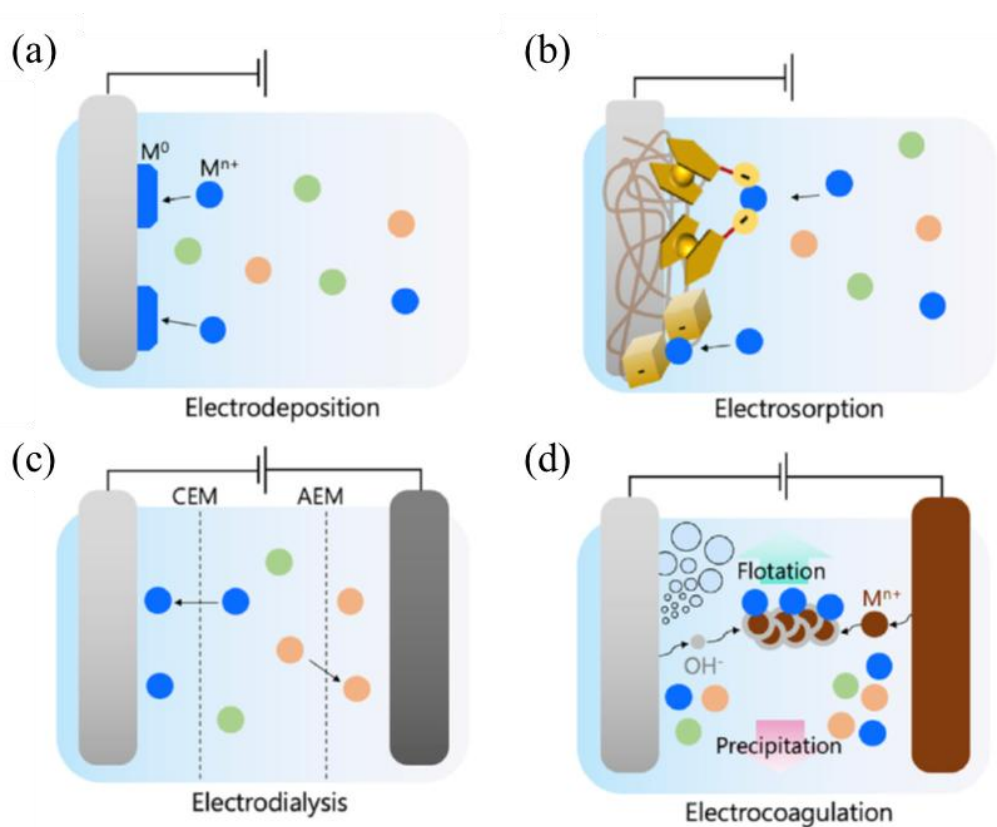


Figure 3.5 Schematic of different electrochemical processes (a) electrodeposition of metal ions on cathodic substrate, (b) electrosorption by non-faradaic CDI or pseudocapacitive faradaic electrodes, (c) electrodialysis, (d) electrocoagulation processes [77].

Electrodeposition (electrowinning) (Figure 3.5(a)) relies on the cathodic reduction of metal ions to their metallic state and deposition of metal cations on the cathode surface. This process is governed primarily by thermodynamic reduction potentials and kinetic factors [77]. While this approach is highly effective for noble and transition metals, its applicability to magnesium is fundamentally constrained by Mg's highly negative reduction potential and the competing hydrogen evolution reaction in aqueous systems [75, 78]. As a result, direct aqueous electrodeposition of magnesium metal is thermodynamically unfavorable, limiting its use to impurity removal or solution conditioning rather than Mg recovery.

Electrosorption-based techniques (Figure 3.5(b)), including capacitive deionization (CDI) and systems employing pseudocapacitive or redox-active electrodes, recover ions through field-assisted adsorption at electrode surfaces [79]. Although these methods can reduce overall ionic strength and enable partial ion separation, their selectivity for Mg^{2+} in the presence of chemically similar ions, such as Ca^{2+} , remains limited. Consequently, electrosorption is more suitable for bulk desalination or pre-concentration than for selective magnesium recovery from complex leachates.

Membrane-based electrochemical separations (Figure 3.5(c)), such as electrodialysis, utilize alternating cation- and anion-exchange membranes to concentrate or separate ionic species under an applied electric field [80, 81]. While effective for salt management, acid-base recovery, and solution conditioning, electrodialysis generally lacks the ion-specific selectivity required to efficiently separate Mg^{2+} from Ca^{2+} in carbonate-rich systems and is further challenged by membrane fouling and scaling.

Electrocoagulation (Figure 3.5(d)) involves the electrochemical generation of metal hydroxide coagulants (typically Al or Fe) that destabilize dissolved species through adsorption and flocculation [82, 83]. Despite its high overall removal efficiency and operational simplicity, electrocoagulation is inherently non-selective and produces substantial sludge volumes, limiting its role to bulk purification rather than targeted recovery of magnesium compounds.

Overall, although electrometallurgical techniques offer valuable tools for solution treatment and impurity management, their application to selective magnesium recovery from secondary resources, particularly dolomitic limestone waste rock, is limited by electrochemical constraints, poor Mg-Ca selectivity, and process inefficiencies. Consequently, these methods are best regarded

as auxiliary or hybrid options that complement hydrometallurgical pathways rather than serving as standalone solutions for magnesium compound production.

3.4.1.3 Biometallurgical process

Biometallurgy represents an environmentally benign alternative to conventional hydrometallurgical processing for the recovery of metals from ores and secondary resources. Unlike purely chemical routes, biometallurgical processes employ the metabolic activity of microorganisms to mediate metal dissolution, transformation, or separation in aqueous systems, typically under mild temperature and pressure conditions. As a result, these processes are often associated with lower energy consumption, reduced reagent demand, and improved environmental compatibility [84].

From a mechanistic standpoint, biometallurgical processing shares similar concepts with hydrometallurgy in that metals are transferred from the solid phase into solution. However, the driving forces are biological rather than purely chemical agents. Microorganisms, including bacteria, archaea, and fungi, can promote metal mobilization by producing organic acids, chelating agents, redox-active metabolites, or extracellular polymers [85]. Depending on the microbial pathway and process objective, biometallurgical techniques can be broadly classified into bio-leaching and bio-oxidation (microbially induced dissolution), bio-reduction (valence-state transformation), bio-flotation (surface modification), bio-precipitation (microbially induced mineral formation), bio-sorption and bio-accumulation (passive or active uptake), and biodegradation-assisted metal release [86].

Despite these diverse mechanisms, the applicability of biometallurgy to magnesium recovery from carbonate-rich secondary resources remains limited. Magnesium-bearing minerals such as dolomite and magnesite are readily soluble under mild acidic conditions, making conventional hydrometallurgical leaching more kinetically favorable than biologically mediated dissolution. Furthermore, biometallurgical processes typically operate on time scales ranging from weeks to months and are sensitive to environmental conditions such as pH, temperature, nutrient availability, and metal toxicity. The presence of high Ca^{2+} concentrations, alkaline carbonatite buffering, and complex impurity matrices in dolomitic limestone waste rock further complicates selective Mg mobilization via microbial routes. Therefore, although biometallurgical processes show potential

for extracting specific base and precious metals from sulfide-rich or refractory wastes, their use in recovering magnesium compounds is typically limited to specialized or pre-treatment uses.

3.4.1.4 Pyrometallurgical process

In the context of magnesium compound recovery from secondary resources, pyrometallurgical processing is rarely employed as a standalone extraction route. Instead, it is most commonly applied as an auxiliary or pre-treatment step designed to enhance subsequent hydrometallurgical leaching efficiency or selectivity. Such hybrid pyrometallurgical-hydrometallurgical approaches aim to modify mineral phases, disrupt refractory structures, and improve metal solubility while reducing reagent consumption during aqueous processing. Direct acid leaching of magnesium-bearing solids using strong inorganic acids (e.g., HCl, HNO₃, and H₂SO₄) can achieve high extraction efficiencies. Nevertheless, this typically requires high acid concentrations and low solid-to-liquid ratios [87, 88]. These conditions significantly increase operating costs and generate large volumes of hazardous effluents. To mitigate these drawbacks, a range of thermal pre-treatment strategies has been developed, including acid baking followed by water leaching, acid roasting followed by water leaching, chlorination roasting, carbochlorination roasting, and calcination-assisted leaching [89-93].

Acid baking involves the reaction of the solid precursor with concentrated acids (typically 95-98 wt.% H₂SO₄ or 37 wt.% HCl) at moderate temperatures (200-400 °C), resulting in the formation of water-soluble sulfate or chloride phases [94]. Acid roasting operates on similar chemical principles but at higher temperatures (>700 °C), promoting the decomposition of thermally unstable impurity phases into water-insoluble species and thereby improving leaching selectivity [87]. While acid baking benefits from lower energy demand, acid roasting generally offers superior impurity rejection at the expense of higher thermal input.

Chlorination-based pre-treatments convert metal oxides, carbonates, or sulfates into soluble chlorides by reacting the solid feed with chlorinating agents such as Cl₂, HCl, or NH₄Cl at temperatures typically ranging from 300 °C to 1000 °C [95]. In carbochlorination, the addition of a carbonaceous reductant lowers the Gibbs free energy of chlorination reactions and enables operation at reduced temperatures (300-700 °C), while also facilitating the formation of reactive gaseous intermediates [96]. These approaches are particularly effective for producing a calcine

amenable to staged leaching, in which highly soluble chlorides can be selectively recovered in early leaching steps while less reactive impurities remain in the solid residue.

Thermal calcination of carbonate- and sulfate-based Mg ores has been explored as a phase-engineering strategy to improve magnesium leachability by converting relatively stable minerals into more reactive oxide phases. Calcination of dolomitic materials at high temperatures ($>900\text{ }^{\circ}\text{C}$) decomposes $\text{CaMg}(\text{CO}_3)_2$ into mixed oxides ($\text{MgO}.\text{CaO}$), which exhibit enhanced thermodynamic solubility in acidic media [97-99]. While high Mg extraction efficiencies have been reported for fully calcined dolomite, this approach is typically accompanied by extensive co-dissolution of calcium, complicating downstream Mg-Ca separation. Partial calcination at intermediate temperatures ($750\text{-}800\text{ }^{\circ}\text{C}$) has therefore been proposed to preferentially decompose magnesium carbonate while retaining calcium as CaCO_3 , yielding mixed $\text{MgO}.\text{CaCO}_3$ phases that can improve Mg selectivity during leaching [100, 101]. Additional selectivity enhancements have been achieved through controlled carbonation or ammonium sulfate leaching, in which calcium is retained in poorly soluble solid phases [23].

Despite these advantages, pyrometallurgical pre-treatment remains constrained by high energy demand, associated CO_2 emissions, and the risk of impurity activation. In dolomitic limestone waste rock, where siliceous and aluminosilicate impurities can constitute up to 10 wt.% of the matrix, thermal treatment may weaken impurity bonding and promote undesired co-leaching during subsequent hydrometallurgical processing. Consequently, although calcination can enhance magnesium reactivity, its application as a pre-treatment step must be carefully evaluated against energy intensity, impurity behavior, and overall process sustainability.

3.4.2 Methods for magnesium metallization

3.4.2.1 Molten salt electrolysis

Molten salt electrolysis is a high-temperature electrometallurgical route that enables the direct conversion of magnesium compounds, particularly MgO or MgCl_2 , into metallic magnesium through a liquid-solid reaction. In this process, magnesium species are reduced in an ionic molten salt medium at temperatures typically between $400\text{ }^{\circ}\text{C}$ and $1300\text{ }^{\circ}\text{C}$, where solid electrolytes are replaced by highly conductive molten salts that facilitate ion transport and charge transfer [47, 102]. From a mechanistic perspective, molten salt electrolysis relies on the cathodic reduction of Mg^{2+} ions suspended or dissolved in fluoride- or chloride-based molten salts, such as $\text{MgF}_2\text{-LiF}$ or

LiCl-KCl systems. Upon application of an external electric current, Mg^{2+} migrates through the molten electrolyte and is reduced at the cathode surface to liquid magnesium ($\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$). Simultaneously, oxide or oxygen-bearing species are oxidized at the anode to form gaseous products such as O_2 , CO , or CO_2 , depending on the anode material (i.e., inert anode like platinum or reactive anode like graphite). To suppress recombination reactions and improve current efficiency, the freshly formed Mg is often absorbed into a dense liquid-metal cathode (e.g., Cu, Ag, or Sn), forming Mg-rich alloys that lower the effective activity of Mg. High-purity Mg is subsequently recovered via vacuum distillation of the alloy [103].

As shown in Figure 3.6, two principal process variants can be distinguished. In the first, electrolysis is conducted below the boiling point of magnesium (1090 °C), and Mg is collected in liquid or alloy form within the electrochemical cell (Figure 3.6(a)). In the second, the process operates at temperatures above the magnesium boiling point, typically in fluoride-based melts, where Mg is generated as a vapor and separated from the molten salt via condensation (Figure 3.6(b)). Although this vapor-phase approach can yield exceptionally high-purity magnesium, it requires substantially higher operating temperatures and energy input [104].

Despite its technical maturity and ability to produce high-purity metal, molten salt electrolysis faces several limitations. Magnesium's low density causes flotation and potential short-circuiting within the cell, while its high solubility in molten salts promotes back-reaction and reduces current efficiency. In chloride-based systems, the need for strictly anhydrous MgCl_2 and the generation of corrosive and toxic chlorine gas impose additional operational and environmental burdens. More broadly, the corrosive nature of molten salts, stringent materials-of-construction requirements, high capital costs, and significant energy demand limit the economic and environmental viability of molten salt electrolysis for magnesium production from secondary resources.

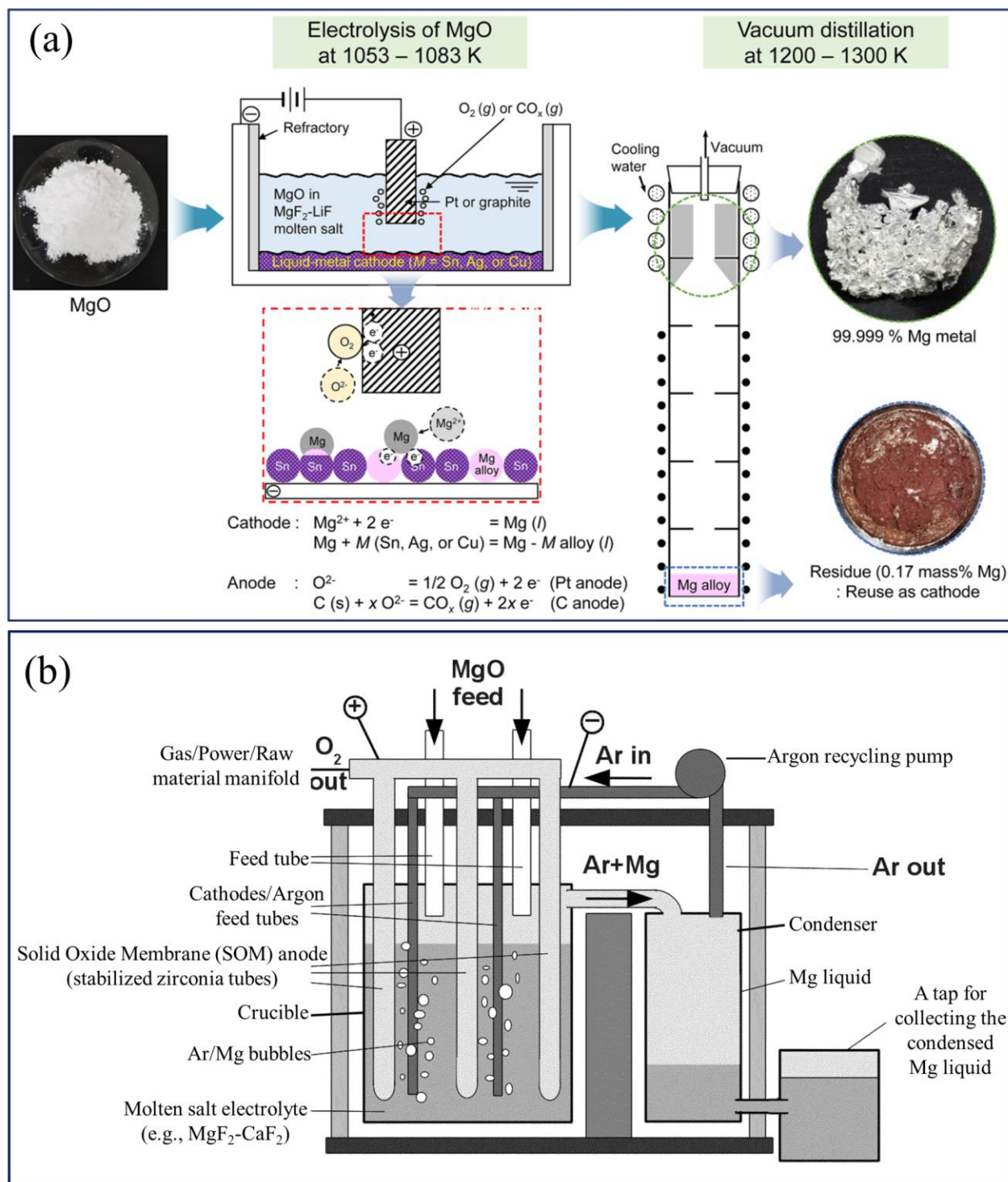


Figure 3.6 Schematic of the electroreduction in molten salt (a) liquid-metal cathode system [103] and (b) salt- and argon-mediated distillation with oxide electrolysis [105].

3.4.2.2 Thermal reduction

Thermal reduction is a reductive pyrometallurgical route in which secondary resources or recovered magnesium compounds are converted into metallic magnesium through high-temperature reactions with a suitable reductant. The driving force for this process arises from the combined effects of elevated temperature and reduced oxygen activity, which thermodynamically favor the formation of Mg vapor or liquid under controlled conditions [106]. In practice, thermal reduction relies on solid-solid or solid-gas reactions conducted at temperatures typically exceeding 1200 °C, often under reduced pressure or controlled atmospheres to shift equilibrium and facilitate Mg volatilization.

Among the various pyrometallurgical approaches, thermal reduction represents the most established and widely implemented route for primary magnesium production. Industrial thermal reduction is predominantly based on silicothermic reduction, in which silicon, commonly introduced as ferrosilicon, serves as the reductant for MgO or calcined dolomite (dolime). This pathway forms the basis of the Pidgeon process, which currently accounts for more than 85% of global magnesium production [107]. In this process, calcined dolomitic feedstocks react with ferrosilicon at a temperature above 1200 °C under a vacuum pressure of 10 Pa, producing magnesium vapor that is subsequently condensed into metallic Mg. Figure 3.7 illustrates the schematic reactor for thermal reduction of MgO to Mg [108, 109].

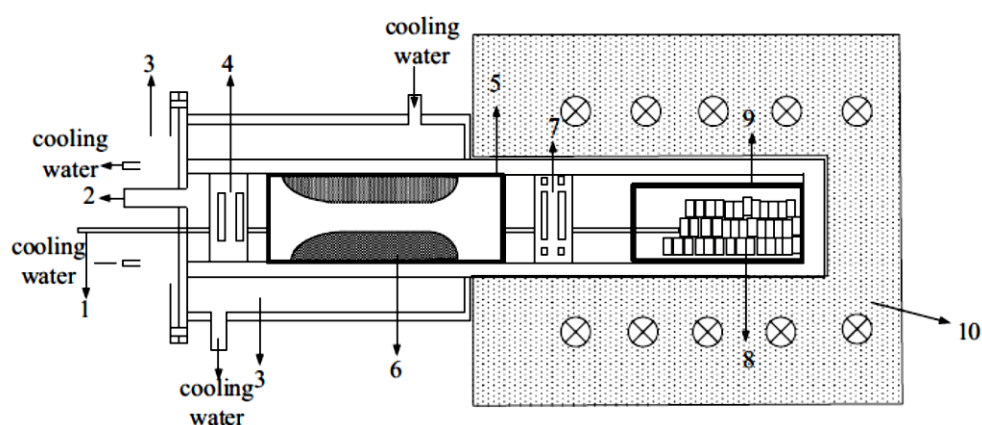


Figure 3.7 Schematic illustration of thermal reduction reactor: 1) thermocouple, 2) vacuum tube, 3) water-cooled jacket, 4) sodium and potassium condenser, 5) magnesium condenser, 6) rough magnesium, 7) thermal cutoff, 8) briquettes, 9) briquettes bucket, 10) furnace [107].

Several industrial variants of silicothermic reduction have been developed to address the batch operation and energy inefficiencies of the conventional Pidgeon process. Notably, the Magnetherm and Mintek processes represent intensified thermal silicothermic reduction technologies designed for semi-continuous or continuous operation. These systems employ higher operating temperatures, electrically heated furnaces, and advanced slag management to improve productivity and thermal efficiency while maintaining the fundamental silicothermic reaction chemistry. Despite differences in reactor design and pressure regime, all commercial thermal reduction processes rely on the same core principle: high-temperature reduction of MgO followed by physical separation of Mg vapor from the reaction zone. In these processes, alumina (Al_2O_3) is also added to lower the melting point of the slag [110]. The primary difference between Mintek and Magnetherm is the pressure level. Mintek operates at atmospheric pressure, enabling more continuous operation, while Magnetherm operates under vacuum in a cyclic, batch mode [111]. Figure 3.8 indicates a schematic illustration of the Mintek process. Also, the properties of these three-silicothermic reductions have been summarized in Table 3.1.

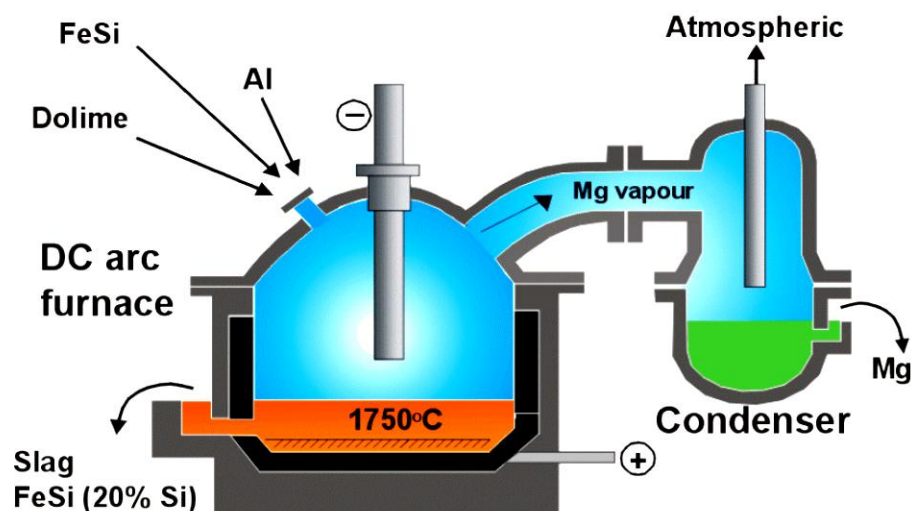


Figure 3.8 The Schematic demonstration of the Mintek Process [112].

Table 3.1 The comparison of the silicothermic reduction processes from metallic magnesium production.

Silicothermic reduction processes	Pidgeon	Magnetherm	Mintek
Reductant	Ferrosilicon (+ Lime)	Ferrosilicon (+ Al/Slag)	Ferrosilicon (+ Al/Slag)
Operation mode	Batch	Semi-continuous	Continuous / Semi-continuous
Temperature	1200 °C	1300-1700 °C	1600-1750 °C
Pressure	Vacuum (10 Pa)	Partial Vacuum (0.05-0.1 atm)	Atmospheric Pressure (1 atm)
Productivity per furnace per day (ton)	0.05	20	100
Capital Cost	Low	Moderate/High	High
Labor Intensity	High	Lower than Pidgeon	Lower than Pidgeon

Owing to its technological maturity, scalability, and compatibility with oxide-based magnesium feedstocks, thermal reduction remains the cornerstone of global magnesium metallization. Its dominance underscores the importance of developing sustainable and low-carbon feed preparation strategies, particularly for secondary resources such as dolomitic limestone waste rock, to integrate effectively with existing and emerging thermal reduction platforms. Details of the contributing parameters and the research pathway for sustainable, low-carbon-emission magnesium production via thermal reduction are discussed in Section 3.5.

3.5 Magnesium metal production by thermal reduction

The efficiency and sustainability of magnesium metal production by thermal reduction are governed by a set of contributing parameters that collectively control reaction thermodynamics, kinetics, and product separation. Among these, feedstock pretreatment, reductant selection, the addition of fluxing agents, and heating strategies play decisive roles in determining magnesium yield, energy consumption, impurity behavior, and overall process feasibility. The influences of

each parameter and the limitations associated with their implementation are critically evaluated in the following subsections.

3.5.1 Pre-treatment of mineral resources

The purpose of pre-treatment for mineral and secondary resources is not only to increase the concentration of the target metal but, more importantly, to engineer a feedstock that is kinetically accessible and chemically compatible with the high-temperature reduction process. Effective pre-treatment can first remove or immobilize impurities that poison reactions or contaminate Mg vapor. Second, it controls mineralogy and phase structure to favor rapid reduction and Mg volatilization. Third, it improves mass and heat transfer by tailoring particle size, porosity, and surface area. Eventually, pretreatment of feedstock standardizes feedstock variability, which is especially important for secondary resources that contain considerable impurities. Consequently, pretreatment plays a key role in improving thermal reduction efficiency and Mg purity. Nonetheless, it also entails trade-offs in energy demand, CO₂ emissions, reagent consumption, and overall process cost.

A range of pre-treatment strategies has been reported, including comminution and liberation, physical separation, chemical conditioning, calcination, and emerging intensification methods such as microwave and ultrasonic treatments [113-116]. Comminution and liberation reduce particle size and increase surface area while promoting the physical liberation of mineral phases from gangue. For thermal reduction, these changes can accelerate reaction kinetics by shortening diffusion distances and improving interfacial contact between the Mg-bearing phase and the reductant. However, finer grinding is energy-intensive and may introduce practical issues such as dust generation, poor bed permeability in fixed-bed reactors, and enhanced sintering at high temperatures, which can reduce porosity and slow reduction rates. Thus, an optimum particle-size distribution often exists that balances kinetics, gas diffusion, and heat transport within the reactor [117].

Following liberation, physical separation methods, such as sieving, gravity separation, magnetic separation, and electrostatic separation, can remove specific gangue fractions and reduce the impurity load delivered to the reduction stage [118]. These methods are attractive because they minimize chemical inputs. However, their effectiveness depends strongly on mineralogical contrast (density, magnetic susceptibility, electrical conductivity) and may be limited when impurities are finely disseminated or chemically bound within Mg-bearing phases. Chemical conditioning (e.g.,

hydraulic washing, selective leaching, or mild acid treatment) and flotation can further reduce problematic impurities and improve feed homogeneity [116, 119]. Nevertheless, chemical pretreatment can increase overall water use and generate waste effluents, and, if applied aggressively, may dissolve desired Mg-bearing phases or introduce salt residues that alter high-temperature behavior. For secondary resources, these separation steps are further challenged by compositional variability and the presence of fine clays or amorphous phases, which can impair separation efficiency and handling [117, 120].

For carbonate-rich Mg feedstocks, calcination is often a critical pre-treatment step because it removes chemically bound CO_2 and converts stable carbonates into more reactive oxide phases. In dolomitic limestone, calcination transforms $\text{CaMg}(\text{CO}_3)_2$ into mixed oxides ($\text{MgO} \cdot \text{CaO}$), increasing reactivity toward reductants and modifying the high-temperature phase behavior relevant to reduction and Mg vapor release [121]. However, calcination also imposes a major energy demand and generates direct CO_2 when fossil fuels are used as the power source. This approach can dominate the carbon footprint unless heat integration, electrification, or CO_2 management is implemented. Moreover, high-temperature calcination can promote sintering and densification, thereby reducing specific surface area and limiting gas-solid transport, which may counteract kinetic benefits if not carefully controlled. Calcination can also alter the speciation of impurities (e.g., silicates, phosphates, iron-bearing phases), potentially increasing their tendency to participate in slag formation or to contaminate Mg vapor during reduction.

More recently, microwave and ultrasonic pre-treatments have been explored as intensification strategies to modify feed microstructure and improve subsequent reduction performance [113, 115, 122, 123]. Microwave irradiation can induce selective heating, thermal stresses, and microcracking at mineral boundaries, potentially enhancing liberation, increasing porosity, and reducing the energy required for comminution. Ultrasonic treatment, particularly in slurry systems, can promote particle fragmentation and surface cleaning via cavitation, thereby improving downstream separation or reactivity [113]. While these methods are often described as green route due to their potential for process intensification, their practical deployment remains constrained by scale-up challenges, energy efficiency at industrial throughput, and strong dependence on feed dielectric properties (for microwave treatment) or slurry handling requirements (for ultrasound treatment). Therefore, their most realistic roles may be targeted pre-conditioning or hybrid integration rather than full replacement of conventional pre-treatment trains.

Overall, pre-treatment plays a crucial role in magnesium thermal reduction by determining the reactive mineralogy, impurity levels, and transport properties of the feedstock. The best pre-treatment method is highly dependent on the specific feedstock and requires balancing enhanced reduction kinetics and Mg purity with factors like energy use, greenhouse gas emissions, waste production, and scalability. These considerations are especially important when processing secondary resources such as dolomitic limestone waste rock.

3.5.2 Reducing agents

A reducing agent, also called a reductant, is a species capable of decreasing the oxygen activity of a system by accepting oxygen from metal oxides, thereby enabling the formation of the metallic phase. While redox tendencies are often introduced using standard reduction potentials, thermal reduction at high temperature is more rigorously governed by oxygen potential and Gibbs free energy relationships (e.g., Ellingham-type considerations). In practice, a reductant is effective when the formation of its oxidized products (e.g., SiO_2 , Al_2O_3 , CO/CO_2 , H_2O) is thermodynamically favored under the operating temperature and pressure, and when the process conditions (i.e., vacuum or atmospheric with inert gas) maintain a sufficiently low partial pressure of magnesium to shift the equilibrium toward Mg vapor [124]. For magnesium production from calcined dolomitic feedstocks, the most common solid reductants are ferrosilicon (silicothermic reduction), aluminum (aluminothermic reduction), and carbon (carbothermic reduction). These processes are often written as solid-solid reactions. However, under practical operating conditions, the reduction pathway is more complex. At elevated temperatures, partial melting, gas formation, or volatilization of reactants and/or products occurs, and the reactions proceed through combined solid-solid, solid-gas, or solid-liquid mechanisms [11, 125, 126]. As a result, reductant selection affects not only reaction thermodynamics but also mass transfer, bed permeability, sintering behavior, and the separation of magnesium vapor or liquid from the reaction zone.

Among these reductants, silicothermic reduction remains the dominant industrial route for magnesium production and underpins the Pidgeon process. Its widespread adoption reflects a balance between thermodynamic driving force, process reliability, and manageable reaction chemistry [127]. Despite its commercialization, silicothermic reduction suffers from high operating temperatures, reliance on vacuum pressure, high energy consumption, excessive CO_2 production, and the formation of silica-rich slags that require appropriate fluxing and residue management

[128]. Aluminothermic reduction offers a stronger reduction potential but is less commonly applied due to higher reductant costs and the formation of refractory alumina-containing residues [129, 130]. In contrast, carbothermic reduction has attracted increasing interest because carbon is inexpensive, widely available, and capable of reducing magnesium oxide under appropriate high-temperature and low-pressure conditions [131]. However, carbothermic routes typically require higher operating temperatures and careful control of pressure and gas composition to prevent back-reactions and ensure efficient magnesium vapor condensation [30, 132].

In addition to solid reductants, gas-phase reducing agents such as hydrogen, carbon monoxide, and methane have been investigated for high-temperature magnesium oxide reduction [29, 133]. Gas-phase reductants can improve reaction kinetics by eliminating solid-solid diffusion barriers and enhancing contact between the reducing species and the metal oxide surface [134]. Among these, methane is particularly attractive because it can simultaneously act as a reducing agent and decomposes into hydrogen and carbon monoxide at high temperatures, generating syngas as a valuable by-product [135]. Nevertheless, gas-phase reduction routes are highly sensitive to temperature, pressure, and gas composition, and their practical viability depends on effective management of reaction equilibria, carbon deposition, and unreacted gas recycling.

Overall, selecting a reductant is vital in thermal magnesium production because it directly affects reaction temperature, energy consumption, impurity interactions, and magnesium recovery efficiency. For secondary resources such as dolomitic limestone waste rock, reductant selection must also account for the presence of calcium and minor impurities, which can alter reaction pathways and slag formation. These considerations highlight the importance of evaluating reducing agents not only on thermodynamic feasibility but also on process integration, scalability, and compatibility with low-carbon magnesium production strategies. Table 3.2 summarizes the main thermal reduction reactions and the thermodynamic operating conditions for the primary reductants, as calculated by the Factsage software.

Table 3.2 The thermodynamically favorable thermal reduction reactions of calcined dolomite or MgO using different reductants.

Process	Reaction	Temperature	Pressure
Silicothermic reduction (Pidgeon)	$2MgO \cdot CaO + (Fe)Si \rightarrow 2Mg_{(g)} + Ca_2SiO_{4(s)} + Fe_{(s)}$	1200-1300 °C	1-10 Pa
Aluminothermic reduction	$6MgO_{(s)} + 2CaO_{(s)} + 4Al_{(s)} \rightarrow 6Mg_{(g)} + 2CaO \cdot Al_2O_{3(s)}$	1100-1600 °C	100 Pa - 1 atm
Carbothermic reduction	$MgO \cdot CaO_{(s)} + 2C_{(s)} \rightarrow Mg_{(g)} + Ca_{(g)} + 2CO_{(g)}$	1500-1700 °C	10-100 Pa
Methanothermic reduction	$MgO_{(s)} + CH_{4(g)} \rightarrow Mg_{(g)} + CO_{(g)} + 2H_{2(g)}$	1200-1800 °C	10 Pa - 1 atm
Carbon monoxide reduction	$MgO_{(s)} + CO_{(g)} \rightarrow Mg_{(g)} + CO_{2(g)}$	2100-2300 °C	1-10 Pa
Hydrogen reduction	$MgO_{(s)} + H_{2(g)} \rightarrow Mg_{(g)} + H_2O_{(g)}$	2000-2200 °C	1-10 Pa

3.5.3 Fluxing agents

In thermal reduction processes, a fluxing agent is added to the feed (mixture of Mg-bearing phase and reductant) to enhance reduction efficiency by lowering the effective melting or softening temperature of the feed and transferring impurities into a separable slag phase [136]. Beyond melting point decrease, fluxes influence reaction performance by adjusting slag chemistry and transport properties (basicity, viscosity, and sometimes electrical conductivity), improving wetting and interfacial contact between reactants, and immobilizing oxide-forming impurities (e.g., Si-, Al-, Fe-, and Ti-bearing phases) that would otherwise hinder Mg vapor generation or contaminate products [137]. In some systems, fluxes can also decrease Mg reoxidation by promoting rapid oxygen capture into stable slag species.

A wide range of fluxes has been reported for calcined dolomite or MgO-based thermal reduction, including fluorides (CaF_2 , MgF_2 , NaF , KF), chlorides (CaCl_2 , NaCl), carbonates (Na_2CO_3 , K_2CO_3), and selected oxides or nitrates used as additives or promoters [138-141]. However, flux selection must balance benefits against drawbacks. Fluoride- and chloride-containing fluxes can improve slag fluidity and phase separation but may increase corrosion, volatilization losses, and environmental impact. Carbonate fluxes can modify basicity and slag formation but may introduce additional CO_2 release and alter gas-solid equilibria. Importantly, an unsuitable flux can introduce new contaminants (e.g., alkali carryover), change slag chemistry in ways that trap Mg-bearing species, or increase processing cost without improving yield. Therefore, selecting an appropriate fluxing agent requires simultaneous consideration of (I) impurity mineralogy of the feed, (II) desired slag viscosity and melting range at operating temperature, (III) compatibility with reactor materials and off-gas constraints, and (IV) cost and availability [18, 142, 143]. These criteria are particularly critical for heterogeneous secondary resources such as dolomitic limestone waste rock, where impurity-driven slagging behavior can dominate the overall feasibility of thermal magnesium production.

3.5.4 Heating model

In pyrometallurgical magnesium production, the heating mode plays an important role in determining energy efficiency, reaction kinetics, and product quality. At present, the majority of industrial pyrometallurgical processes rely on fossil-fuel combustion as the primary heat source, which is directly associated with high greenhouse gas emissions and energy consumption. The electrification of thermal reactors using renewable energy, through technologies such as induction, plasma, solar, electrical resistance, geothermal, and microwave heating, has therefore emerged as a key strategy for decarbonizing pyrometallurgy. Beyond the choice of energy source, the mechanism by which heat is delivered to the reacting solids fundamentally influences process performance. As schematically illustrated in Figure 3.9(a), in conventional heating, heat is first applied to the reactor walls and subsequently transferred to the feed via convection, radiation, and conduction. This indirect heat transfer results in long heating times, substantial thermal inertia, and pronounced temperature gradients between the particle surface and core [144]. In fixed-bed or briquetted systems commonly used for thermal reduction of magnesium-bearing solids, such gradients can promote sintering and pore collapse, thereby reducing gas permeability and hindering

magnesium vapor transport [145, 146]. Furthermore, prolonged exposure to high temperatures results in greater energy losses [20].

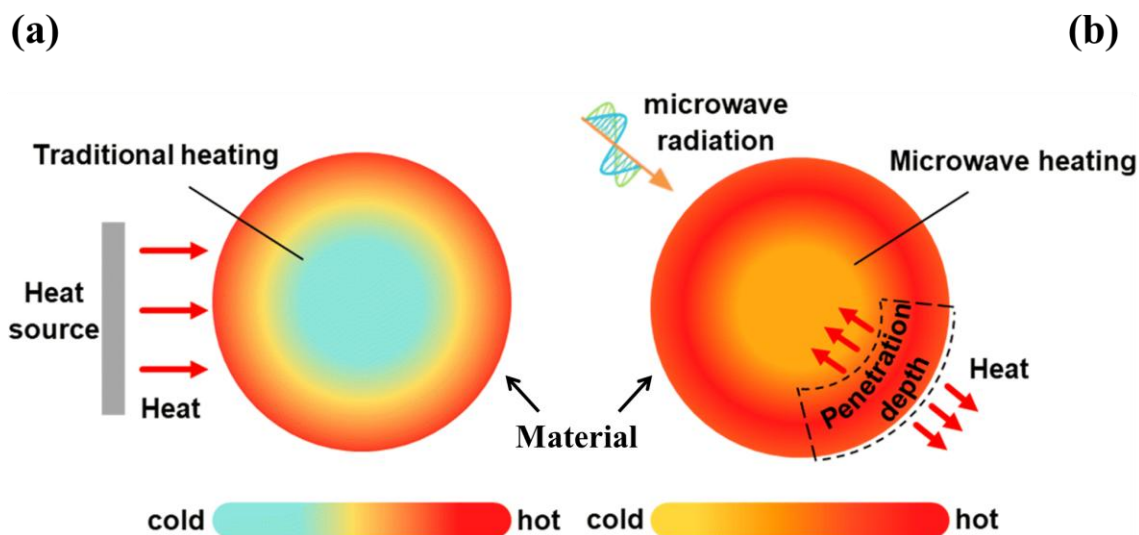


Figure 3.9 Temperature distribution pattern in (a) conventional heating, (b) microwave heating, adapted from [147].

Non-conventional heating approaches seek to overcome these limitations by altering the heat-transfer pathway. Among them, microwave heating is particularly distinctive because it enables volumetric energy dispersion through direct interaction between electromagnetic fields and dielectric materials [148]. As depicted in Figure 3.9(b), instead of relying on external heat transfer, microwave energy is absorbed within the material and converted into heat throughout the bulk, often producing higher temperatures in the interior than at the surface. This inversion of the temperature profile contrasts markedly with conventional heating and can significantly accelerate reaction kinetics while suppressing surface-driven sintering and side reactions in the surrounding environment [149-152]. In addition to volumetric heating, microwave irradiation offers several advantages, including rapid heating rates, reduced thermal lag, and improved temperature uniformity [20]. Importantly, many mineral phases and reductants exhibit significantly different dielectric properties, enabling selective microwave absorption. Such selectivity can lead to localized heating at reactive interfaces, enhancing solid-solid or gas-solid reaction efficiency without uniformly raising the reactor temperature [20, 153]. Several studies have also reported apparent decrease in activation energy under microwave irradiation, suggesting the presence of microwave-specific (non-thermal) effects, although the extent and origin of these effects remain a topic of debate [133, 154-156].

Taken together, the aforementioned features position electrified thermal reduction by microwave heating as a promising alternative to conventional heating for magnesium reduction, particularly in systems constrained by slow heat transfer, sintering, gas-bulk side reactions, or excessive energy consumption.

3.6 Microwave heating-assisted thermal reduction

A microwave is a type of electromagnetic wave with a wavelength ranging from 1mm to 1m, corresponding to frequencies between 0.3 and 300 GHz. As illustrated in Figure 3.10(a), microwave radiation propagates as mutually perpendicular oscillating electric (E) and magnetic (H) fields that travel at the speed of light. Industrial and laboratory microwave heating systems most commonly operate at 0.915 GHz and 2.45 GHz, frequencies chosen to avoid interference with telecommunication bands and widely adopted in commercial applicators [20]. In contrast to conventional furnaces, where heat is delivered from the reactor walls to the feed by conduction, convection, and radiation, microwave processing applies electromagnetic energy directly into the material. This difference can produce rapid volume heating, inverted temperature profiles, and selective heating of specific phases, which are particularly relevant for heterogeneous mineral-reductant mixtures. The ability of a material to convert microwave energy into heat depends on its electromagnetic response and, in most mineral systems at 0.915-2.45 GHz, is dominated by electric-field interactions rather than magnetic effects. As shown in Figure 3.10(b), electric-field heating is commonly described through polarization and charge-transport mechanisms, including dipolar polarization, ionic conduction, electronic polarization, and interfacial (Maxwell-Wagner) polarization [157, 158]. In practice, not all mechanisms contribute equally to microwave frequencies. Dipolar polarization is prominent in polar liquids and hydrated solids, where dipoles attempt to follow the oscillating field and dissipate energy through frictional relaxation. Ionic conduction arises from the oscillatory motion of mobile charge carriers. It is often a major source of loss in conductive solids such as molten salts and moist mineral matrices because charge motion induces Joule heating. Electronic polarization involves the displacement of the electron cloud relative to the nuclei and is generally associated with a high-frequency response. At 2.45 GHz, it contributes mainly through the material's overall permittivity rather than being a dominant loss channel. Interfacial polarization becomes important in multiphase and porous solids, such as ore-

reductant mixtures, where charge accumulation at phase boundaries can significantly increase dielectric losses.

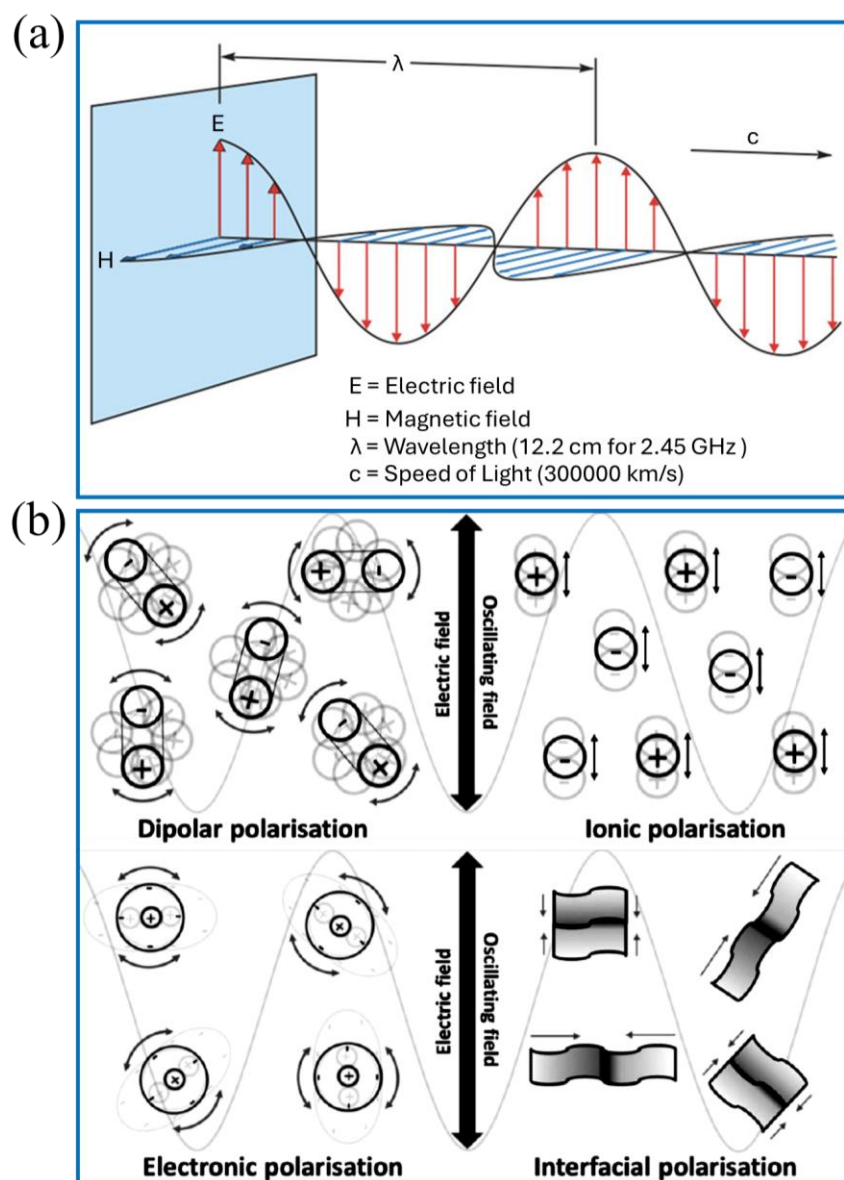


Figure 3.10 (a) Electromagnetic energy propagation of the microwave [159] and (b) Mechanism of microwave heating caused by the electrical field [157].

In addition to dielectric losses (E-field), magnetic losses (H-field) may contribute to heating in magnetic materials, conductors, and semiconductors. Although the main mechanism of magnetic heating is less well known than that of dielectric heating, proposed mechanisms for this field include eddy-current (Joule) losses induced by time-varying magnetic fields, hysteresis losses associated with magnetization reversal, and resonance phenomena such as domain-wall or

electron-spin resonance in certain magnetic oxides [160]. It is worth noting that for many mineral feedstocks at 2.45 GHz, magnetic losses are often secondary to dielectric losses, and their contribution depends strongly on the specific magnetic susceptibility, electrical conductivity, and microstructure of the material.

Given these complexities, the performance of microwave-assisted thermal reduction cannot be generalized from electromagnetic frequency alone. It must be evaluated based on the dielectric responses of each phase and the mixture, as well as the electromagnetic penetration depth and the power-absorption distribution. These aspects are discussed in the following subsections.

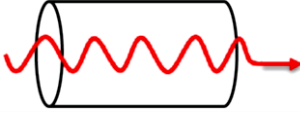
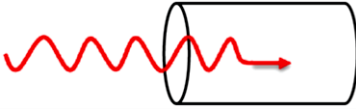
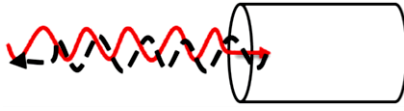
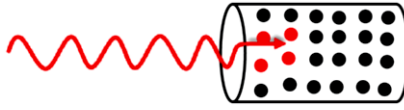
3.6.1 Dielectric Response

The interaction of materials with microwave radiation is commonly described by grouping materials into broad behavioral classes, depending on how incident electromagnetic waves are transmitted, absorbed, or reflected. Table 3.3 summarizes a practical classification into (I) low-loss dielectrics (transparent materials), (II) lossy dielectrics (absorbers), and (III) electrical conductors (reflectors). Although this classification is helpful for conceptual discussion, it should be regarded as qualitative rather than definitive, since microwave coupling depends strongly on factors such as frequency, temperature, porosity, crystal phase, and microstructure [161]. For example, many ceramics and oxide minerals exhibit low loss at room temperature but become strong microwave absorbers at elevated temperatures due to increased conductivity and dielectric loss [162-164]. Conversely, some materials heat initially only when coupled with susceptors or conductive additives [165].

In low-loss dielectrics (e.g., quartz, PTFE), the electromagnetic wave can propagate through the material with limited attenuation because dielectric losses are small. Such materials may still experience weak heating in practice, especially if impurities, bound water, or interfacial polarization mechanisms are present, but their microwave coupling is usually not strong enough for rapid volumetric heating. In contrast, lossy dielectrics (e.g., water, SiC) exhibit significant energy dissipation within the bulk, so the field penetrates to a finite depth and gradually attenuates as absorbed energy is converted to heat. The absorber category is particularly relevant to heterogeneous mineral systems, in which certain phases or additives preferentially absorb microwave energy and can serve as internal heat sources. Electrical conductors (e.g., bulk metals) predominantly reflect microwaves due to the rapid screening of the electric field at the surface (skin

effect). However, assuming a conductor has no heating is an oversimplification that is not universally accurate. Thin metallic films, metal powders, and metal-dielectric composites can absorb microwave energy through resistive and eddy-current losses, and can generate localized heating, especially near percolation thresholds or at sharp features where field enhancement occurs [166, 167].

Table 3.3 Classification of materials based on their response to microwave radiation

Interaction	Schematic illustration	Relevant materials
Transparent (low dielectric loss)		Quartz, Teflon, glass, sulfur, and most plastics.
Absorber (high dielectric loss)		Water, carbon, SiC, Fe ₃ O ₄ , ceramics, wet materials
Conductor (reflector)		Bulk metals and metal alloys like copper, aluminum, stainless steel
Mixed absorber (variation in dielectric loss)		Polymers, ceramics, and metal composites

For electric-field-dominated microwave heating, the dielectric response is quantified by the complex permittivity (ε^*), which describes both polarization capability and energy dissipation under a sinusoidal electric field [168]:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \quad (3.1)$$

Here, ε' (dielectric constant) represents the capacity to store electromagnetic energy, whereas ε'' (dielectric loss factor) represents the capacity to dissipate electromagnetic energy into heat. Considering different polarization mechanisms (i.e., dipolar, interfacial, ionic, and electronic), the effective dielectric properties can also be expressed as follows [165]:

$$\varepsilon' = \varepsilon'_{\text{dipolar}} + \varepsilon'_{\text{interfacial}} + \varepsilon'_{\text{ionic}} + \varepsilon'_{\text{ionic}} \quad (3.2)$$

$$\varepsilon'' = \underbrace{\varepsilon''_{\text{dipolar}} + \varepsilon''_{\text{interfacial}} + \varepsilon''_{\text{ionic}} + \varepsilon''_{\text{ionic}}}_{\text{Polarization Loss}} + \underbrace{\frac{\sigma}{2\pi f}}_{\text{Conduction Loss}} \quad (3.3)$$

where σ is the electrical conductivity of the material (S/m), and f is the frequency of the radiation (2.45 GHz). For many non-magnetic materials, the magnetic contribution is comparatively small and the dominant heating originates from dielectric and conductive losses. Nevertheless, complex permeability (μ^*) cannot be neglected in magnetic or strongly conducting systems, where magnetic loss mechanisms or induced currents may contribute to total power absorption.

A convenient indicator of microwave heating capability is the loss tangent, which quantifies a material's capacity to convert absorbed electromagnetic energy into heat. This parameter can be estimated as follows [169]:

$$\tan\delta_\varepsilon = \frac{\varepsilon''}{\varepsilon'} \quad (3.4)$$

In general, higher $\tan\delta_\varepsilon$ indicates stronger conversion of absorbed electromagnetic energy into heat. However, $\tan\delta_\varepsilon$ should be interpreted carefully. A high $\tan\delta_\varepsilon$ does not automatically guarantee efficient microwave heating at scale because heating also depends on field distribution, penetration depth, thermal conductivity, and sample geometry [170, 171]. Moreover, the dielectric properties of most materials are not constant. The values of ε' and ε'' can vary substantially with temperature, composition, moisture content, and phase changes. As a result, the microwave response of mineral-reductant mixtures can change during heating, which may cause hotspot formation if absorption rises rapidly with temperature [172, 173].

For many mineral-processing applications, an effective microwave-absorbing solid typically exhibits moderate ε' combined with sufficiently high ε'' to enable rapid energy dissipation [174]. As a rule of thumb, materials with $\tan\delta_\varepsilon$ values above 0.05 at the operating frequency of 2.45 GHz are often considered readily microwave-heatable [168]. Carbonaceous reductants (e.g., carbon black, char, graphite) are widely used to enhance microwave coupling, but their heating behavior is more accurately described by conductive (electronic) losses and interfacial polarization rather than purely dipolar mechanisms. In mixed metal oxide-carbon systems, this selective coupling can

be advantageous by concentrating heat at reaction interfaces. Nevertheless, it can increase the potential for non-uniform heating. Therefore, careful control of homogeneity and reactor electromagnetic design is required.

3.6.2 Penetration Depth and Power Absorbed

Microwave heating differs fundamentally from conventional furnace heating because electromagnetic energy can penetrate within the material rather than being delivered only from boundaries. The extent to which a microwave field penetrates into a solid determines whether heating is volumetric or confined near the surface, which directly affects temperature uniformity, hotspot formation, and the feasibility of scaling microwave-assisted processes.

The attenuation coefficient (α) describes the exponential decay of electromagnetic wave amplitude inside a material. In other words, it indicates how easily electromagnetic waves can penetrate into the material. The penetration depth (d_p) is commonly defined as the distance at which the microwave power decreases to $1/e$ ($\approx 36.8\%$) of its value at the surface. Therefore, d_p is a practical measure of how deep microwave heating can occur before the field becomes too weak to contribute significantly to volumetric energy absorption. The penetration depth is related to the attenuation coefficient by:

$$d_p = \frac{1}{\alpha} \quad (3.5)$$

For a general lossy medium in which both dielectric and magnetic losses may contribute, α can be expressed as [165, 175]:

$$\alpha = \frac{\sqrt{2}\pi f}{c} \sqrt{\mu' \varepsilon'} \left[\sqrt{1 + \left(\frac{\varepsilon''}{\varepsilon'}\right)^2 \left(\frac{\mu''}{\mu'}\right)^2 + \left(\frac{\varepsilon''}{\varepsilon'}\right)^2 + \left(\frac{\mu''}{\mu'}\right)^2} - \left(1 - \frac{\varepsilon''}{\varepsilon'} \frac{\mu''}{\mu'}\right) \right]^{\frac{1}{2}} \quad (3.6)$$

where c is the speed of light (3×10^8 m/s), and f is the microwave frequency.

A key point for mineral processing is that d_p is not a fixed property. It depends strongly on frequency, temperature, material porosity, and composition [153, 176]. In heterogeneous ore-reductant mixtures, the effective penetration depth is also influenced by phase distribution (e.g., carbon networks), evolving microstructure during heating, and phase transformations (e.g.,

dehydration, decarbonation, sintering, melting) [177-179]. Consequently, penetration depth measured at room temperature may not accurately represent the actual behavior under the reactive high-temperature conditions encountered during Mg-bearing solid thermal reduction.

When magnetic losses are negligible ($\mu''=0$) and materials interact only with the electric field, the penetration depth simplifies to the standard dielectric form:

$$d_p = \frac{c}{\sqrt{2\pi f \sqrt{\mu' \epsilon'}}} [\sqrt{1 + \tan^2 \delta_\epsilon} - 1]^{-\frac{1}{2}} \quad (3.7)$$

This expression highlights the competing requirements for effective microwave processing. Materials with low $\tan \delta_\epsilon$ exhibit large penetration depths and behave as transparent media. In this kind of material, the field penetrates deeply but deposits little energy per unit volume. In contrast, strongly lossy materials may absorb microwaves efficiently but exhibit small d_p , leading to near-surface heating, steep internal temperature gradients, and thermal runaway if heat removal and mixing are insufficient. For practical applications, the ratio of sample thickness (D) to penetration depth is a useful design indicator. As a rule of thumb, reported optimum microwave absorption often occurs near $D/d_p \approx 2.4$ [20]. However, this guideline is not universal and must be interpreted alongside boundary conditions, reactor geometry, and heat conduction within the sample, especially for reactive porous beds.

Table 3.4 summarizes representative values of $\tan \delta_\epsilon$ and d_p for reflectors, transparent, and microwave absorbers at specified frequencies and temperatures. These values illustrate two important trends relevant to microwave-assisted reduction. First, many structural ceramics and refractories have very large penetration depths at room temperature and therefore require susceptors or absorptive additives for efficient heating. Second, carbonaceous materials typically exhibit relatively small penetration depths and strong microwave absorption, enabling selective heating of the reductant phase in metal oxide-carbon mixtures. This selectivity can accelerate interfacial reactions, but it also increases the potential of hotspots and non-uniform temperature fields if the mixture is poorly homogenized or if the electromagnetic field distribution is not well controlled [160, 180, 181].

Table 3.4 The $\tan\delta_\epsilon$ and d_p of some reflector, transparent, and microwave absorbing materials [182-192].

Microwave interaction	Material	$\tan\delta_\epsilon$	d_p (cm)	Frequency (GHz)	Temperature (°C)
Reflector	Al	-	0.00017	2.45-2.5	25
	Cu	-	0.00013	2.45-2.5	25
	Au	-	0.00015	2.45-2.5	25
	Ag	-	0.00013	2.45-2.5	25
	Zr	-	0.00067	2.45-2.5	25
Microwave transparent	Alumina	0.001	1265	2.45-2.5	25
	Fused quartz	0.0003	7573	2.45-2.5	25
	Borosilicate glass	0.0012	1570	2.45-2.5	25
	Teflon	0.00048	5640	2.45-2.5	25
	Mullite	0.0015	1020	2.45-2.5	25
	Porous alumina fiberboard	0.00003	42100	2.45-2.5	25
	Yttria stabilized zirconia	0.0011	>500	2.216 or 2.45	25
	PVC	0.0056	403	2.45-2.5	25
	Polystyrene	0.0003	7620	2.45-2.5	25
	Silicon	<0.012	>396	1	25
	Silicon Nitride	<0.001	>1220	2.216 or 2.45	25
	Boron Nitride	<0.0005	>3500	3	25
Microwave absorber	Water	0.15	3	2.45-2.5	25
	SiC	0.37	1.93	2.45-2.5	25
	Carbon black (20 μm)	0.23	5.75	2.45	25
	Graphite powder (20-80 μm)	0.36-0.67	1.34-2.09	2.45	25
	Graphitized carbon powder (60-80 mesh)	0.4-1	0.5-0.9	2.45	25
	Activated Carbon	0.31-0.9	0.7-3.43	2.45	25
	Charcoal	0.14-0.38	6-11	2.45	25
	Carbon Fibers	0.45-0.5	0.5-0.7	8.2	25
	Carbon Nanotube	1.11	0.2	8	25

The local rate of microwave-to-heat conversion depends on both material losses and the internal electric and magnetic field strengths. The volumetric heat generation rate (Q_{MW}) can be written as [193]:

$$Q_{MW} = \underbrace{\pi f \epsilon'' |E|^2}_{\text{Heating by Electric Field}} + \underbrace{\pi f \mu'' |H|^2}_{\text{Heating by Magnetic Field}} \quad (3.8)$$

Where E (V/m) and H (Amp/m) are the internal electric and magnetic field amplitudes. This relationship emphasizes that strong microwave heating requires not only a lossy material (high ϵ'' and μ'') but also a favorable field distribution inside the reactor. In practice, E and H are spatially non-uniform due to standing waves, cavity design, and sample geometry, which is a major reason why microwave processes can exhibit localized overheating even when bulk-average temperatures appear moderate [194, 195].

Neglecting heat losses, the average heating rate can be estimated as:

$$\frac{\Delta \bar{T}}{\Delta t} = \frac{\bar{Q}_{MW}}{\rho C_p} \quad (3.9)$$

where ρ and C_p , are the material's density (kg/m^3) and specific heat capacity (J/kg.K), respectively. $\Delta \bar{T}$ is the average temperature rise (K), $\bar{Q}_{MW}$ is the average heat generation rate (W/m^3), and Δt denotes the exposure time. This expression provides a useful first-order comparison between materials but should be applied carefully for reactive systems, since ρ , C_p , ϵ'' , and even field distribution may change significantly as reactions proceed. These considerations motivate the need to evaluate dielectric response together with penetration depth and power absorption to rationalize heating uniformity, reaction acceleration, and process scale-up in microwave-assisted carbothermic reduction.

3.6.3 Microwave-assisted carbothermic reduction

Microwave-assisted carbothermic reduction has been widely investigated for the extraction of various metals from oxide-based feedstocks, as summarized in Table 3.5. These studies consistently demonstrate that microwave heating can dramatically accelerate carbothermic reactions, enabling high reduction efficiencies at atmospheric pressure and significantly shorter reaction times compared to conventional heating. The reported systems span a wide range of

oxides, including Fe-, Ni-, Zn-, Sb-, and Si-bearing materials, with reduction efficiencies frequently exceeding 90% within 10-60 min at temperatures between 750 °C and 1200 °C. This body of work clearly establishes microwave-assisted carbothermic reduction as an effective intensification strategy for pyrometallurgical processing.

The effectiveness of microwave-assisted carbothermic reduction arises primarily from the strong microwave absorption of carbonaceous materials, which occurs predominantly through electronic conduction losses and interfacial polarization rather than ionic mechanisms [196, 197]. Under microwave irradiation, carbon particles heat rapidly and selectively, whereas most metal oxides remain comparatively weak absorbers at the same frequency and temperature [198]. This contrast in dielectric response leads to localized interfacial heating at metal oxide-carbon contact points, where reduction reactions are initiated. As a result, the reaction zone can reach temperatures substantially higher than the measured bulk temperature, thereby accelerating reduction kinetics without raising the overall reactor temperature to the same extent as in conventional heating [199].

This interfacial heating mechanism can provide several advantages for magnesium production. First, the localized temperature rise can enhance MgO reduction rate and promote the rapid formation and volatilization of Mg vapor, which is essential for shifting the equilibrium of carbothermic reactions toward completion [200]. Second, because energy is applied directly at reactive interfaces rather than transferred from external furnace walls, microwave heating can reduce thermal lag and shorten the time required to reach reactive conditions [201]. Third, selective heating of carbon can mitigate extensive sintering or particle coarsening of the oxide matrix, thereby preserving porosity and gas permeability, which are critical for Mg vapor transport and removal from the reaction zone [202, 203].

Despite this growing literature, magnesium production by microwave-assisted carbothermic reduction remains strikingly underexplored. To date, only a single study, reported by Yoshikawa and Morita in 2003, has demonstrated the direct carbothermic reduction of MgO using microwave heating under atmospheric pressure [204]. In that work, MgO mixed with graphite was reduced at 1600 °C under microwave irradiation, achieving a maximum reduction efficiency of approximately 46% within 10 min. While this study was important in proving the feasibility of rapid atmospheric pressure carbothermic reduction of MgO, it left several fundamental questions unresolved.

First, the reaction environment in the Yoshikawa-Morita study was constrained by the isolation of the reaction zone using firebrick, which limited effective purging of gaseous products with argon. This restriction likely influenced the local partial pressures of magnesium vapor and carbon monoxide, both of which play critical roles in shifting the equilibrium of MgO reduction. Second, the study provided limited characterization of reaction residues and products, making it difficult to assess the extent of side reactions, sintering, or reoxidation. Third, the condensation behavior of magnesium vapor at atmospheric pressure, especially when temperature gradients exist between the reaction and collection zones, has not been thoroughly studied, even though it is a crucial bottleneck in Mg recovery outside vacuum systems.

In addition, the influence of microwave-specific phenomena was not conclusively resolved. The relative contributions of localized interfacial heating, bulk temperature gradients, and potential non-thermal microwave effects were not distinguished. The reported reduction efficiency may therefore reflect a complex combination of selective carbon heating, transient hotspot formation, and reactor-scale thermal non-uniformity rather than intrinsic reaction kinetics. Furthermore, the effect of the initial magnesium-bearing phase (e.g., MgO morphology, particle size, or degree of aggregation) on microwave coupling and reduction behavior was not examined, limiting the generalizability of the results.

In contrast to the scarcity of MgO-focused studies, microwave-assisted thermal reduction of magnesium-containing feedstocks using alternative reductants has received limited but notable attention. Recent work has demonstrated magnesium production from magnesite using aluminum and carbon mixture reductants under microwave irradiation, achieving moderate Mg yields at lower temperatures [205]. Other studies have explored vacuum microwave-assisted silicothermic reduction of calcined dolomite using ferrosilicon, reporting Mg recoveries up to 71% [206]. While these approaches confirm that microwave heating can enhance magnesium production, they do not address the central challenge of achieving high-yield carbothermic Mg production at atmospheric pressure, which remains the most economically and environmentally attractive route if successfully realized.

In total, the literature summarized in Table 3.5 highlights a clear imbalance. Microwave-assisted carbothermic reduction is well studied for many metal oxides, yet magnesium production, despite its strong thermodynamic dependence on temperature, vapor pressure, and gas-solid transport, has

received minimal systematic investigation. The unresolved issues identified in the Yoshikawa-Morita study, combined with the demonstrated success of microwave-assisted carbothermic reduction for other metals, underscore a critical knowledge gap. Addressing this gap requires a comprehensive investigation that integrates controlled microwave heating, rigorous temperature and gas management, detailed phase and microstructural characterization, and systematic evaluation of feedstock chemistry.

Consequently, the present dissertation focuses on developing and critically assessing microwave-assisted carbothermic reduction pathways for magnesium production from dolomitic limestone waste rock. By resolving the limitations of prior studies and balancing the selective and volumetric nature of microwave heating, this research aims to establish a robust foundation for rapid, high-yield magnesium production under atmospheric pressure.

Table 3.5 Representative studies on microwave-assisted carbothermic and thermal reduction of metal oxides.

Feed	Reductant	Microwave frequency (GHz)	Reaction temperature (°C)	Reaction Pressure (atm)	Reaction time (min)	Reduction efficiency (%)	Product	Ref.
Magnesium oxide	Graphite	2.45	1600	1	10	46	Mg	[204]
Laterite nickel	Anthracite coal	NA	1150	1	30	91.17 92.44	Fe Ni	[207]
Ilmenite	Graphite	2.45	850	1	20	93.21	Fe	[70]
Diatomaceous earth	Graphite	2.45	1680	1	20	NA	Si	[208]
Zinc ferrite	Graphite	2.45	850	1	20	98	Zn	[209]
Nickel(II) oxide	Graphite	2.45	900	1	12.5	86.7	Ni	[210]
Rice hull ash	Graphite	2.45	1564	1	15	NA	Si	[211]
Antimony(III) Oxide	Anthracite coal	2.45	758	1	56	92.19	Sb	[212]
Zinc-bearing dusts	Coke dry quenching	2.45	1150	0.001	20	99.68 94.64	Zn Fe	[213]
Hematite	Biochar	2.45	1000	1	30	93.32	Fe	[214]
Spent zinc-manganese batteries	Coke	2.45	1000	1	30	89.5	Zn	[215]
Stainless steel dust	Biochar	2.45	1200	1	30	91.03 87.04	Fe Cr	[216]
Magnesia	Aluminum and graphite	2.45	1050	1	17	44.37	Mg	[205]
Calcined dolomite	Ferrosilicon	2.45	1000	0.00002	80	71%	Mg	[206]

CHAPTER 4 ARTICLE 1 - UNVEILING THE ROLE OF CARBONATE IN DOLOMITIC LIMESTONE FOR EFFICIENT LEACHING OF MAGNESIUM FROM PHOSPHATE MINE WASTES

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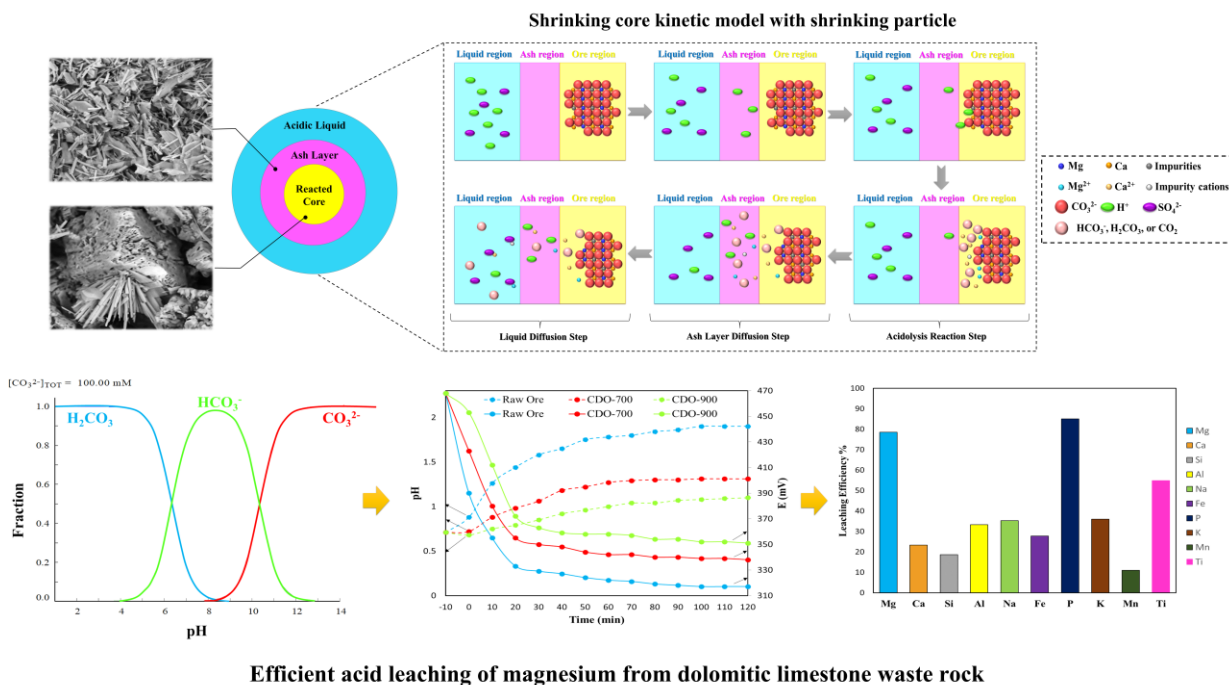
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4.1 Abstract

The recovery of magnesium as a critical metal from industrial wastes rather than traditional mining has attracted significant attention due to environmental concerns and mining limitations. In this research, we investigated the role of carbonate in acid leaching utilizing diluted sulfuric acid to efficiently extract Mg from dolomitic limestone, a phosphate mine waste rock. As the main objective, we elucidated how carbonate phase transformation influences impurities' co-leaching from thermodynamic and kinetic aspects. In this regard, the leaching behavior of dolomitic limestone was compared with calcined ore at 700 °C and 900 °C, where the CO₂ was liberated from MgCO₃ and CaCO₃, respectively. The CO₂ volatilization raised the hydrophilicity of the ore and increased the average surface area from 2 m²/g to 6 m²/g. During the leaching process, phase transformation impacted the lixiviant redox potential and caused a 35 mV decrease for dolomitic limestone leachate compared to calcined ore at 900 °C. The alteration of physicochemical properties of feed and lixiviant redox potential arising from the carbonate phase could inhibit the access of H⁺ to impurities, reducing the co-leaching of impurities from 87% to 36%. Adopting a solid-to-liquid ratio of 10 g/L in 0.5 M H₂SO₄ at 80°C was the optimum condition for 100% magnesium extraction and simultaneous crystallization of 75% calcium as needle-shaped CaSO₄·2H₂O. Based on the kinetic modeling, magnesium leaching obeyed the shrinking core model with shrinking particle size. The leaching rate was controlled by diffusion through the ash product layer, with an activation energy of 16 kJ/mol.

Keywords: Waste recovery; Magnesium extraction; Calcium crystallization; Thermodynamic; Kinetics

Graphical Abstract



Efficient acid leaching of magnesium from dolomitic limestone waste rock

4.2 Introduction

Over the past decade, there has been a growing utilization of critical metals and rare earth elements in renewable technologies aimed at mitigating greenhouse gas emissions and tackling global warming and climate change. Magnesium (Mg) is a strategic critical metal with a density (1.74 g/cm^3) of about three-fifths that of aluminum and one-fifth that of steel. This distinctive lightweight characteristic positions Mg as a suitable candidate for substitution with aluminum in the automotive industry and aerospace [217, 218]. Furthermore, Mg finds application in diverse sectors, including the electronics industry, battery technology, chemical processing, military equipment, and healthcare, owing to its exceptional features such as electrical conductivity, energy storage capacity, catalytic activity, machinability, thermal stability, corrosion resistance, and biocompatibility [17, 219]. Despite the escalating demand for Mg, the US Department of Energy (DOE) has categorized magnesium as one of the most critical metals from 2025 to 2035 based on its importance for energy applications and supply risk [220]. In addition, the available Mg mines encounter the rapid depletion of high-grade Mg minerals, resulting in the formation of low-grade Mg ores [221]. Therefore, discovering secondary resources to sustain Mg in the market chain

becomes crucial. In response to this challenge, closed-loop recycling of Mg derived from industrial or urban wastes, rather than the traditional linear extraction from mines, can be a promising approach.

The phosphate mine wastes are appropriate secondary resources for recycling critical metals. Diverse valuable minerals exist in phosphate mine wastes, such as quartz, montmorillonite, illite, palygorskite, dolomitic limestones, calcite, and residual fluorapatite [57, 222]. Among these minerals, dolomitic limestone possesses significant potential for contributing not only to the Mg but also to the calcium (Ca) market chain. Dolomitic limestone is a sedimentary waste rock primarily composed of calcium magnesium carbonate ($\text{MgCa}(\text{CO}_3)_2$), which is known as dolomite, with the addition of several impurities, including SiO_2 , Al_2O_3 , P_2O_5 , TiO_2 , Fe_2O_3 , MnO , K_2O , and Na_2O [57]. The extraction of one ton of phosphate rock in Morocco generates between 3 to 11 tons of waste rocks. Up to 16 wt.% of the extracted orebody contains dolomitic limestone waste rock [57-59]. Consequently, recycling dolomitic limestone instead of landfill disposal suggests a two-fold advantage by valorizing phosphate waste rock and mitigating the adverse environmental impacts. Furthermore, adopting phosphate waste for Mg production proves to be more economically viable and environmentally sustainable than directly mining primary Mg resources.

The recovery of Mg from secondary sources can be conducted typically through pyrometallurgy, biometallurgy, and hydrometallurgy processes. Among these methods, hydrometallurgy offers higher recovery efficiency than biometallurgy and lower energy consumption than pyrometallurgy [17, 223]. Hydrometallurgy consists of a hybrid process. In the first step, the metals in the solid feed are dissolved in an acidic lixiviant by utilizing either inorganic (e.g., H_2SO_4 , HCl , and HNO_3) or organic acids (e.g., oxalic acid, citric acid, ascorbic acid, and acetic acid) [224, 225]. Afterward, the dissolved metals are recovered from the liquid phase using different separation techniques such as precipitation, CO_2 mineralization, evaporation, electrowinning, electrodialysis, solvent extraction, ionic exchange, and membrane filtration [226, 227]. Leaching is crucial in the hydrometallurgical process since dissolving non-targeted metals can complicate the subsequent recovery step and reduce separation efficiency [228]. Comprehending the interaction between the materials and lixiviant is imperative for achieving optimal leaching efficiency and the selective extraction of target metals. Although many studies have investigated the dissolution of Mg from dolomitic ores, the majority have been allocated to natural dolomite with high Mg concentrations

(approximately 20-25 wt.%) and impurities less than 1 wt.% [229-233]. However, the dolomitic limestone sourced from Moroccan phosphate mine wastes has a low Mg concentration (10-16 wt.%) with impurities exceeding 10 wt.%, posing challenges for efficient Mg leaching. Focusing on the analogous dolomitic minerals with low Mg concentrations, two thermal solutions have been proposed to upgrade Mg concentration and increase its leaching efficiency. The first approach is the pre-calcination of dolomitic minerals at a temperature above 900 °C, inducing the phase transformation of $\text{MgCa}(\text{CO}_3)_2$ to $\text{MgO} \cdot \text{CaO}$. According to investigations of Schurecht [97], Fouda et al. [98], and Royani et al. [99], various inorganic acids, such as HNO_3 and HCl , exhibited the capability to leach more than 90 % of Mg from dolomitic minerals calcined at 900 °C. However, the main issue associated with this approach is the simultaneous dissolution of Ca at high concentration. Due to the chemical resemblance of Ca to Mg, their separation after the leaching process is difficult. To overcome this challenge, pre-calcination at temperatures between 750 °C to 800 °C has been proposed as the second approach that causes CO_2 liberation from magnesium carbonate, creating $\text{MgO} \cdot \text{CaCO}_3$. Studies of Amer [100] and Caceres and Attiogbe [101] indicated that CaCO_3 has lower solubility than MgO in aqueous solution. Therefore, hydration and carbonation of $\text{MgO} \cdot \text{CaCO}_3$ in an autoclave at 140-200 °C under CO_2 flow with pressure in the 5-10 atm range can assist in Mg leaching by reducing Ca dissolution. In addition, Huang et al. [23] revealed the leaching of $\text{MgO} \cdot \text{CaCO}_3$ via ammonium sulfate $((\text{NH}_4)_2\text{SO}_4)$ enables Mg dissolution while retaining Ca in the form of solid gypsum.

Despite the advantages of the mentioned approaches to enhance Mg leaching, no studies have investigated the effect of phase transformation on the co-leaching of impurities. Particularly, in the case of dolomitic limestone wastes, the co-leaching of impurities is a bottleneck because around 10-11 wt.% of the ore is composed of SiO_2 , Al_2O_3 , P_2O_5 , TiO_2 , Fe_2O_3 , MnO , K_2O and Na_2O . Elevated temperatures during thermal treatment may weaken bonds of impurities, thereby exacerbating the risk of co-leaching [234]. Moreover, pre-calcination at high temperatures is energy-intensive, increasing operating costs and heightening greenhouse gas emissions.

According to recent research, carbonation of lixiviants with CO_2 can assist in recovering transition and rare earth metals from acidic liquor [235-237]. Evaluation of the literature leaves a clue that the carbonate phase in dolomitic limestone waste can be a means to suppress the co-leaching of

impurities and increase the efficient leaching of Mg from dolomitic limestone waste. Nevertheless, no study has investigated this main objective yet.

Therefore, this study aims to comprehensively investigate the effect of the carbonate phase in dolomitic limestone waste for efficient leaching of Mg. To reach this main objective, three specific objectives were engaged as follows. For the first specific objective, CO_2 liberation from MgCO_3 and CaCO_3 in dolomitic limestone waste was studied through the thermodynamic evaluation with Facstage and thermogravimetric analysis. In the second objective, Mg was leached from dolomitic limestone waste and from calcined ores using diluted sulfuric acid (H_2SO_4). Regarding this specific objective, the impact of the carbonate phase on the efficient leaching of Mg was evaluated based on the acidolysis reactions derived from thermodynamic calculations, alterations of pH and potential of lixiviant during the leaching process, and changes of morphology, textural properties, and crystal phase of dolomitic limestone waste before and after of calcination. It is important to note that employing diluted H_2SO_4 can be considered a model of acid waste reusability generated during the wet processing of phosphoric acid, which can cause environmental benefits. The third specific objective was allocated to the kinetic study of Mg leaching from dolomitic limestone waste. This specific objective assisted in optimizing the leaching process by elucidating the leaching reaction rate, mechanism pathway, rate-controlling step, and activation energy.

4.3 Experimental

4.3.1 Materials and reagents

Dolomitic limestone waste, sourced from OCP's phosphate mine wastes in Morocco, was characterized via the Quantitative Evaluation of Materials by Scanning Electron Microscopy (QEMSCAN; 650F, USA) to identify the modal mineralogy and quantitative distribution. The results depicted in Figure 4.1 reveal the presence of more than eight distinct minerals in the dolomitic limestone waste rock. The main minerals of which the mass distribution exceeded 4 wt.% include dolomite (about 78 wt.%), calcium silicate (about 14 wt.%), and quartz (about 4 wt.%). Approximately 6 wt.% of the dolomite mineral was completely liberated, while 92 wt.% remained associated with silicates. Further chemical composition analysis was conducted using X-ray fluorescence spectrometry (XRF; Malvern Panalytical-Epsilon 3XLE, UK). As presented in Table 4.1, the dolomitic limestone waste primarily comprises CaO (35 wt.%), MgO (16 wt.%), SiO_2 (8

wt.%), P_2O_5 (1 wt.%), and Al_2O_3 (wt.1%). In addition, minor constituents, including Fe_2O_3 , TiO_2 , MnO , Na_2O , and K_2O , account for 0.51 wt.% of the waste rock.

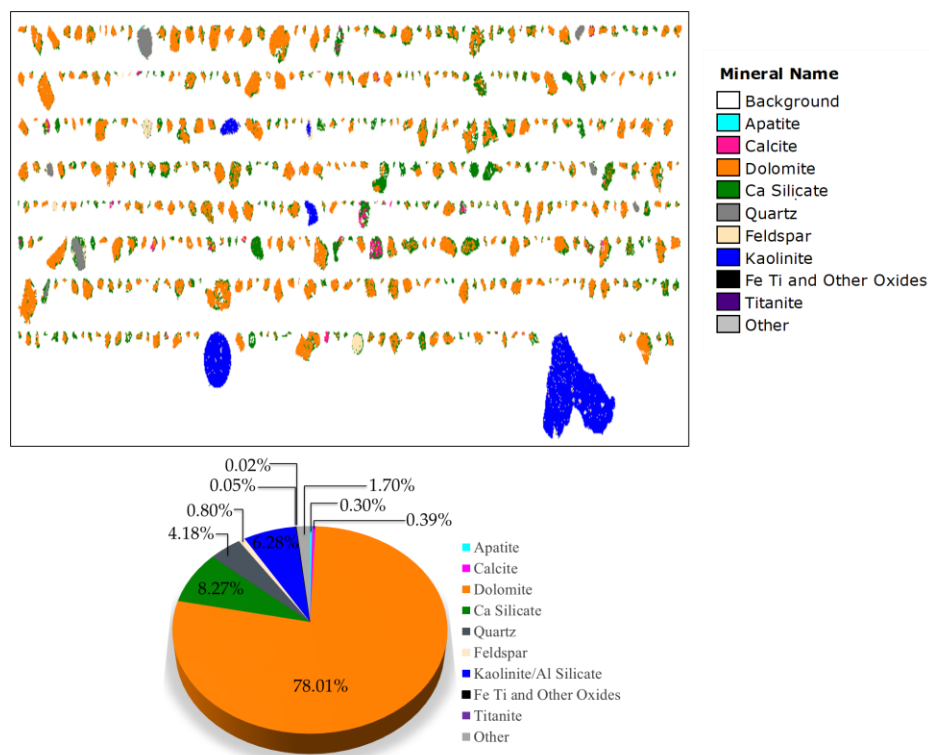


Figure 4.1 Mineralogy of dolomitic limestone waste rock.

Table 4.1 The composition of dolomitic limestone characterized by XRF analysis.

Component	MgO	CaO	SiO ₂	P ₂ O ₅	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO	Na ₂ O	K ₂ O	LOI
Mass (wt.%)	16	35	8	1	1	0.1	0.1	0.1	0.2	0.01	38-47

The received ore was ground and sieved to uniform particle sizes of 45 μm , 63 μm , 90 μm , and 150 μm with ASTM mesh numbers of 325, 230, 170, and 100. To assess the carbonate phase impact on efficient Mg leaching, the 45 μm ore was calcined to 700 °C and 900 °C in a muffle furnace at a rate of 5 °C/min, aligning with thermodynamic evaluations and thermogravimetric analyses. In the following sections, the calcined ores at 700 °C and 900 °C are denoted as CDO-700 and CDO-900.

Elemental compositions of dolomitic limestone, CDO-700, and CDO-900 were determined via inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent 5110, USA). A

certain weight of samples was digested in aqua regia at 100 °C for 24 h in a block digestion system (DigiPREP LS; SCP SCIENCE, Canada). As illustrated in Table 4.2, dolomitic limestone waste contains approximately 10 wt.% Mg, 20 wt.% Ca, 3 wt.% Si, 0.3 wt.% Al, 0.2 wt.% P, and 0.3 wt.% other impurities (Fe, Ti, Mn, Na, and K). Calcination at 700 °C and 900 °C increased Mg and Ca concentrations from 10 wt.% to 24 wt.% and from 20 wt.% to 36 wt.%, respectively. All chemicals used were analytical grade, and solutions were prepared with distilled water. Sulfuric acid (H₂SO₄, purity > 95 wt.%) for leaching was obtained from MilliporeSigma Canada.

Table 4.2 The elemental composition of dolomitic limestone, CDO-700, and CDO-900 measured by ICP-OES analysis.

Sample	Mass percentage (wt.%)									
	Mg	Ca	Si	Al	Na	Fe	P	K	Mn	Ti
Dolomitic limestone	9.65	20.01	2.80	0.26	0.07	0.03	0.22	0.04	0.07	0.06
CDO-700	16.14	29.70	2.93	0.27	0.06	0.13	0.08	0.05	0.01	0.01
CDO-900	24.02	36.62	3.61	0.39	0.04	0.19	0.12	0.05	0.02	0.01

4.3.2 Procedure of acid leaching by diluted H₂SO₄ and kinetic study

Leaching experiments were conducted in a 250 mL three-neck round-bottom flask with an electromagnetic stir mantle (Glas-Col, Canada). Two necks housed a thermocouple type J and a pH meter probe (Thermo Scientific™ VSTAR13, Canada), with the central neck connected to an Allihn condenser to maintain a constant solid-to-liquid ratio (S/L). The solution temperature was adjusted for each experiment before adding the weighed ore and stirring at 500 rpm with a magnetic stirrer. To assess the carbonate phase effect, dolomitic limestone, CDO-700, and CDO-900 were introduced into a 0.3 M H₂SO₄ solution at 80 °C with an S/L ratio of 10 g/L. It is worth noting that the acid concentration and S/L ratio for this assessment were determined through thermodynamic simulations and mass balance calculations, ensuring the leaching of over 80% of magnesium from dolomitic limestone waste. Additionally, the experiments were conducted at the maximum feasible temperature to expedite the acidolysis reactions. After 120 min at constant temperature and

agitation, the solid and liquid were separated via vacuum filtration. The solution was filtered with 0.45 μm nylon syringe filters (Fisher Scientific, Canada) and diluted with 5 wt.% HNO_3 solution to prevent supersaturation for ICP-OES analysis. Solids were rinsed and dried at 80 $^\circ\text{C}$ for 15 h. For kinetic studies, dolomitic limestone was leached with diluted H_2SO_4 for varying times from 1 min to 120 min. Reactions were stopped during specific intervals, and the liquid and solid were separated based on the abovementioned procedure. Liquid samples were analyzed via ICP-OES to track metal concentration changes. The study investigated contributing parameters, including temperature (20 $^\circ\text{C}$ to 80 $^\circ\text{C}$), acid concentration (0.2 M to 0.5 M), S/L ratio (10 g/L to 80 g/L), and initial ore particle size (45 μm to 150 μm). The leaching efficiency (E_i) of metals was calculated using Equation (4.1):

$$E_i(\%) = \frac{m_{i,\text{leachate}}}{m_{i,\text{ore}}} \times 100 = \frac{C_{i,\text{leach}} V_{\text{leach}}}{f_{i,\text{ore}} m_{\text{ore}}} \times 100 \quad (4.1)$$

where $m_{i,\text{leachate}}$ and $m_{i,\text{ore}}$ represent the mass of metal i in leachate (mg) and in initial ore (mg), respectively. $C_{i,\text{leach}}$ and V_{leach} are ascribed to the concentration of metal i in leachate measured by ICP-OES (mg/L) and the volume of leachate solution (L). In addition, m_{ore} and $f_{i,\text{ore}}$ are signs of the total mass of initial ore (mg) and mass fraction of metal i in initial ore. The leaching selectivity of magnesium was calculated based on Equation (4.2) [238]:

$$S_{\text{Leaching}}(\%) = \frac{\frac{E_{\text{Mg}} m_{\text{Mg,ore}}}{MW_{\text{Mg}}}}{\sum_i \frac{E_i m_{i,\text{ore}}}{MW_i}} \times 100 \quad (4.2)$$

where $m_{i,\text{ore}}$, and MW_i are the mass of metal i in the initial ore (mg) and the molecular weight of metal i (mg/mol). E_{Mg} , $m_{\text{Mg,ore}}$, and MW_{Mg} also represent the leaching efficiency of Mg (%), the mass of Mg in the initial ore (mg), and the molecular weight of Mg (mg/mol).

All the leaching experiments were repeated three times, and the results presented in the following sections are the average of these replications.

4.3.3 Thermodynamic simulation

Thermodynamic simulations were conducted with FactSage 8.3 software. The predominant regions for the Mg-Ca-O-C system at atmospheric pressure and varied temperatures were simulated by the Predom toolbox via classical phase diagrams. Changes in enthalpy and Gibbs free energy during acidolysis were calculated using the Reaction Toolbox. Mineral data were extracted from the FToxid database, while thermodynamic data for ions and pure substances in solution were elicited from the FThelg and FactPS databases, respectively. Species distribution diagrams for the H-C-O phase as a function of pH were generated using Medusa-Hydra software.

4.3.4 Characterization and analytical techniques

The mineralogy of dolomitic limestone waste rock was identified by the Quantitative Evaluation of Materials by Scanning Electron Microscopy (QEMSCAN; 650F, USA) equipped with a TESCAN Integrated Mineral Analyzer (TIMA, Tescan Vega TC x64, USA). The elemental analysis of dolomitic limestone waste was determined by X-ray fluorescence (XRF; Malvern Panalytical-Epsilon 3XLE, United Kingdom). The crystal structures of ores and solid residual were characterized by X-ray diffraction measurement using Cu K α radiation (XRD; Bruker D8 ADVANCE; USA). Morphological characteristics were analyzed using scanning electron microscopy (SEM, Hitachi TM3030 Plus, Japan) coupled with energy-dispersive X-ray spectroscopy (EDS) for surface elemental composition and distribution. Thermolysis behavior was monitored by thermogravimetric analysis (TGA; TA Instruments-550, USA) under N₂ and CO₂ atmospheres (heating rate: 5 °C/min). Specific surface area, pore volume, and pore size were assessed via N₂ adsorption-desorption isotherms using Quantachrome Autosorb-1 (Quantachrome Instruments, USA), applying Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. Hydrophilicity was analyzed through optical contact angle measurements (CA; DataPhysics Instruments-OCA25, Germany). pH and redox potential (E) changes during acid leaching were recorded using a pH meter (Thermo Scientific™ VSTAR13, Canada). Metal concentration changes in the liquid phase were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent 5110, USA).

4.4 Results and discussion

4.4.1 Thermal pretreatment for phase transformation

Pure dolomitic limestone comprises Mg and Ca atoms arranged in layers separated by carbonate groups. High-temperature calcination liberates CO_2 from dolomitic limestone hexagonal unit cells, forming metal oxides, commonly known as dolime (MgO-CaO). Thermodynamic simulation and thermogravimetric analysis were conducted to determine the conditions for these phase transformations. Figure 4.2(a) illustrates the predominance area for the Mg-Ca-O-C system at atmospheric pressure and temperatures ranging from 630 °C to 930 °C. Dolomite ($\text{MgCa}(\text{CO}_3)_2$), calcite (CaCO_3), magnesia (MgO), quicklime (CaO), and calcium dioxide (CaO_2) are the major phases of Mg and Ca under varying conditions. At high CO_2 partial pressure, MgCO_3 and CaCO_3 are dominant phases. Decreasing CO_2 partial pressure at constant O_2 partial pressure leads to MgCO_3 conversion to MgO , while calcium remains in its carbonate phase. Further reduction in CO_2 and O_2 partial pressures results in complete CO_2 liberation from dolomite, yielding dolime. Notably, CaO_2 and MgO are obtained when O_2 partial pressure is maintained above 100 atm, while CO_2 partial pressure is reduced below 1 atm, corresponding to calcination temperature.

The achieved thermodynamic simulation concurs with the common scenario of two-step dolomite calcination reported by McIntosh et al. [239]. According to this scenario, dry thermal calcination of dolomite generates active dolomite ($\text{MgCaCO}_3 \cdot \text{CO}_3^*$). This unstable phase subsequently converts to a metastable precursor ($\text{CaCO}_3 \cdot \text{Mg(O)} \cdot \text{CO}_2$), where CO_2 is liberated from defects on the dolomite surface and Mg^{2+} cations occupy the leaving O^{2-} ions. The metastable precursor is unstable at high temperatures and thus is converted to MgO-CaCO_3 immediately. In the second step, increasing temperatures induce instability in the calcite structure within the MgO-CaCO_3 composite, resulting in the formation of MgO-CaO under elevated thermal conditions.

According to Figure 4.2(a), temperature significantly affects the predominance phase areas. With increasing temperature from 630 °C to 930 °C, the predominance areas of dolomitic limestone and calcite decrease, while those of MgO , CaO , and CaO_2 increase. Furthermore, the calcination temperature of dolomitic limestone required for producing MgO-CaO rises with increasing CO_2 partial pressure. These findings indicate the tendency of Mg and Ca to exist in oxide forms at higher temperatures. To estimate the temperature range for the conversion of dolomitic limestone to MgO-

CaCO_3 and MgO-CaO , changes in Gibbs free energy and enthalpy of reactions were calculated as a function of temperature under atmospheric pressure using the Reaction toolbox of FactSage. Figure 4.2(b) illustrates the changes in Gibbs free energy and enthalpy for generating MgO-CaCO_3 and MgO-CaO from dolomitic limestone. Positive enthalpy values indicate the endothermic nature of both calcination stages. Below 480 °C, no thermal decomposition occurs, as indicated by the positive ΔG of reactions. However, raising the temperature from 480 °C to 750 °C results in a negative ΔG for the first stage of thermal decomposition while remaining positive for the second stage. Consequently, the formation of the MgO-CaCO_3 phase is feasible within the temperature range of 480 °C to 750 °C under atmospheric pressure. Beyond 750 °C, both stages exhibit negative ΔG , implying the complete conversion of dolomitic limestone to MgO-CaO under atmospheric pressure.

Based on the preceding thermodynamic calculation, dolomitic limestone waste was calcined at 700 °C and 900 °C to yield MgO-CaCO_3 and MgO-CaO , respectively. CO_2 mass balance was assessed via TGA analysis. Figures 4.2(c) to 4.2(e) depict the TGA curves of dolomitic limestone waste, CDO-700, and CDO-900. All samples exhibited negligible weight loss of approximately 1% below 300 °C, attributed to the decomposition of adsorbed water molecules on the ores' surfaces. TGA of dolomitic limestone under N_2 (Figure 4.2(c)) showed a 47% weight loss starting at 480 °C and ending at 800 °C. This substantial weight loss corresponds to CO_2 liberation from MgCO_3 and CaCO_3 in the dolomite structure, aligning with the theoretical mass balance (47.8%) and LOI mass percentage estimated from XRF results (47 wt.%).

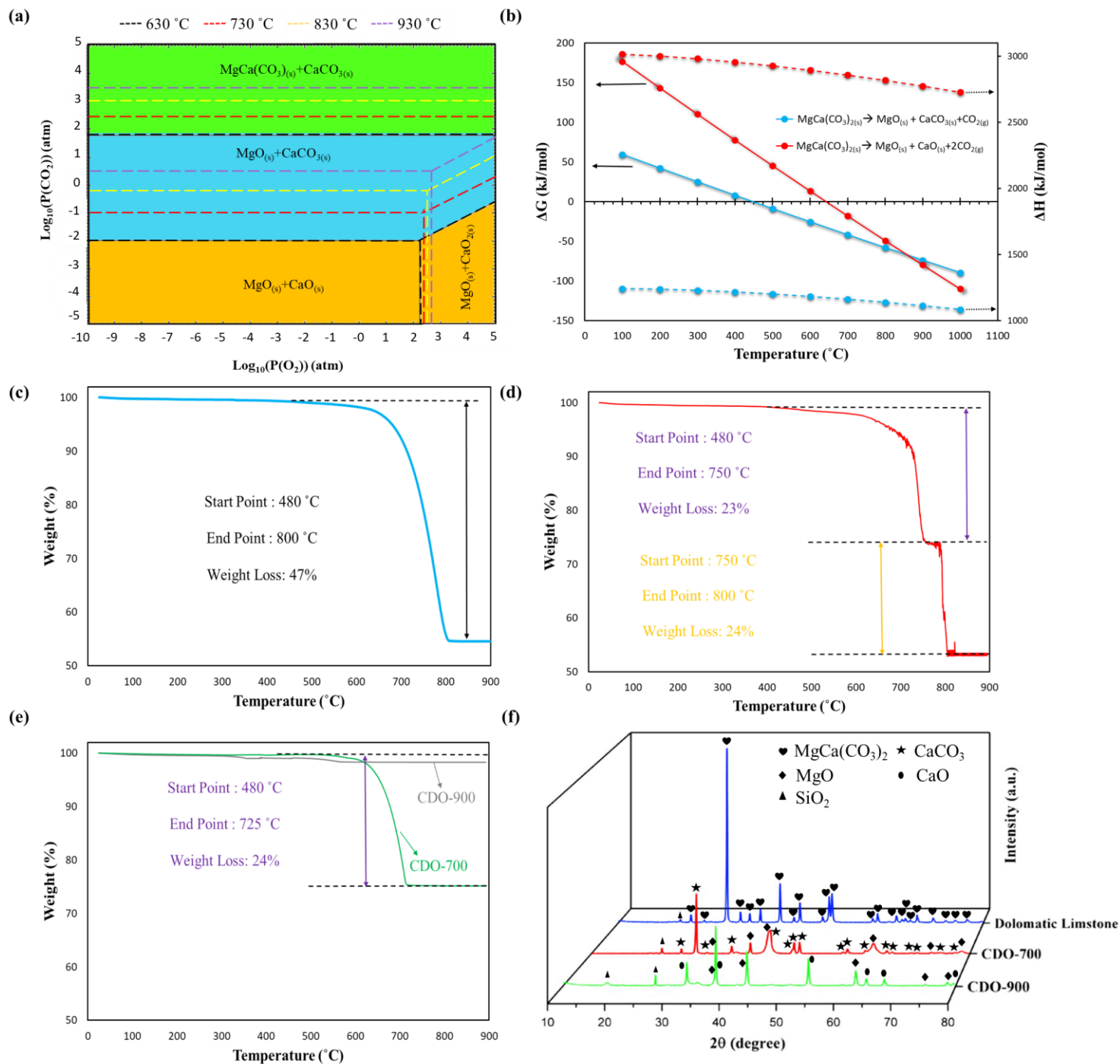


Figure 4.2 (a) Predominance area diagrams for the system of Mg-Ca-C-O at different temperatures and isobar condition; (b) changes of Gibbs free energy and enthalpy versus time during calcination of dolomitic limestone; (c) TGA of dolomitic limestone under N_2 atmosphere; (d) TGA of dolomitic limestone under CO_2 atmosphere; (e) TGA of CDO-700 and CDO-900 under N_2 atmosphere; (f) XRD patterns of dolomitic limestone, CDO-700, and CDO-900.

In contrast to the thermodynamic calculation, the TGA plot of dolomitic limestone under N_2 revealed a unified weight loss, suggesting a single-stage dolomitic limestone decomposition process. This discrepancy arises because the $MgCO_3$ decomposition step overlaps with the $CaCO_3$ decomposition step during TGA measurement under the N_2 atmosphere [24]. Applying CO_2 as the purging gas during TGA measurement can help distinguish between the two-step dolomitic limestone calcination processes [239, 240]. As depicted in Figure 4.2(d), two-step CO_2 liberation was observed during dolomitic limestone calcination from ambient to 900 °C under a CO_2 atmosphere. The 23% mass loss, occurring from 480 °C to 750 °C, is attributed to CO_2 volatilization from $MgCO_3$ in dolomitic limestone waste. Subsequently, a 24% mass loss was observed until 800 °C, corresponding to CO_2 liberation from $CaCO_3$ in dolomitic limestone. Based on these findings, 700 °C and 900 °C were selected for dolomitic limestone calcination to produce MgO - $CaCO_3$ and MgO - CaO minerals. Figure 4.2(e) illustrates the TGA of CDO-700 and CDO-900. Considering the respective graphs, a 23.5% weight loss was observed for CDO-700 from 570 °C to 725 °C, consistent with the theoretical mass percent of CO_2 in $CaCO_3$. Therefore, dolomitic limestone calcination at 700 °C resulted in the formation of MgO - $CaCO_3$. Additionally, negligible weight loss was observed below 400 °C for CDO-900 due to moisture evaporation, indicating complete conversion of dolomitic limestone to MgO - CaO after calcination at 900 °C.

Figure 4.2(f) exhibits the XRD patterns of dolomitic limestone waste, CDO-700, and CDO-900. The diffraction peaks at 2θ of 24.1°, 30.9°, 33.5°, 35.3°, 37.4°, 41.1°, 43.8°, 45°, 49.3°, 50.6°, 51.1°, 51.3°, 58.9°, 59.8°, 62°, 63.4°, 64.4°, 65.1°, 66.1°, 67.4°, 70.5°, 72.9°, 74.7°, 77° and 79.7°, which were equivalent with Miller index of (012), (104), (006), (015), (110), (113), (021), (202), (024), (018), (116), (009), (211), (122), (10.10), (214), (208), (119), (125), (300), (00.12), (217), (02.10), (128) and (220), demonstrated the rhombohedral structure of dolomitic limestone (JCPD card No. 00-011-0078). Regarding the XRD pattern of CDO-700, the diffraction peaks of dolomitic limestone were considerably decreased by calcination at 700 °C, while diffraction peaks of MgO and $CaCO_3$ appeared simultaneously. The sharp peaks at 2θ of 29.4°, 31.4°, 39.4°, 43.2°, and 47.1° with the Miller index of (104), (006), (113), (202), and (018) were attributed to the rhombohedral crystal structure of $CaCO_3$ with $R\bar{3}c$ space group (JCPD card No. 01-072-1214). In addition, the dominant peak at 2θ of 42.9°, 62.3°, 74.6°, and 78.6°, corresponding to the Miller index of (200), (220), (311), and (222), indicated the formation of the cubic crystal structure of MgO with $Fm\bar{3}m$ space group (JCPD card No. 01-071-1176). According to the XRD pattern of CDO-900, CO_2 was

completely liberated from dolomitic limestone, creating MgO and CaO. Herein, the diffraction peaks at 32.2° , 37.3° , 53.8° , 64.1° , 67.3° , and 79.6° with Miller index of (111), (200), (220), (311), (222), and (400) were ascribed to the cubic structure of CaO with $Fm\bar{3}m$ space group (JCPD card No. 01-080-7710).

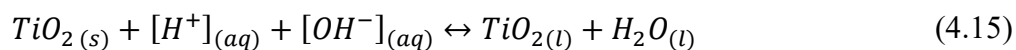
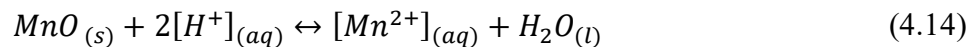
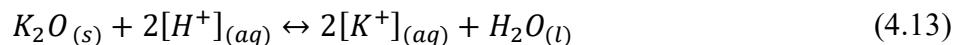
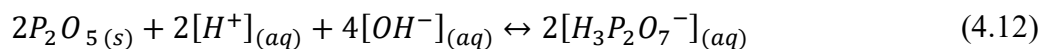
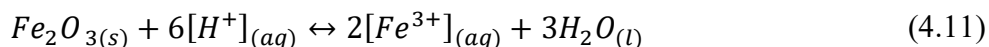
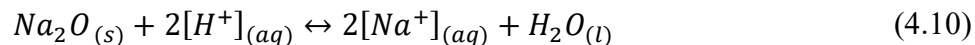
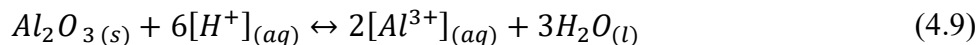
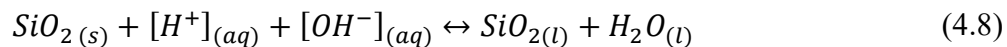
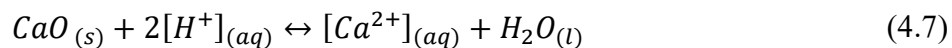
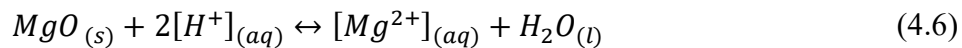
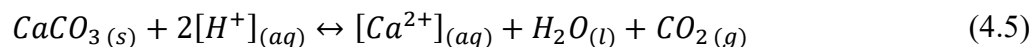
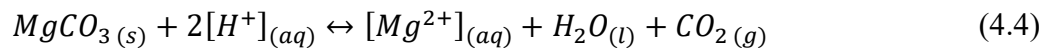
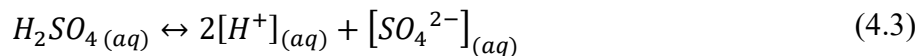
In light of thermodynamic, thermogravimetric, and crystallography evaluations, it is evident that the calcination of dolomitic limestone follows a two-step CO_2 liberation. The formation of MgO- CaCO_3 can be achieved at 480°C to 750°C , while MgO-CaO is produced at temperatures above 750°C .

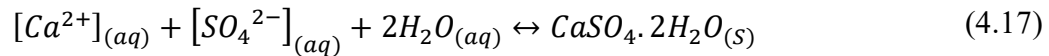
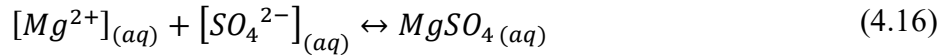
4.4.2 Inorganic acid leaching

The effect of the carbonate phase on efficient Mg leaching was studied through acid leaching of dolomitic limestone, CDO-700, and CDO-900 in a 0.3 M H_2SO_4 solution at 80°C for 2 h. Figures 4.3(a) to 4.3(c) illustrate the leaching efficiency of elements in dolomitic limestone waste and calcined ores. According to this figure, CO_2 liberation notably influenced metal dissolution. In pure dolomitic limestone, 79% of Mg, 85% of P, and 55% of Ti were leached by diluted H_2SO_4 , while the leaching efficiency for other metals remained below 36%. In contrast, CO_2 volatilization from MgCO_3 at 700°C (i.e., CDO-700) aided metals digestion in inorganic acid, resulting in a leaching efficiency exceeding 70% for all metals except calcium (26%). A similar trend was observed for CDO-900, where complete decarbonization at 900°C enhanced the leaching efficiency of Mg, Si, Al, Na, Fe, P, K, Mn, and Ti to above 87%. The leaching efficiency of Ca also increased from 23% to 32% due to the phase transformation of $\text{MgCa}(\text{CO}_3)_2$ to MgO-CaO. Figure 4.3(d) indicates the Mg leaching selectivity from dolomitic limestone, CDO-700, and CDO-900. As shown in this figure, the CO_2 liberation from MgCO_3 decreased the Mg leaching selectivity from 82% to 67%. Complete CO_2 liberation from MgCO_3 and CaCO_3 led to a decline in Mg leaching selectivity by up to 59%. The decrease in Mg leaching selectivity is attributed to the increase in co-leaching of other metals as a consequence of CO_2 liberation.

During the acid leaching, chemical bond disruption is accompanied by various redox reactions. To gain deeper insight into the effect of carbonate phase on efficient Mg leaching, changes in Gibbs free energy and enthalpy for acidolysis of dolomitic limestone and calcined dolomitic limestones were calculated using the FactSage Reaction toolbox. It is important to note that FactSage

databases do not include a cationic phase for Ti, Si, and P. Therefore, $\text{SiO}_{2(l)}$, $\text{H}_3\text{P}_2\text{O}_7^-$, and $\text{TiO}_{2(l)}$ were adopted due to their similar oxidation states. Reactions (4.3) to (4.17) represent possible reactions for inorganic acidolysis of metals present in dolomitic limestone and calcined ores.





In the initial stage of the leaching process, H_2SO_4 ionizes into H^+ and SO_4^{2-} through a reaction with water molecules (Reaction (4.3)). The dissociation constant (K_a) for this reaction is approximately 1.2×10^4 , indicating the acidic strength of H_2SO_4 [56]. Subsequently, H^+ ions attack the metal compounds' frameworks, releasing metal cations through redox reactions (Reactions (4.4) to (4.15)). According to Figures 4.3(e) and 4.3(f), the enthalpy and Gibbs free energy changes for all these reactions are negative. Negative ΔH indicates exothermic acidolysis of metal oxides and carbonates in an H_2SO_4 solution. Thus, more energy is released during metal cation extraction than is needed to break bonds in dolomitic limestone waste and calcined ores. Negative ΔG also signifies the spontaneous digestion of dolomitic limestone waste and calcined ores in H_2SO_4 solution at temperatures ranging from 20 °C to 100 °C. Comparing enthalpy changes, ΔH of MgO (-147 kJ/mol) and CaO (-192 kJ/mol) acidolysis at 80 °C were 5 and 12 times more negative than for $MgCO_3$ (-30 kJ/mol) and $CaCO_3$ (-15 kJ/mol) acidolysis. This discrepancy may arise from the diverse bond energies of reactants and products in the acid-leaching process. In metal oxides' structure, metal cations have ionic bonds with oxygen [241]. When MgO and/or CaO encounter an acidic solution, these ionic bonds break, generating Mg^{2+} and Ca^{2+} cations. These cations are then surrounded by multiple water molecules, forming ion-dipole interactions [242]. As the interactions after metal dissolution are stronger and more stable than those of solid MgO , CaO , and water, enthalpy changes yield negative values. For metal carbonates, metal cations are attracted to the delocalized electrons in the carbonate ion, forming an ionic bond [243]. Typically, metal carbonates are insoluble in pure water. However, when $MgCO_3$ and/or $CaCO_3$ encounter diluted H_2SO_4 , hydronium ions from the acid attack the metal carbonates, yielding metal cations and CO_3^{2-} anions [244]. Multiple water molecules separate the Mg^{2+} and Ca^{2+} cations by forming ion-dipole interactions, while CO_3^{2-} anions protonate with hydronium ions, creating HCO_3^- a weak acid. As the interaction after metal carbonate leaching is less stable and less strong than those after metal oxides, ΔH of $MgCO_3$ and $CaCO_3$ leaching is less negative than MgO and CaO leaching. Similar to enthalpy changes, ΔG of MgO (-118 kJ/mol) and CaO (-186 kJ/mol) were more negative compared to $MgCO_3$ (-63 kJ/mol) and $CaCO_3$ (-65 kJ/mol) at 80 °C. These thermodynamic

calculations, consistent with experimental results (Figures 4.3(a) to 4.3(c)), illustrate that metal oxides are more soluble than metal carbonates and are more prone to participating in acidolysis reactions. Figure 4.3(e) shows that released Mg^{2+} and Ca^{2+} cations can react with SO_4^{2-} generated from diluted H_2SO_4 to form MgSO_4 and CaSO_4 (Reactions (4.16) and (4.17)). Although MgSO_4 remains soluble, CaSO_4 is insoluble and can precipitate as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

Figure 4.3(g) and Table 4.3 present the crystal phase and chemical assays of residuals collected after leaching dolomitic limestone, CDO-700, and CDO-900. According to Figure 4.3(g), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is the predominant crystal phase in the residue obtained after the leaching process. As shown in Table 4.3, the primary metals present in the leaching residue of dolomitic limestone are Ca (82 wt%), Mg (13 wt%), Si (3 wt%), Al (1 wt%), and Fe (1 wt%). Following complete CO_2 liberation at 900 °C, the mass percentage of Ca in the leaching residue increased from 82 wt% to 93 wt% due to the enhanced digestion of other metals.

Despite MgCO_3 and CaCO_3 exhibiting lower leaching efficiency compared to MgO and CaO , carbonates phase notably suppressed the co-leaching of other impurities in dolomitic limestone, particularly Si and Al as major impurities. Three main reasons can explain this phenomenon. Firstly, CO_3^{2-} anions released during the acid leaching of metal carbonates affect the concentration of H^+ within the aqueous medium. To assess this effect, changes in pH and redox potential (E) during the leaching of dolomitic limestone and calcined ores were recorded over the acidolysis process time.

Table 4.3 The elemental compositions of the residuals obtained from the leaching of dolomitic limestone, CDO-700, and CDO-900, were measured using ICP-OES analysis.

Sample	Mass percentage (wt.%)									
	Mg	Ca	Si	Al	Na	Fe	P	K	Mn	Ti
Dolomitic limestone	13.05	81.67	3.00	1.00	0.13	1.00	0.04	0.11	0.04	0.01
CDO-700	9.14	89.65	0.71	0.12	0.07	0.27	0.02	0.01	0.01	0.00
CDO-900	6.27	93.00	0.46	0.06	0.02	0.19	0.01	0.00	0.01	0.00

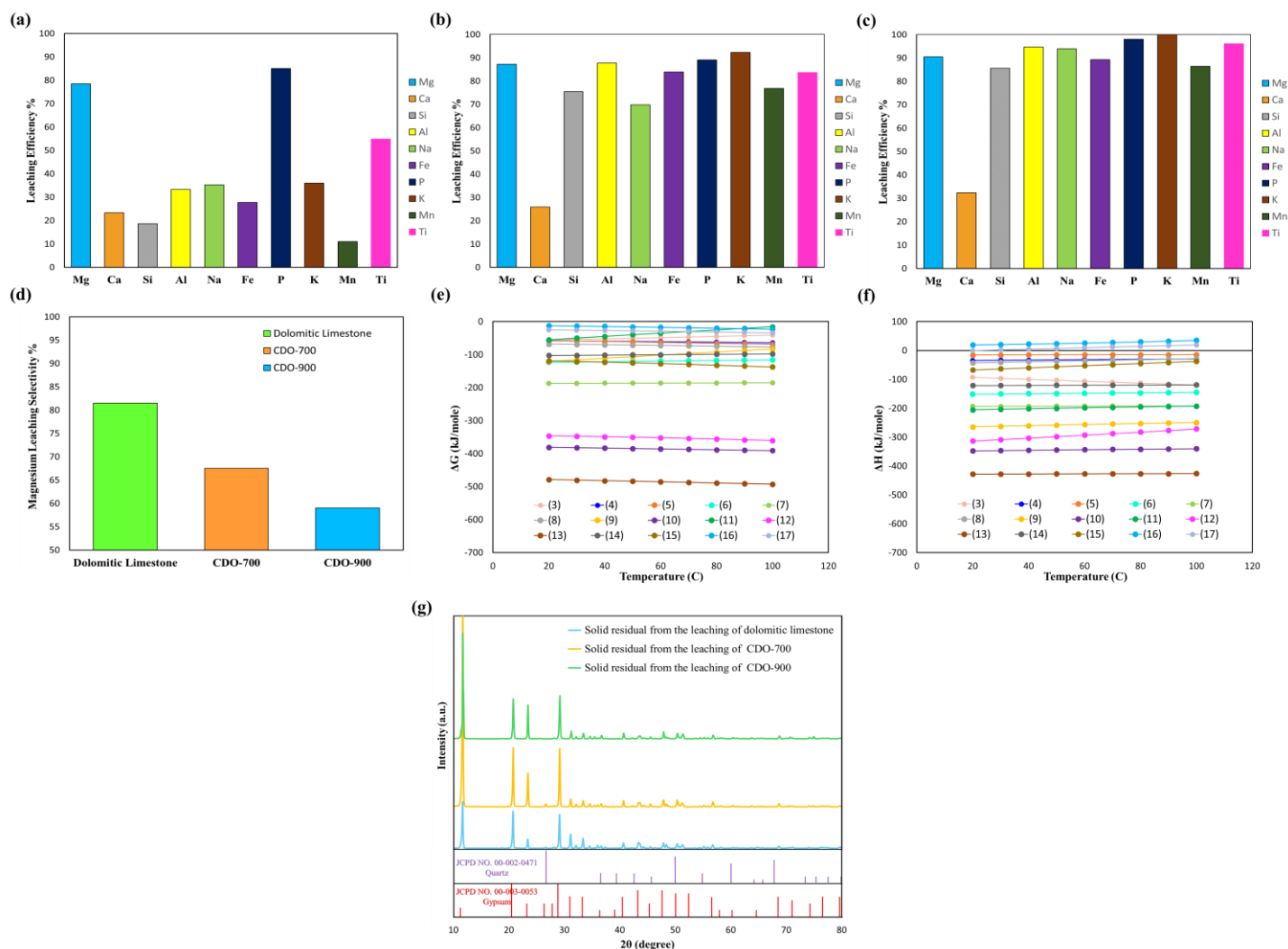


Figure 4.3 Acid leaching by 0.3 M H_2SO_4 at 80 °C with S/L of 10 g/L (a) dolomitic limestone, (b) CDO-700, and (c) CDO-900; (d) Mg leaching selectivity; (e) variation of Gibbs free energy as a function of temperature for Reactions (4.3) to (4.17); (f) variation of enthalpy as a function of temperature for Reactions (4.3) to (4.17); and (g) crystal phases of residuals obtained from the leaching of dolomitic limestone, CDO-700, and CDO-900.

As shown in Figure 4.4(a), the pH of the medium increased over time and stabilized above 20 min, while the redox potential decreased, leveling off after 20 min. The rise in pH and decrease in E result from H^+ consumption and the generation of metal cations. According to Figure 4.4(a), the final pH of the leachate after the dissolution of dolomitic limestone waste reached approximately 2, less acidic than after leaching of CDO-700 (pH=1.3) and CDO-900 (pH = 1). Moreover, a more significant decline in the E of the medium occurred after the leaching of dolomitic limestone waste (from 468 mV to 317 mV) compared to CDO-700 (from 468 mV to 340 mV) and CDO-900 (from 468 mV to 352 mV). These results indicate that the leaching of metal carbonates consumes more

H^+ than metal oxides. As shown in Figure 4.4(b), CO_3^{2-} consumes H^+ and converts to HCO_3^- and H_2CO_3 at pH below 12. Eventually, H_2CO_3 decomposes into water and CO_2 gas in the aqueous medium. Therefore, during the leaching of dolomitic limestone, a major concentration of H^+ is allocated to the dissolution of metal carbonates, leaving a lower concentration of H^+ available for extracting impurities compared to CDO-700 and CDO-900, resulting in lower co-leaching efficiency.

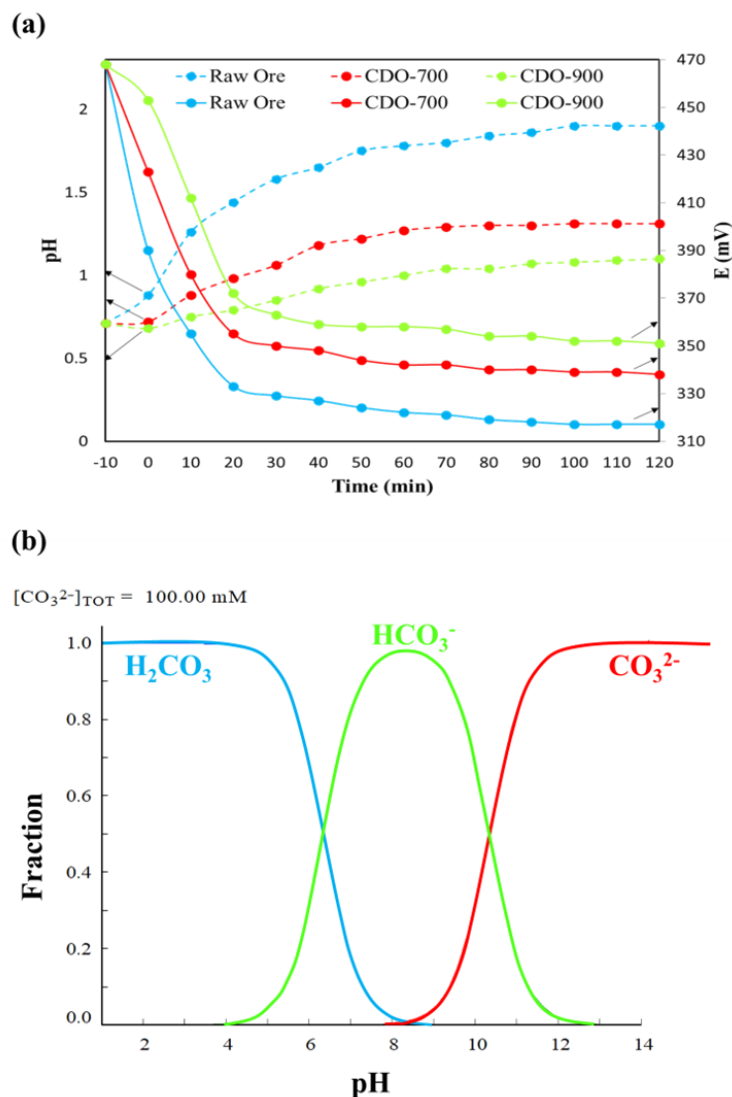


Figure 4.4 (a) pH-E changes during acid leaching; and (b) distribution and content of CO_2 in the hydrometallurgical process at different pH.

The second reason lies in the impact of the carbonate phase on the wettability of dolomitic limestone waste. Figure 4.5 illustrates the dynamic contact angle of 0.5 M H_2SO_4 with dolomitic limestone waste, CDO-700, and CDO-900. A contact angle below 90° indicates the hydrophilicity of dolomitic limestone and calcined dolomitic limestones in an acidic solution. At 0 s, the contact angle of CDO-900 (16°) and CDO-700 (20°) was lower than dolomitic limestone (34°) due to CO_2 liberation. Because carbon has hydrophobicity, CO_2 liberation enhances ore hydrophilicity and increases leaching agent accessibility to impurities in ore, causing higher co-leaching. At 2 s (Figures 4.5(a-3) and 4.5(b-3)), the contact angle of H_2SO_4 with dolomitic limestone and CDO-700 rose to 49° and 25° , respectively, indicating gas evolution during acid leaching and approve the consumption of H^+ with the carbonate phase. Despite the passage of all acidic solution droplets through CDO-900 and CDO-700 after 5 s (Figures 4.5(b-4) and 4.5(c-5)), a by-product layer covered the surface of dolomitic limestone (Figure 4.5(a-4)). Thus, carbonate phase in dolomitic limestone can prevent the co-leaching of impurities by consuming H^+ and limiting the access of leaching agents to impurities.

The third reason for inhibiting co-leaching in the presence of the carbonate phase is linked to the geometric and textural attributes of dolomitic limestone waste and calcined ores. Figure 4.6 displays the SEM-EDS and mapping of dolomitic limestone waste, CDO-700, and CDO-900, respectively. Dolomitic limestone (Figure 4.6(a-1)) exhibited a cubic structure with an average side length of $43\text{ }\mu\text{m}$. Calcination of dolomitic limestone (Figures 4.6(b-1) and 4.6(c-1)) did not alter the overall morphology. However, CO_2 liberation created small holes on the surface of CDO-700 and CDO-900. The number of holes on CDO-900 surpassed that on CDO-700 due to complete CO_2 volatilization. As depicted in Figures 4.6(a-2) and 4.6(b-2), dolomitic limestone waste and CDO-700 primarily consisted of Mg, Ca, O, and C. Compared to dolomitic limestone waste, C and O mass percentages decreased in CDO-700 due to CO_2 liberation from MgCO_3 . In CDO-900, all carbon vanished, leaving Mg, Ca, and O as the principal elements.

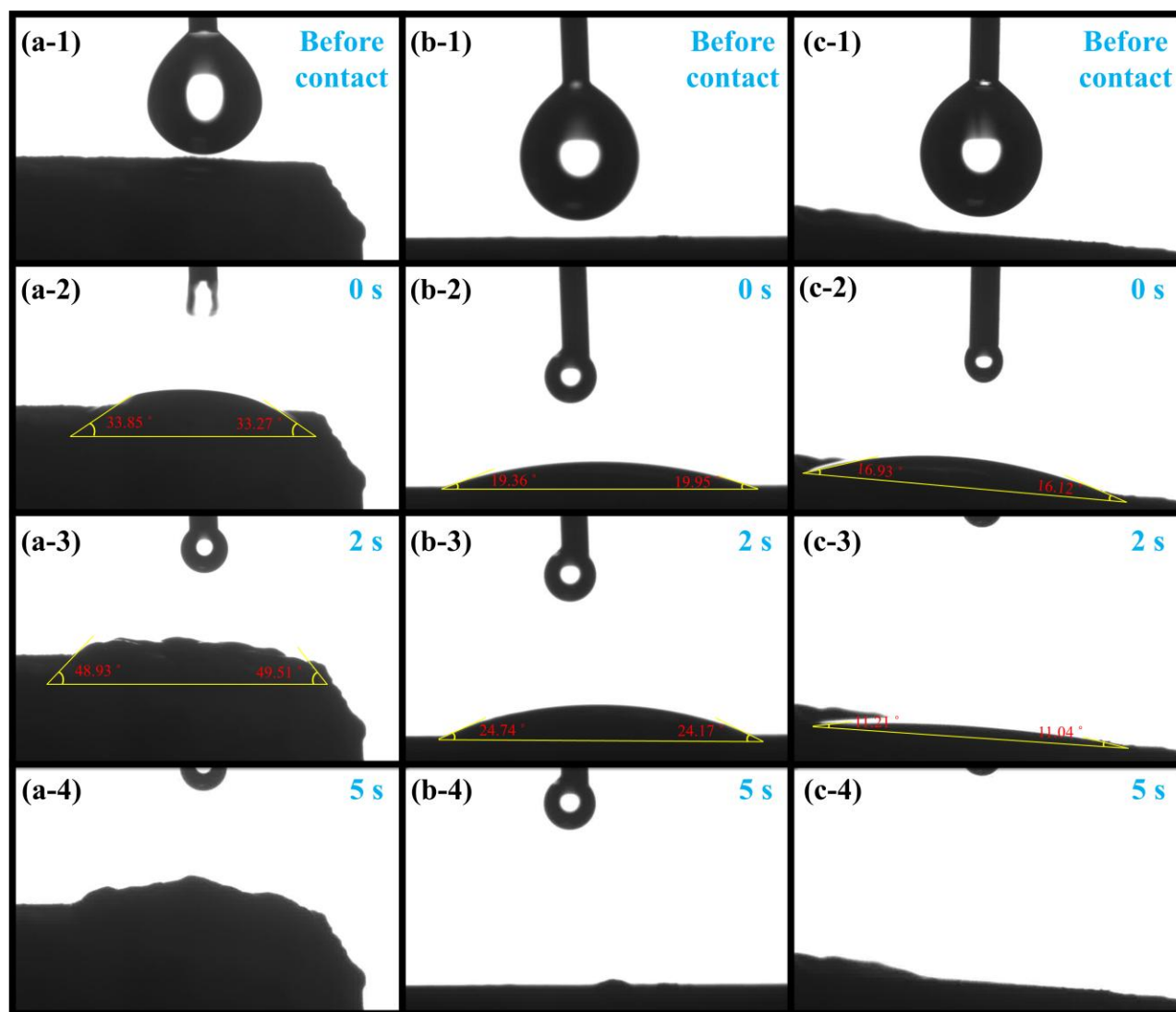


Figure 4.5 Wettability of (a) dolomitic limestone, (b) CDO-700, and (c) CDO-900 with 0.3M H_2SO_4 .

Additionally, Si and Al, identified as major surface impurities by EDS analysis, were observed across all samples. Their distribution on the surfaces of dolomitic limestone waste and calcined variants is illustrated in Figures 4.6(a-3) to 4.6(c-3). These images reveal a dense layer of Mg, Ca, and O on the surface of all samples, with Si and Al impurities dispersed within. In the mapping of dolomitic limestone (Figure 4.6(a-3)), carbon showed similar dense patterns as Mg, Ca, and O, suggesting that most of the surface was occupied by $\text{MgCa}(\text{CO}_3)$. However, CO_2 liberation, as indicated in Figures 4.6(b-3) and 4.6(c-3), reduced carbon congestion on the surface of calcined dolomitic limestones, making Si and Al impurities more accessible.

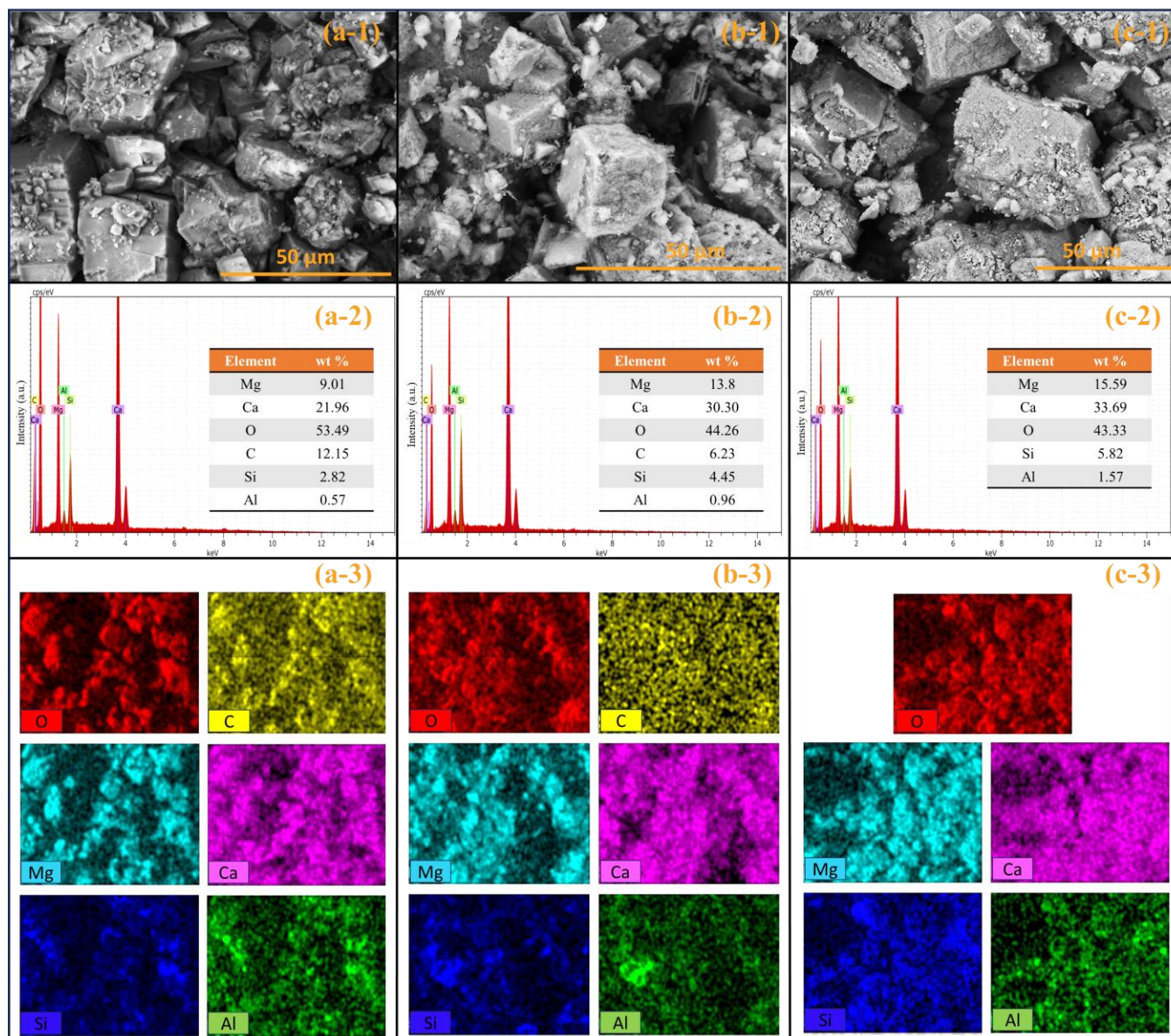


Figure 4.6 SEM images of (a-1) dolomitic limestone, (b-1) CDO-700, and (c-1) CDO-900; EDS analysis of (a-2) dolomitic limestone, (b-2) CDO-700, and (c-2) CDO-900; and elemental mapping of (a-3) dolomitic limestone, (b-3) CDO-700, and (c-3) CDO-900.

Figure 4.7 and Table 4.4 present the BET results obtained from dolomitic limestone and calcined ores. The data in Table 4.4 indicate that phase transformation enhanced the textural properties of dolomitic limestone waste. The average surface area increased from 2 m^2/g to 4 m^2/g and 6 m^2/g upon calcination at 700 $^{\circ}\text{C}$ and 900 $^{\circ}\text{C}$, respectively. This improvement corresponds to the formation of surface holes due to CO_2 liberation. According to the IUPAC classification, all hysteresis loops are categorized as type IV isotherms, indicating mesoporous and macroporous

materials, while the loops behaved as type H3, representing non-rigid aggregates of plate-like particles [245, 246].

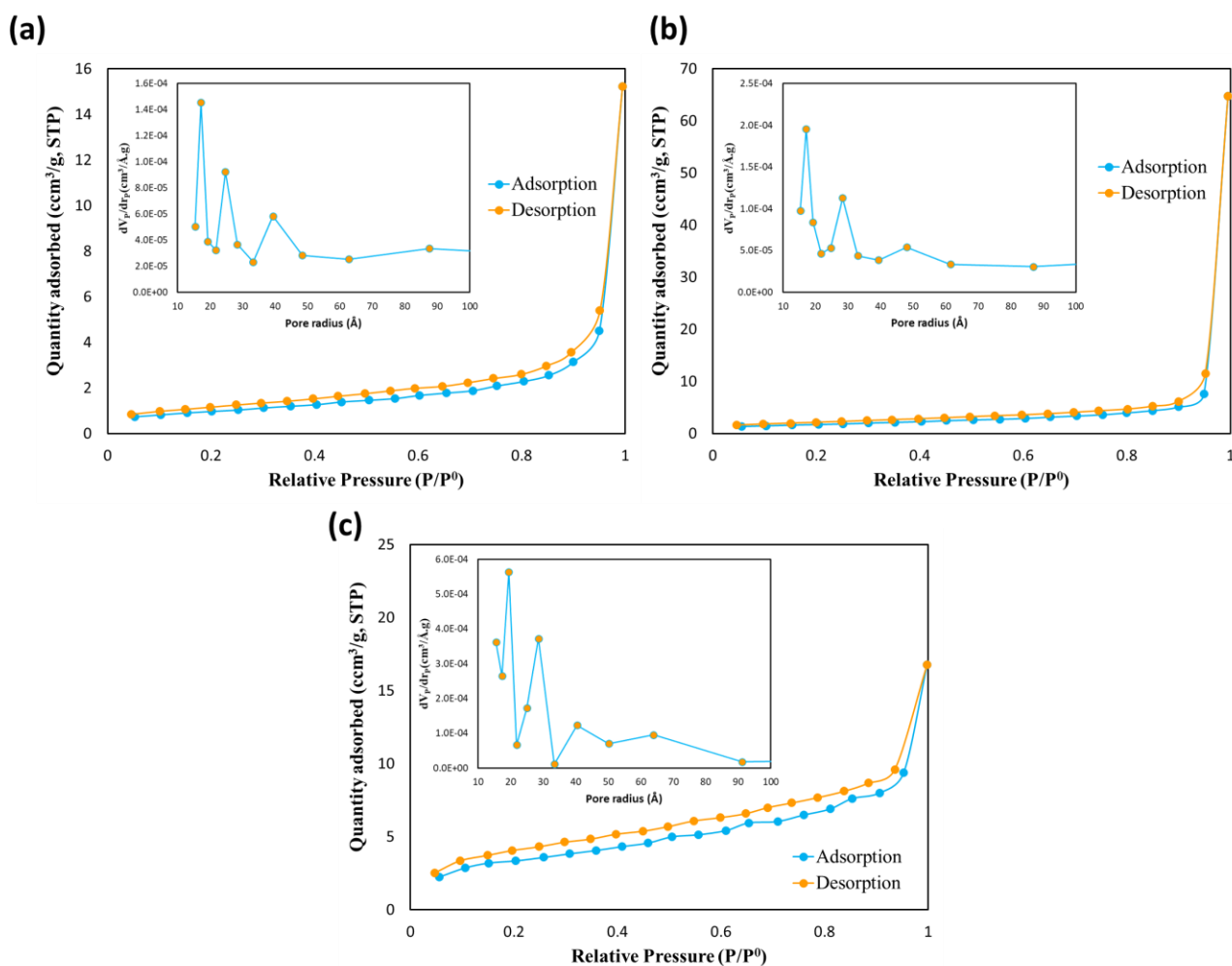


Figure 4.7 N₂ adsorption-desorption isotherm and pore size distribution (inserted plot) of (a) dolomitic limestone, (b) CDO-700, and (c) CDO-900.

Table 4.4 The surface area and pore volume of dolomitic limestone, CDO-700, and CDO-900 were measured using BET analysis.

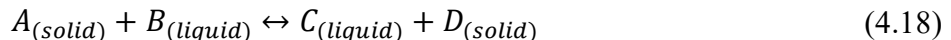
Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)
Dolomitic limestone	2.41	0.02
CDO-700	4.42	0.09
CDO-900	6.06	0.11

Considering the geometry and textural properties, the improved accessibility of leaching agents to impurities in the calcined ore frames resulted from reduced carbon congestion and increased surface area. Consequently, the co-leaching of Si, Al, Na, Fe, P, K, Mn, and Ti was heightened in CDO-700 and CDO-900 compared to dolomitic limestone waste.

To sum up, the carbonate phase significantly influences the efficient leaching of Mg. If the objective is to extract all metals in phosphate mine waste, carbonate phase transformation to oxide may aid this goal. Conversely, direct leaching of the carbonate phase would be advantageous for efficiently Mg leaching from dolomitic limestone waste. This assertion holds implications for the broader aim of efficiently leaching critical metals from secondary mineral resources through CO₂ mineralization. This outlook can pave the pathway for carbon capture utilization and storage (CCUS) as well as valorization of mineral wastes.

4.4.3 Kinetic study for inorganic acid leaching of dolomitic limestone

The thermodynamic analysis assesses the feasibility of a reaction to achieve equilibrium by minimizing Gibbs free energy or maximizing entropy. It focuses solely on a reaction's initial and final states, omitting intermediate steps. To address this limitation, a kinetic study examines the time required to reach equilibrium, defining reaction rates, mechanisms, rate-controlling steps, and activation energy for metal leaching. Acid leaching of mineral resources constitutes a liquid-solid heterogeneous reaction, generally represented by Reaction (4.18). In this reaction, acid acts as the leaching agent (reactant B), reacting with mineral resources (reactant A) to dissolve a portion of reactant A (yielding product C) and produce solid residuals (product D).



To analyze this heterogeneous liquid-solid reaction, three key kinetics models are utilized: the progressive conversion model (PCM), the shrinking core model (SCM), and the shrinking particle model (SPM) [247, 248]. In PCM, also known as the grain kinetics model, particles possess high porosity with interconnected grains. The leaching agent in the liquid phase can diffuse within the particle pores, reacting throughout the entire particle volume. In this model, particle size remains constant during the leaching process. SCM describes the consumption of solid particles via surface reactions and is divided into two categories: (I) SCM with constant particle size and (II) SCM with

shrinking particles. In SCM with constant particle size, metal dissolution initiates from the particle surface and progresses to the core without altering the total particle size. It assumes that the ash product layer formed during acidolysis reactions maintains the same thickness as the dissolved metals, thus keeping the total particle size unchanged. Conversely, SCM with shrinking particle size posits that the ash product layer lacks thickness akin to dissolved metals. Consequently, both the ash product layer and particle core progressively shrink during acid leaching. SPM resembles SCM with shrinking particles, wherein the core size decreases throughout the leaching process. Nonetheless, in SPM, no ash product layer forms around the particle core during leaching.

To determine the appropriate kinetic model for the Mg leaching from dolomitic limestone waste, changes in particle size and crystal phase of ore during acidolysis in diluted H_2SO_4 were assessed. SEM-EDS and XRD analyses (Figures 4.8(a) and 4.8(b)) depict the evolution of dolomitic limestone morphology and composition during acid leaching with 0.5 M H_2SO_4 . SEM images revealed the transformation of the cubic structure of dolomitic limestone into a needle-shaped structure after 60 min of acidolysis, coinciding with a decrease in Mg mass percentage from 9 wt.% to near zero, indicating Mg dissolution. Additionally, the average particle size of dolomitic limestone reduced from 43 μm to 4.6 μm during this period. Notably, the mass percentage of Ca remained relatively stable throughout the acidolysis reaction. Partial acidolysis reactions at 5 min and 20 min intervals demonstrate the formation of needle-shaped products adhering to the cubic dolomitic limestone structure, implying the creation of an ash product layer. XRD analyses reveal $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as the primary crystal phase of this ash product layer. As acidolysis reaction time increased, dolomitic limestone XRD peaks diminished while gypsum peaks intensified. After 60 min of acid leaching, gypsum became the dominant phase, signifying complete Mg dissolution in the liquid phase. The reduction in core particle size and formation of a smaller ash product layer during acid leaching affirms the SCM with shrinking particle size.

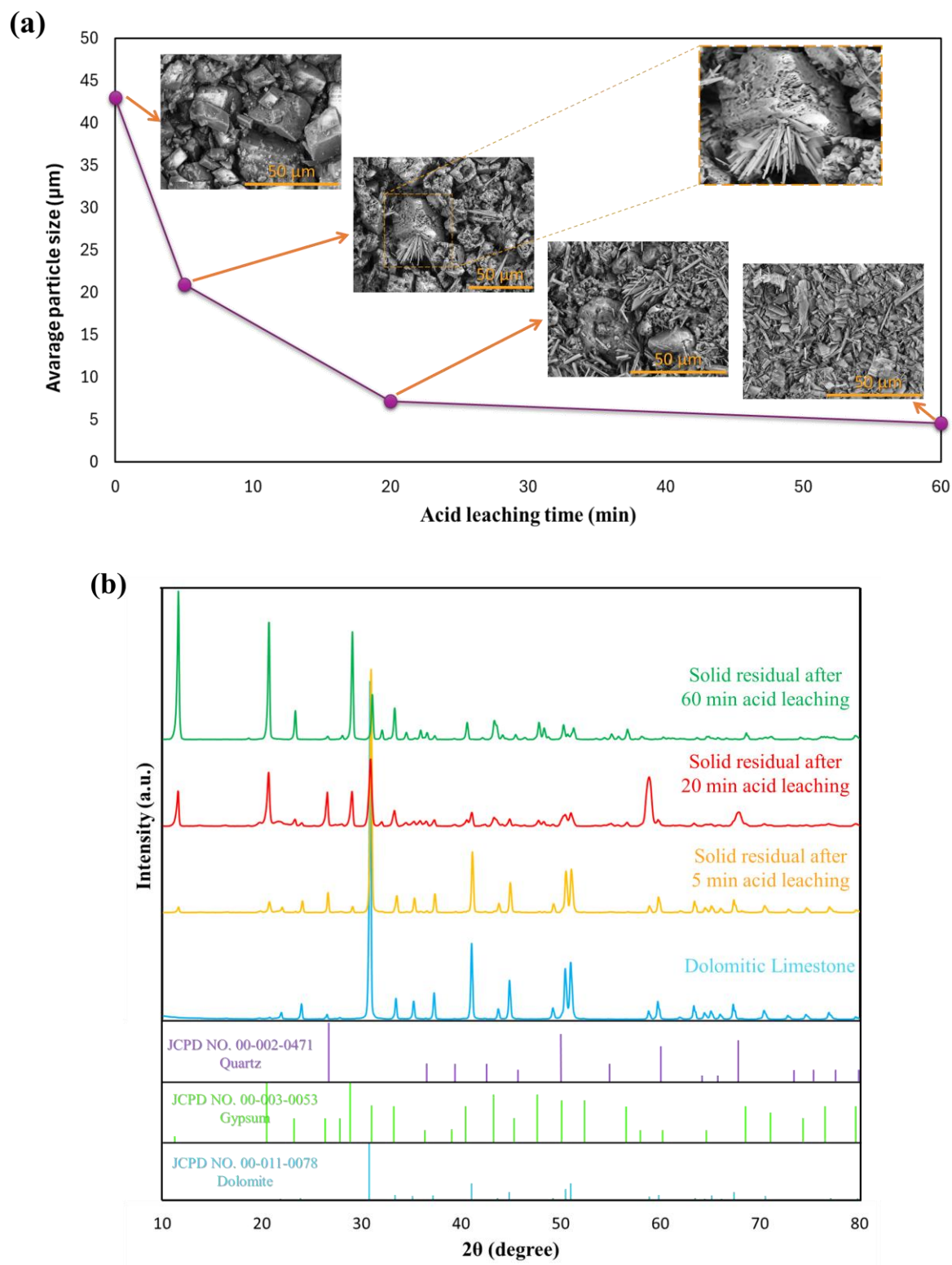


Figure 4.8 Changes in (a) structural properties and (b) crystal phases of dolomitic limestone as a function of acid leaching time.

As exhibited in Figure 4.9, the SCM with shrinking particle size occurs in six sequential steps. Initially, the acid-leaching agents permeate the liquid boundary layer, reaching the surface of the ash product layer. Subsequently, the reactants diffuse through the ash product layer in the second step and reach the particle surface. In the third step, the acid-leaching agents interact with particles, resulting in the generation of metal cations and solid residuals. The fourth and fifth steps entail the migration of dissolved metal cations through the ash product layer to the bulk liquid phase. Finally, in the sixth step, the dissolved metal cations diffuse into the liquid boundary layer. This mechanism underscores three pivotal steps: (I) permeation of the reactants through the liquid boundary film, (II) diffusion of the reactants through the ash product layer, and (III) surface acidolysis reactions.

If the permeation of the reactants controls the Mg leaching through the liquid boundary film, the reaction rate will obey Equation (4.19) [249]:

$$x_i = k_{LD}t \quad (4.19)$$

If the Mg leaching is controlled by the diffusion of the reactant through the ash product layer, the reaction rate will follow Equation (4.20) [250, 251]:

$$1 - \frac{2}{3}x_i - (1 - x_i)^{\frac{2}{3}} = k_{AD}t \quad (4.20)$$

If the surface acidolysis reaction is the controlling step, the reaction rate will follow Equation (4.21) [250, 251]:

$$1 - (1 - x_i)^{\frac{1}{3}} = k_{CR}t \quad (4.21)$$

It is also possible that both diffusion of the reactant through the ash product layer and surface acidolysis reaction control the reaction rate. In this case, Wadsworth and Dickinson suggested Equation (4.22) to govern the Mg leaching reaction rate [250]:

$$\frac{1}{3}Ln(1 - x_i) + (1 - x_i)^{-\frac{1}{3}} - 1 = k_{CD}t \quad (4.22)$$

For the above equations, x_i represents the leaching efficiency of the target metal (%), here is Mg. k_{LD} , k_{AD} , k_{CR} , and k_{CD} are the apparent rate constants for liquid boundary film diffusion, ash product layer diffusion, surface acidolysis, and mixed diffusion and reaction, respectively (min^{-1}). t also refers to the leaching process time (min). A fitting between experimental data and Equations (4.19) to (4.22) should be performed to determine the rate-controlling step. The step with the highest correlation coefficient (R^2) will be selected as the rate-controlling step.

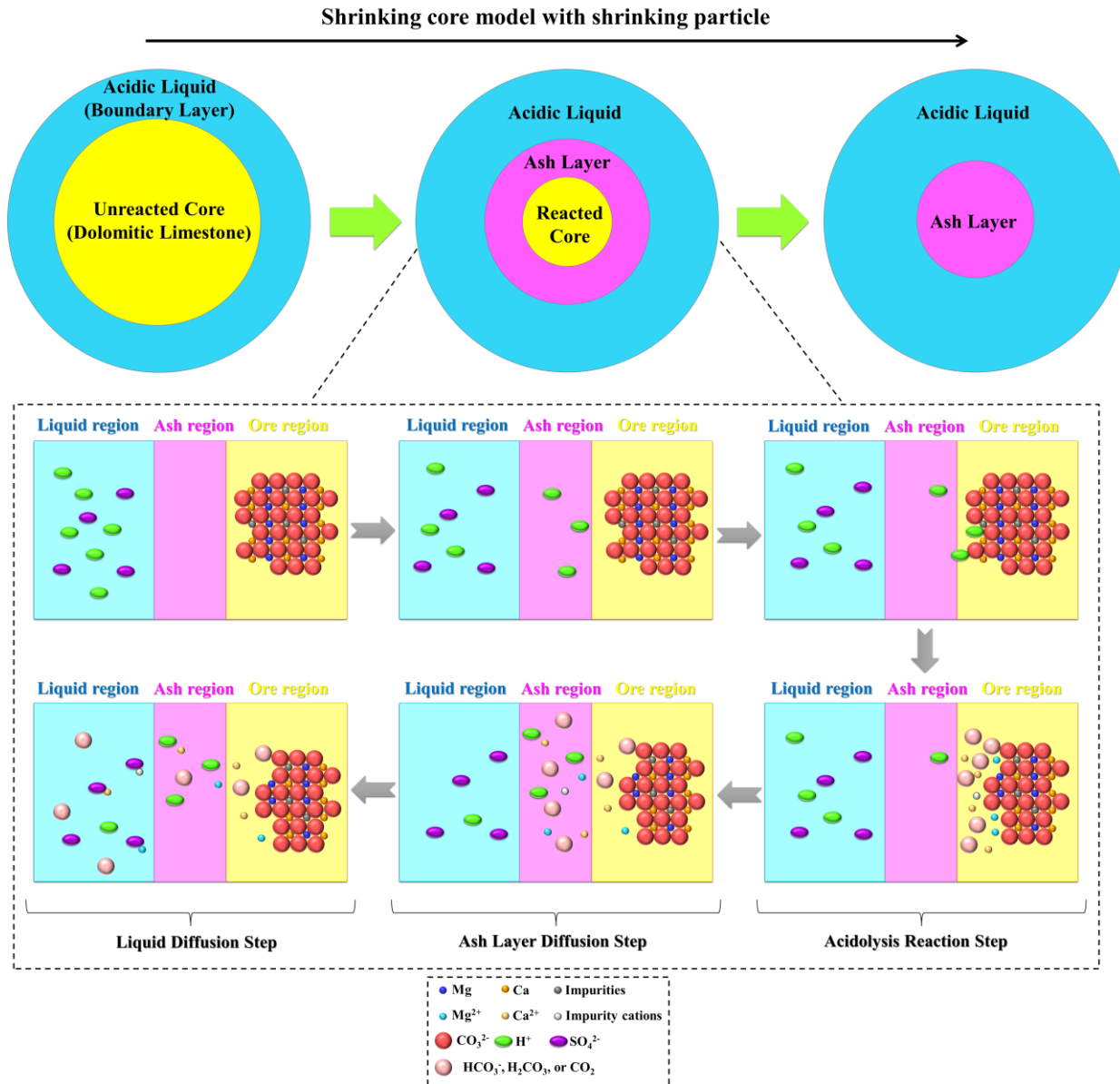


Figure 4.9 Schematic illustration of dolomitic limestone acid leaching mechanism in accordance with the shrinking core model with shrinking particle size.

4.4.3.1 Temperature effect

Dolomitic limestone leaching in diluted acid was performed at different temperatures from 20 °C to 80 °C to find the rate-controlling step. Figure 4.10(a) presents the Mg leaching efficiency from dolomitic limestone waste with an average particle size of 45 μm using 0.3 M H_2SO_4 and an S/L ratio of 10 g/L during 120 min. Across all leaching temperatures, Mg dissolution exhibited a rapid increase within the initial 10 min, followed by a slower progression after 20 min. According to this figure, temperature positively impacted the Mg leaching efficiency. Mg leaching during 120 min increased from 42% to 78% by raising the temperature from 20 °C to 80 °C. Moreover, the slope of plots during the initial stage noticeably increased with temperature, implying faster acidolysis reactions at higher temperatures. These improvements can be attributed to increased ion activity and enhanced solubility of metal cations at higher temperatures. The ionization of H_2SO_4 is heightened at elevated temperatures, resulting in greater H^+ generation [249]. In addition, diffusion of ions and solubilities of metal cations is higher at elevated temperatures [252]. Consequently, elevated temperatures accelerated acidolysis reactions and improved Mg leaching due to rapid H_2SO_4 ionization, enhanced ionic conductivity, and increased dissolution of metal cations.

Figures 4.10(b) to 4.10(e) depict the fitting of experimental data obtained at various temperatures with liquid boundary film diffusion, ash product layer diffusion, surface acidolysis, and mixed diffusion and reaction steps, respectively. According to these figures, diffusion through the ash product layer yielded the highest correlation coefficients, with R^2 greater than 0.99, indicating its role as the rate-controlling step. The lowest correlation coefficient was observed for diffusion through the liquid boundary film, which was expected given the experimental conditions. Since the acid leaching experiments were conducted under vigorous stirring, external mass transfer from the liquid boundary phase to the ash product layer was rapid. Therefore, diffusion of the reactant through the liquid boundary film could not be the rate-controlling step.

The apparent activation energy for Mg leaching from dolomitic limestone waste can be calculated by the Arrhenius equation, which correlates the rate constant of a chemical reaction to the absolute temperature (Equation (4.23)):

$$k = A_0 \exp\left(-\frac{E_a}{RT}\right) \quad (4.23)$$

where k is the apparent rate constant, A_0 is the Arrhenius pre-exponential factor or frequency factor (min^{-1}), E_a is the apparent activation energy (kJ/mol), T is the leaching temperature (K), and R is the universal gas constant ($8.314 \text{ J}/(\text{mol}\cdot\text{K})$). Equation (4.23) can be rearranged in logarithmic form as follows:

$$\ln(k) = \ln(A_0) - \frac{E_a}{RT} \quad (4.24)$$

According to Equation (4.24), the E_a and A_0 can be obtained from the slope and intercept of the plot of $\ln(k)$ versus $\frac{1}{T}$. As shown in Figure 4.10(f), $\ln(k)$ is linearly dependent on $\frac{1}{T}$ with a correlation coefficient of 0.96. Based on this plot, the E_a and A_0 of Mg leaching from dolomitic limestone were 16 kJ/mol and 1.17 min^{-1} , respectively. In the context of chemical engineering, activation energy below 20 kJ/mol indicates that internal diffusions are the rate-controlling steps [253], while activation energy exceeding 40 kJ/mol suggests that chemical reactions control the reaction rate [254]. When activation energy falls within the range of 20 kJ/mol to 40 kJ/mol , both diffusion and chemical reactions play a role in controlling the reaction rate [255]. Our kinetic study aligns with these principles, indicating that the diffusion of H^+ to the particle surface through the ash product layer controls the rate of Mg leaching from dolomitic limestone waste.

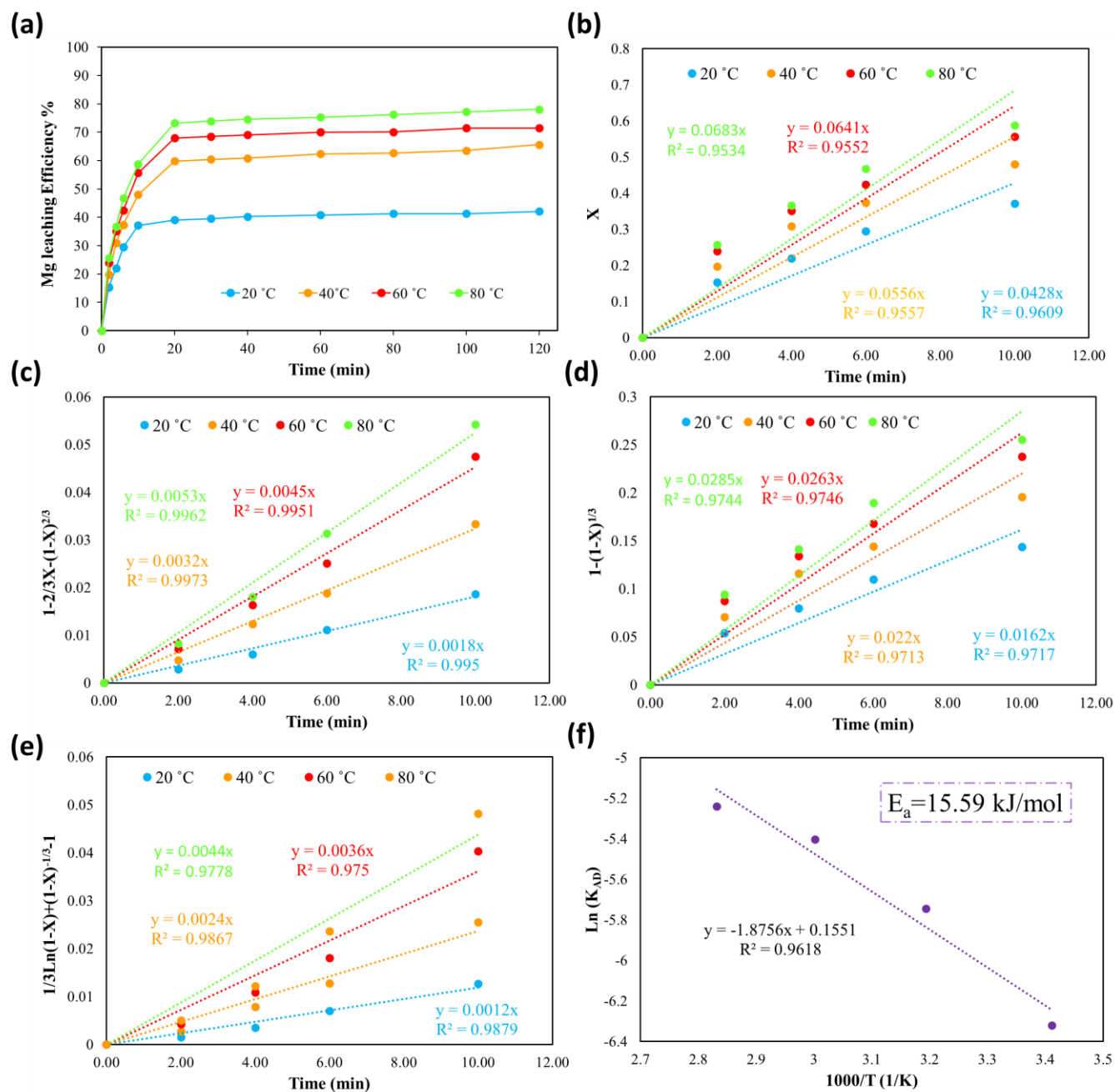


Figure 4.10 (a) The effect of temperature on the Mg leaching efficiency; (b) kinetic fitting curve controlled with liquid boundary film; (c) kinetic fitting curve controlled with diffusion through the ash product layer; (d) kinetic fitting curve controlled with chemical reaction; (e) kinetic fitting curve controlled with both diffusion through the ash product layer and chemical reaction; and (f) logarithmic plot of Arrhenius for acid leaching of Mg.

4.4.3.2 Acid concentration effect

Figure 4.11(a) illustrates the impact of H_2SO_4 concentration on Mg leaching efficiency. The experiments were conducted at 80 °C using a 45 μm dolomitic limestone and an S/L ratio of 10 g/L. Increasing the H_2SO_4 concentration from 0.2 M to 0.4 M significantly enhanced Mg leaching efficiency from 65% to 96% over 120 min. This improvement is attributed to heightened H^+ generation, enhanced leaching agent diffusion, and increased probability of H^+ collision with dolomitic limestone particles [252]. Further increasing the H_2SO_4 concentration from 0.4 M to 0.5 M has a slight positive effect, boosting Mg leaching efficiency from 96% to 100%. Theoretically, Reactions (4.3) to (4.17) suggest that 0.46 M H_2SO_4 is needed for complete Mg digestion from dolomitic limestone. Therefore, our findings indicate that 0.5 M H_2SO_4 is adequate for complete Mg digestion.

As shown in Figure 4.11(a), the reaction rate surged in the initial 10 min, escalating with higher acid concentrations. However, beyond the 20 min process, the reaction rate tapered off across all acid concentrations. This decline in reaction rate can be ascribed to the rapid consumption of H^+ by Mg, Ca, and carbonate at the onset of the process. Consequently, substantial Mg dissolution and CaSO_4 formation occurred within a short duration. The encasement of the dolomitic limestone core with CaSO_4 as a by-product hinders the diffusion of remaining H^+ , resulting in a decelerated leaching reaction rate.

Figures 4.11(b) and 4.11(c) demonstrate the fitting of experimental data obtained at various acid concentrations with ash product layer diffusion and logarithmic plots of the apparent reaction rate constant versus acid concentration, respectively. As shown in Figure 4.11(b), the correlation coefficients for all concentrations exceed 0.99, indicating that internal diffusion through the ash product layer governs Mg leaching at different H_2SO_4 concentrations. Regarding Figure 4.11(c), the apparent reaction rate constant linearly increases with higher acid concentration. Thus, the apparent reaction rate constant of Mg leaching follows a first-order relationship with H_2SO_4 concentration.

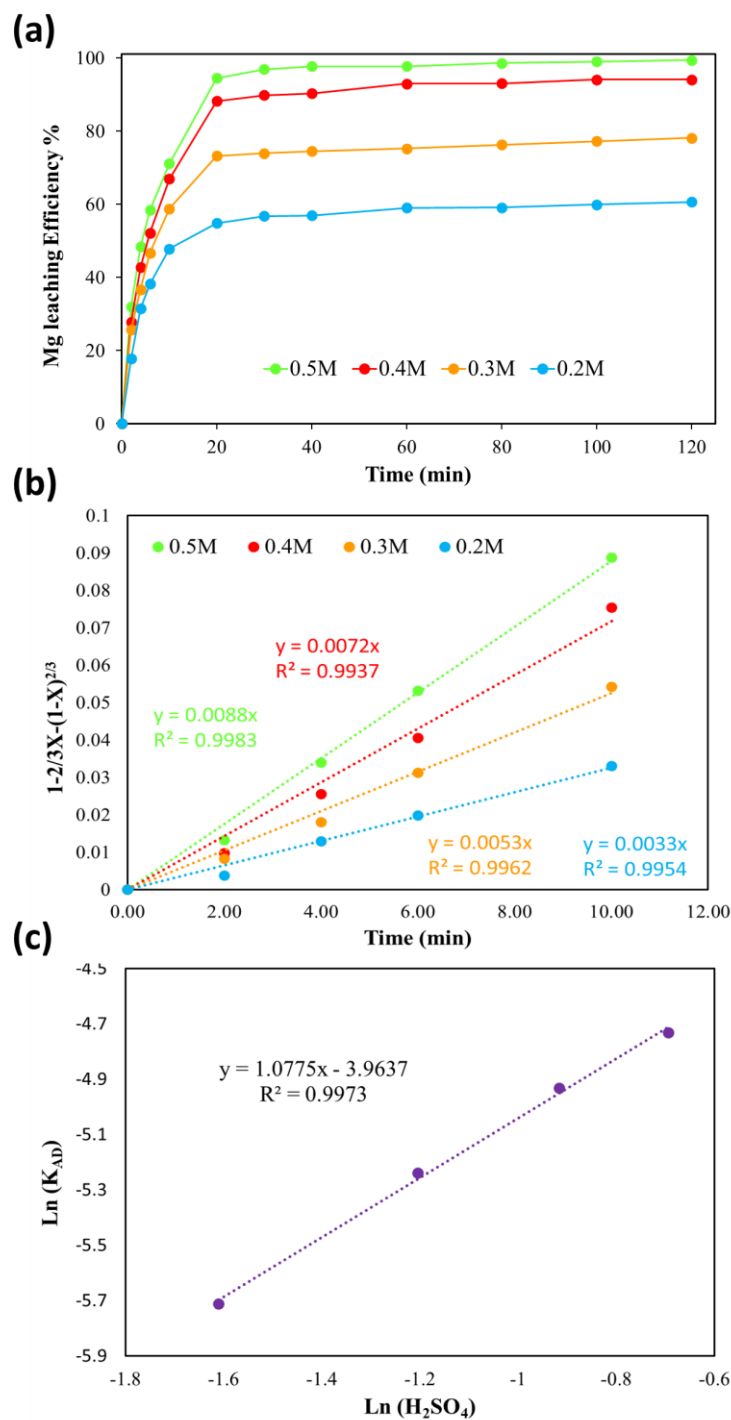


Figure 4.11 (a) The effect of H_2SO_4 concentration on Mg leaching efficiency; (b) kinetic fitting curve controlled with diffusion through the ash product layer; (c) the logarithmic plot of K_{AD} versus H_2SO_4 concentration.

4.4.3.3 Solid-to-liquid ratio effect

Figure 4.12(a) indicates the impact of the solid-to-liquid ratio (S/L) on the Mg leaching efficiency. Leaching experiments were conducted using 45 μm dolomitic limestone in a 0.5 M H_2SO_4 solution at 80 $^\circ\text{C}$ to assess this parameter. The figure shows that the S/L ratio negatively affected Mg leaching efficiency. Increasing the S/L ratio from 10 g/L to 80 g/L resulted in a 40% decrease in Mg leaching efficiency. Two main reasons account for this negative effect. Firstly, increasing the S/L ratio reduces the concentration of H^+ relative to the dolomitic limestone particle, thereby decreasing the probability of acidolysis reaction due to insufficient H^+ concentration, leading to lower Mg leaching efficiency [256]. Secondly, increasing the S/L ratio enhances the diffusion resistance of the leaching agent, resulting in lower accessibility and collision of H^+ with the surface of dolomitic limestone particles, thus leading to lower leaching efficiency [253].

Figures 4.12(b) and 4.12(c) demonstrate the fitting of experimental data obtained at different S/L ratios with ash product layer diffusion and a logarithmic plot of the apparent reaction rate constant versus S/L ratio, respectively. Based on Figure 4.12(b), the correlation coefficients for all S/L ratios exceed 0.99, indicating that internal diffusion through the ash product layer controls Mg leaching at varying S/L ratios. Concerning Figure 4.12(c), the slope of the logarithmic plot of the apparent reaction rate constant versus the S/L ratio was -0.25. Thus, the apparent reaction rate constant of Mg leaching exhibits zero-order kinetics with respect to the S/L ratio.

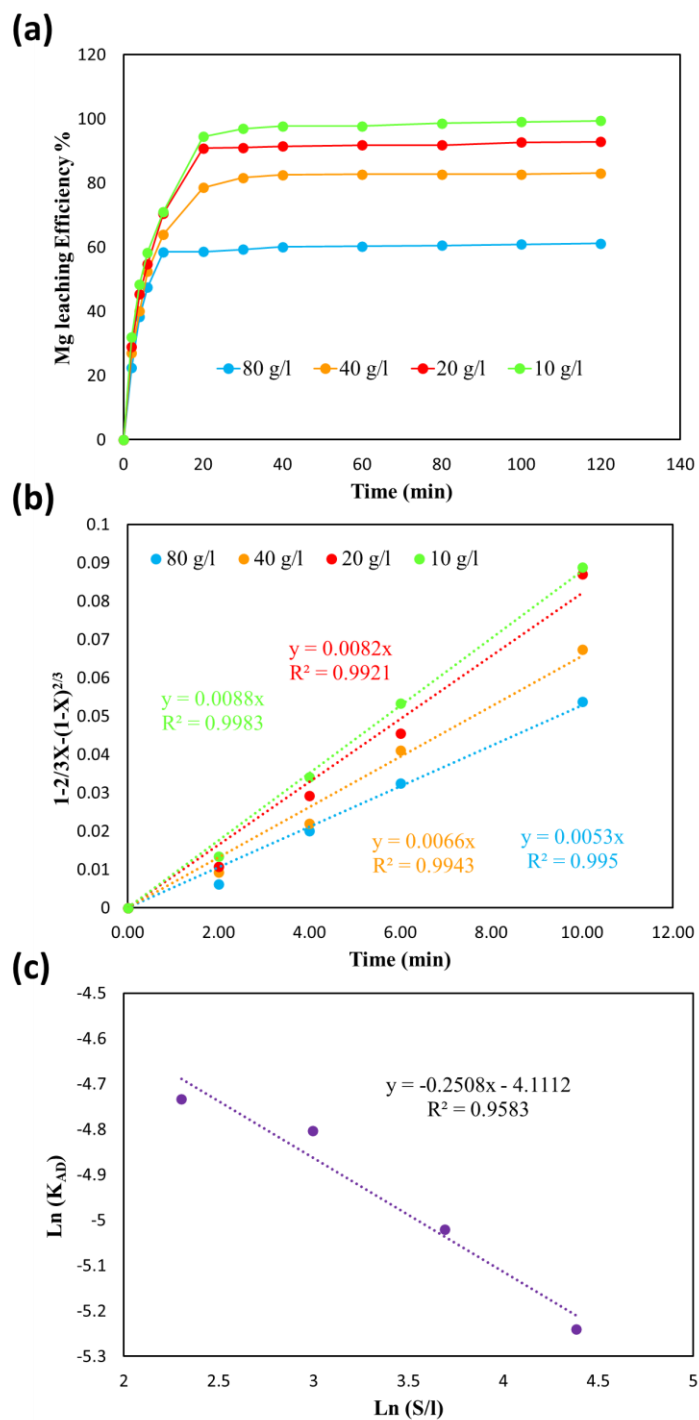


Figure 4.12 (a) The effect of S/L ratio on Mg leaching efficiency; (b) kinetic fitting curve controlled with diffusion through the ash product layer; (c) logarithmic plot of K_{AD} versus S/L ratio.

4.4.3.4 Particle size effect

Figure 4.13(a) exhibits the impact of particle size on Mg leaching efficiency. This investigation was conducted at a leaching temperature of 80 °C with an S/L ratio of 10 g/L in a 0.5 M H₂SO₄ solution. Increasing the particle size had a negative effect on Mg dissolution, with leaching efficiency decreasing from 100% for an average particle size of 45 µm to 57% for an average particle size of 150 µm over a 120 min leaching period. The decline in leaching efficiency with increasing average particle size is attributed to changes in specific surface area. Fine particles, compared to coarse ones, possess a higher specific surface area per unit mass of dolomitic limestone, providing more reactive sites accessible to leaching agents and thereby enhancing acidolysis and leaching efficiency [250]. Additionally, fine particles are less prone to agglomeration during leaching compared to coarse particles, enabling leaching agents to swiftly access suspended fine particles, further improving Mg leaching efficiency.

Figures 4.13(b) and 4.13(c) demonstrate the fitting of experimental data for average particle size with ash product layer diffusion and a logarithm plot of the apparent reaction rate constant versus the S/L ratio, respectively. Based on Figure 4.13(b), the correlation coefficients for all average particle sizes exceed 0.99, indicating that internal diffusion through the ash product layer governs Mg leaching from dolomitic limestone with varying particle sizes. Regarding Figure 4.13(c), the slope of the logarithm plot of the reaction rate versus the average particle size ratio was -0.7. Thus, the apparent reaction rate constant of Mg leaching follows a first-order trend with respect to the inverse of the particle size.

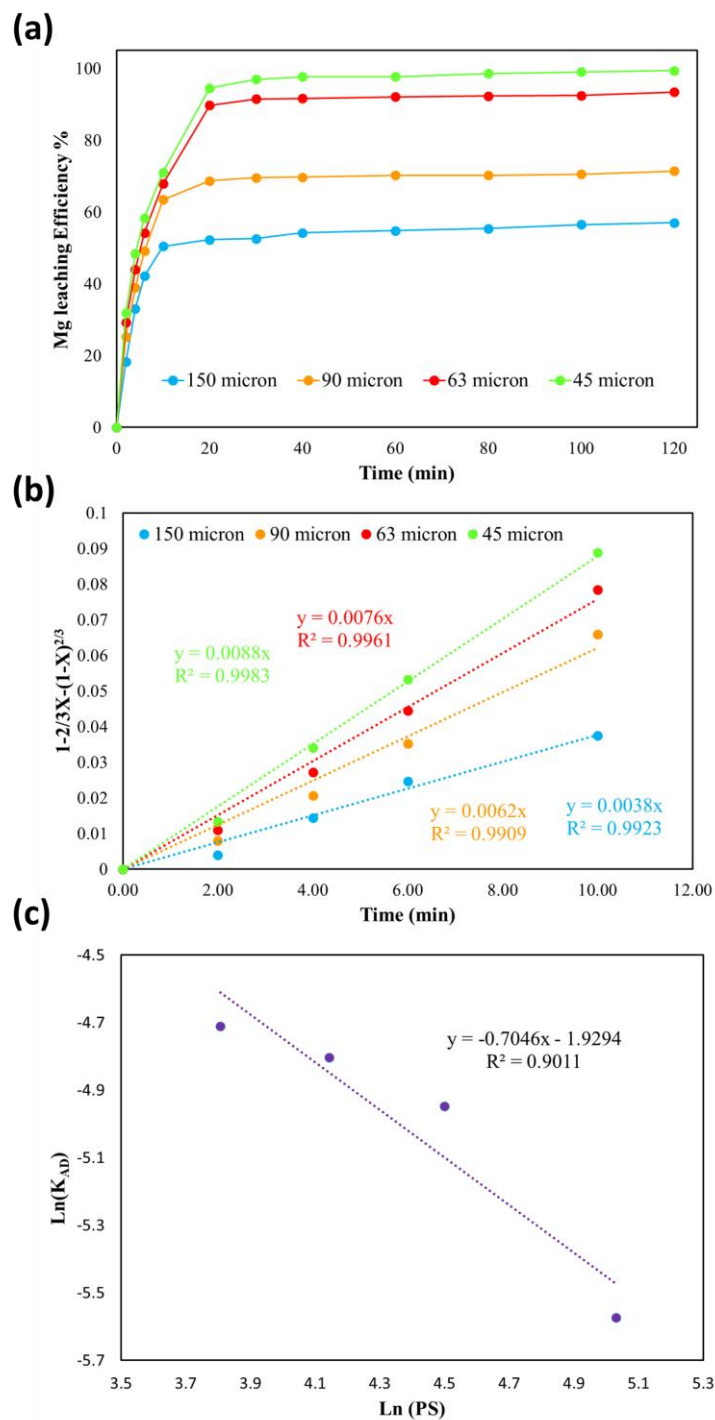


Figure 4.13 (a) The effect of particle size on Mg leaching efficiency; (b) kinetic fitting curve controlled with diffusion through the ash product layer; (c) logarithmic plot of K_{AD} versus particle size.

4.4.3.5 Semi-empirical kinetic model

The results from temperature, H_2SO_4 concentration, S/L ratio, and average particle size effects suggest that inorganic acid leaching of Mg from dolomitic limestone waste follows the SCM with shrinking particle size, controlled by internal diffusion through the ash product layer. The semi-empirical kinetic model for Mg leaching from dolomitic limestone can be expressed as follows, incorporating Equation (4.20), the activation energy, and the order of the apparent rate constant with respect to H_2SO_4 concentration, S/L ratio, and average particle size:

$$1 - \frac{2}{3}x - (1 - x)^{\frac{2}{3}} = k_{AD}t = A_0 \exp\left(-\frac{E_a}{RT}\right) [H_2SO_4]^a \left[\frac{S}{L}\right]^b [PS]^c t \quad (4.25)$$

$$1 - \frac{2}{3}x - (1 - x)^{\frac{2}{3}} = 1.17 \exp\left(-\frac{15.59}{RT}\right) [H_2SO_4] \left[\frac{S}{L}\right]^{-0.25} [PS]^{-0.7} t \quad (4.26)$$

where x is the Mg leaching efficiency (%) at leaching time t (min), T is the leaching temperature (K), R is the universal gas constant (8.314 J/(mol·K)), $[H_2SO_4]$ is the concentration of sulfuric acid (M), $\frac{S}{L}$ is the solid-to-liquid ratio (g/L), and PS is the average particle size (μm).

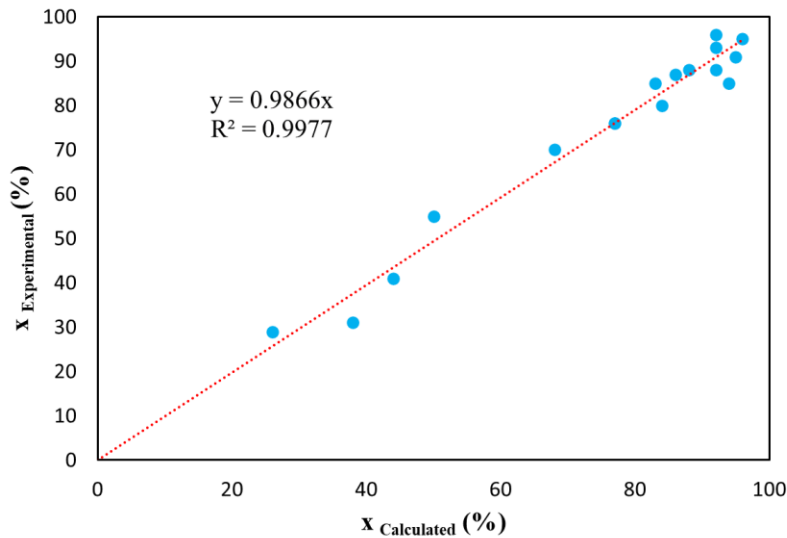


Figure 4.14 Comparison of experimental results and predicted results obtained from the semi-empirical kinetic model for acid leaching of Mg by dilute H_2SO_4 .

According to the proposed semi-empirical kinetic model, increasing temperature and acid concentration while decreasing the S/L ratio and average particle size enhances Mg leaching efficiency from dolomitic limestone waste. To validate the model, Mg acid leaching was performed under different conditions from those in the kinetic study. Figure 4.14 compares experimental values with those calculated from the model at various operating conditions. The figure demonstrates excellent agreement between the proposed model and experimental data, indicating its capability to predict Mg leaching efficiency from dolomitic limestone waste across the selected ranges of temperature, H_2SO_4 concentration, S/L ratio, and average particle size in this study.

4.5 Conclusion

In this research, efficient leaching of Mg from dolomitic limestone waste rock was achieved by elucidating the role of carbonate in acid leaching with diluted H_2SO_4 . The solid-liquid interactions of metals and lixiviant were evaluated thermodynamically and kinetically inside a stirring batch system with the aid of TGA, ICP-OES, XRF, XRD, SEM-EDS, QEMSCAN, contact angle, and BET characterization techniques. Pre-calcination of dolomitic limestone waste involved a two-stage decomposition in which CO_2 was liberated from MgCO_3 and CaCO_3 at $700\text{ }^\circ\text{C}$ and $900\text{ }^\circ\text{C}$. Utilization of diluted H_2SO_4 assisted efficient separation of Mg and Ca from dolomitic limestone waste, yielding soluble MgSO_4 and insoluble $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with a reaction enthalpy of -114 kJ/mole . Drawing an analogy between the leaching of dolomitic limestone and calcined ore at $700\text{ }^\circ\text{C}$ and $900\text{ }^\circ\text{C}$ revealed that the carbonate phase can act as an inhibitor and reduce the co-leaching of Si, Al, Na, Fe, P, K, Mn, and Ti from 87% to 26 %. The main reasons for the inhibition of impurities co-leaching associated with the carbonate phase in dolomite limestone waste were decreasing the hydrophilicity and the surface area of the ore, along with lowering the lixiviant reduction potential due to the consumption of the leaching agents. Developing the semi-empirical kinetic models indicated that Mg leaching follows the first-order kinetic regarding H_2SO_4 concentration and the inverse of the particle size while is zero-order with respect to the S/L ratio. At the optimum condition (0.5 M H_2SO_4 , S/L ratio of 10 g/L, particle size of $45\text{ }\mu\text{m}$, and reaction temperature of $80\text{ }^\circ\text{C}$), 15.59 kJ/mole energy was required to reach 100% Mg leaching efficiency with 75% Ca crystallization.

4.6 Acknowledgments

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CHAPTER 5 ARTICLE 2 - SELECTIVE RECYCLING OF CRITICAL METALS FROM THE DOLOMITIC LIMESTONE WASTE THROUGH MULTI-STEP ALKALINE PRECIPITATION INTEGRATED WITH CO₂ CARBONATION

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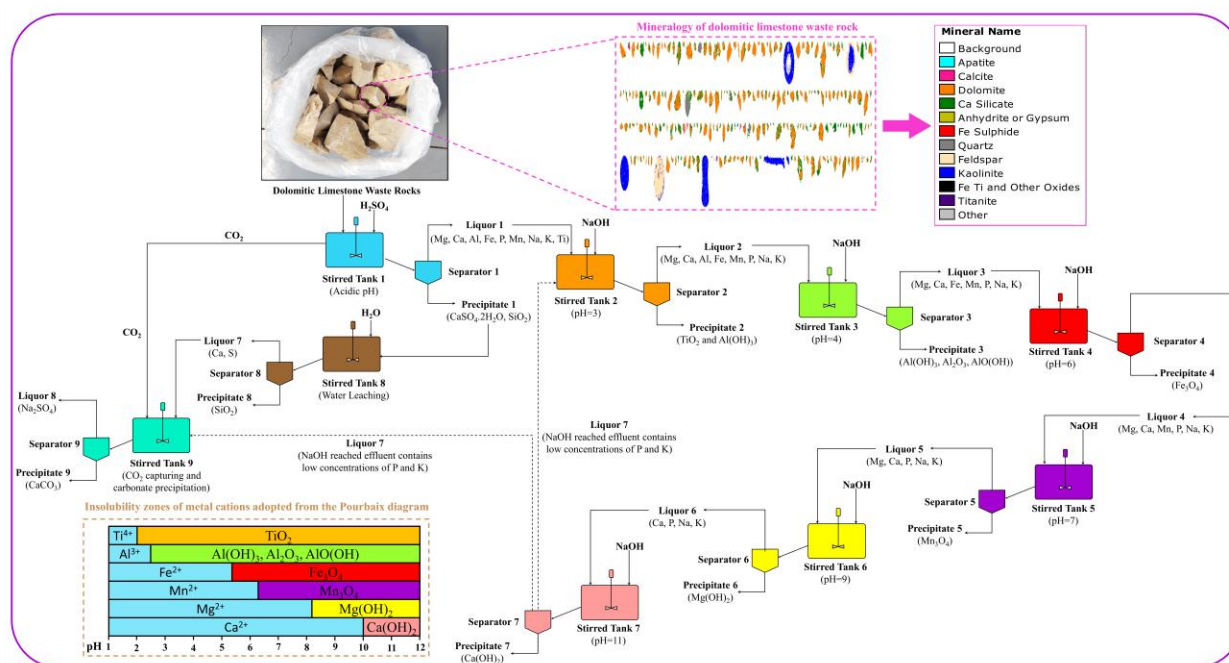
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5.1 Abstract

Waste valorization provides a sustainable pathway for metals resource management and environmental remediation. In this study, we presented a carbon-neutral hydrometallurgical process for selectively recycling critical metals from dolomitic limestone leachate, a waste stream of phosphate mining. By incorporating thermodynamic simulation with experimental works, we achieved high-purity recovery of magnesium, calcium, aluminum, iron, manganese, and titanium via stepwise alkaline precipitation integrated with CO₂ carbonation. This process eliminates the need for redox agents or stabilizers. Thermodynamic simulations revealed that increasing temperature widened the pH gap between metal insolubilities, enabling selective precipitation at lower pH. Higher NaOH concentrations enhanced the supersaturation factor by 10²-10⁸ orders, thus accelerating precipitation. Experimental optimization of pH, temperature, and NaOH concentration enabled selective recycling of 97% Ti, 99% Al, 96% Fe, 91% Mn, 98% Mg, and 90% Ca at distinct pH thresholds 3, 4, 6, 7, 9, and 11, respectively. The NaOH effluent was repurposed to capture CO₂ arising from the acid leaching step and to synthesize NaHCO₃. The obtained NaHCO₃ was further utilized for calcium recovery as CaCO₃. Economic assessments supported the viability of this closed-loop process for recovering value-added products, including Mg(OH)₂, Ca(OH)₂, Fe₃O₄, Mn₃O₄, Al(OH)₃, and TiO₂. This work advances circular economy strategies by transforming mining waste into valuable metal resources while promoting carbon neutrality.

Keywords: Waste valorization; Selective recovery; Critical metals; Sustainable chemistry; hydrometallurgy; CO₂ Capturing

Graphical Abstract



5.2 Introduction

The development of technologies powered by renewable energy is essential globally to mitigate climate change and achieve net-zero carbon emissions. Critical metals and rare earth elements play a pivotal role in this progress. However, the limited availability of primary resources and restrictive trade policies create challenges in meeting the growing demand for these strategic metals [257-259]. To address these challenges, recycling metals from secondary resources, such as industrial wastes and end-of-life products, presents a promising solution. This approach enables a circular economy, promotes sustainable metal production, and reduces environmental harm [260-262]. According to Moroccan mining databases, phosphate extraction generates substantial quantities of waste, with 3-11 tons of waste rocks produced per one ton of phosphate ore [57, 58]. Approximately 16 wt% of this waste comprises dolomitic limestone, a sedimentary rock mainly composed of $\text{MgCa}(\text{CO}_3)_2$ [59]. Dolomitic limestone waste contains various elements from different groups of the periodic table, including alkaline earth metals (Mg and Ca), alkali metals (Na and K), transition metals (Fe, Mn, and Ti), post-transition metals (Al), metalloids (Si), and nonmetals (P) [57]. Consequently, dolomitic limestone waste rock presents a potential secondary

resource for recycling strategic metals, offering an opportunity to reduce the environmental footprint and valorize phosphate mining waste.

Among the current technologies, hydrometallurgy is a favored technique for recovering valuable metals from secondary resources. This hybrid process involves leaching metals from the solid feed into a solution using organic or inorganic lixiviants, followed by the extraction of dissolved metals through various separation processes, such as precipitation, flotation, CO₂ mineralization, membrane separation, electrodialysis, electrowinning, ion exchange, and solvent extraction [263-265]. The choice of the separation process strongly depends on leachate complexity, dissolved metals concentration, desired product purity, process costs, and environmental impacts. Given these criteria, precipitation is particularly advantageous due to its simplicity, selectivity, cost-effectiveness, energy efficiency, and compatibility with closed-loop recycling strategies [266, 267]. This separation involves using various precipitants to react with metal cations, forming insoluble metal compounds through single or double ionic replacement reactions. As summarized in Table A.1, some recent studies have investigated the Mg separation from the leachate of secondary resources by different precipitants like sodium hydroxide (NaOH), calcium hydroxide (Ca(OH)₂), ammonia hydroxide (NH₄OH, also known as water ammonia (NH₃.H₂O), ammonia solution, aqua ammonia, or aqueous ammonia (NH_{3(aq)}), ammonium carbonate ((NH₄)₂CO₃), and sodium carbonate (Na₂CO₃) [23, 232, 268-272]. Despite the efficiency of NH₄OH as a precipitant, its low alkalinity decreases the precipitation rate and increases the process time, especially for solutions with low metal cation concentrations. Alkaline salts such as NaOH and KOH have exhibited the potential for rapidly separating critical metals with high recovery efficiency [273, 274]. However, selective separation with high purity of precipitates has remained a significant obstacle due to the co-precipitation of other metals with the target metal. To the best of our knowledge, no research has examined stepwise alkaline precipitation of magnesium and calcium from Moroccan dolomitic limestone waste rock. The similar physicochemical properties of Mg and Ca make their separation more difficult. Notably, the presence of 15-20 wt% of impurities in this waste rock, including Ti, Si, Al, Fe, and Mn, complicates the selective separation of Mg and Ca with high purity. These gaps underscore the need for a comprehensive study on separating low-concentration transition metals from high-concentration alkaline earth metals in Moroccan dolomitic limestone waste rock by stepwise alkaline precipitation, focusing on enhancing selectivity and minimizing co-precipitation challenges.

Therefore, the main object of this study is to develop a sustainable and carbon-neutral process for selective recovery of Mg, Ca, Al, Fe, Mn, and Ti by employing NaOH as a single precipitant without the addition of extra oxidants, reductants, or stabilizing agents. To achieve this goal, five specific objectives will be pursued as follows. First, the feasibility of selective separation through a single precipitant will be evaluated via thermodynamic simulation using Factsage and Medusa-Hydra. This step will determine the possible precipitation reactions, supersaturation factor, and operational boundaries as functions of pH and oxidation-reduction potential (ORP). Second, the impact of contributing parameters, including leach liquor pH, reaction temperature, NaOH concentration, and stabilization time (i.e., a time allocated after each NaOH addition stage to ensure the precipitation reaction is completed and the pH level remains stable), will be comprehensively investigated in a series of batch reactors to optimize precipitation efficiency and enhance the purity of the precipitates. Third, the crystal structure, morphology, and elemental composition of precipitates will be characterized by XRD, SEM, EDS-mapping, and ICP-OES techniques. Fourth, the carbon neutrality of the process will be evaluated by capturing CO₂ via NaOH-enriched effluent and the subsequent production of sodium bicarbonate (NaHCO₃). In this step, the produced NaHCO₃ will be utilized to separate calcium from the residue of the acid-leaching step. Eventually, the potential viability and economic feasibility of the proposed hydrometallurgical process will be preliminarily assessed through the characterization and quantification of solid and liquid products. In this step, the capital and operating expenditures (Capex and Opex) of the proposed process for large-scale operations will be calculated based on the mass balance, and the minimum breakeven processing rate required to maintain a positive cash flow will be determined.

5.3 Experimental

5.3.1 Materials and reagents

The dolomitic limestone waste was supplied by OCP from the phosphate mine in Morocco. The leach liquor of dolomitic limestone was prepared according to our previous work through dilute acid leaching by 0.5 M H₂SO₄ at 80 °C for 60 min [275]. All chemicals were in analytical grade and used as received without further purification. Sulfuric acid (H₂SO₄; purity > 95 wt%) as leaching agent, sodium hydroxide (NaOH; pellet with purity > 99 wt%) as precipitant, and nitric acid (HNO₃, 70%) as ICP-based acid solution were purchased from MilliporeSigma Canada.

Standard buffer solutions at pH 4.01, pH 7.00, and pH 10.01 were purchased from Fisher Scientific Canada. In addition, all solutions throughout the experiments were prepared using distilled water.

5.3.2 Procedure of selective precipitation by sodium hydroxide

The selective recovery of metals from the leach liquor of dolomitic limestone occurred in an electromagnetic stir mantle using a four-neck round-bottom flask. Three necks of the flask were connected to the Allihn condenser, thermocouple type J, and pH meter probe. The remaining neck was connected with a 100 mL burette containing specific NaOH concentrations (0.1M, 0.5M, and 1M). Two series of alkaline precipitation were performed: single-step and multi-step precipitation. Single-step precipitation was employed to discover the insolubility zone of dissolved metals for selective precipitation, while multi-step precipitation was applied to duplicate the industrial process. In both precipitation processes, the temperature of leachate and agitation speed were first adjusted at the range of 20-80 °C and 500 rpm, respectively, and kept constant throughout the experiments. Before the precipitation test, the pH meter was calibrated by standard solutions at three defined pH values of 4.01, 7.00, and 10.01. In the single-precipitation process, the pH was raised slowly from 1 to 12 by adding 1M NaOH solution to the leachate dropwise. Herein, a certain stabilization time was allocated at each pH level to ensure complete precipitation and reach a stable pH level. During regular pH intervals from 1 to 12, a certain volume of solution was collected with a syringe and filtered with 0.22 µm nylon syringe filters (Fisher Scientific, Canada). Subsequently, the filtered solution was diluted with a certain volume of 5 wt% HNO₃ and sent for ICP-OES analysis.

After determining the insolubility zone of digested metals as a function of process temperature, NaOH concentration, and stabilization time, the multi-step precipitation was conducted to simulate the industrial process and recover desired products. In this procedure, the pH of the dolomitic limestone leach liquor was adjusted to the target level with NaOH solution, as defined by single precipitation experiments. Each precipitation step involved stirring the mixture for 60 min at 80 °C, followed by vacuum filtration to separate the solid and liquid phases. The resulting solid was rinsed several times with distilled water, dried at 80 °C for 10 h, and then characterized using various analytical techniques. For all precipitation experiments, the recovery efficiency (R_i) was calculated based on the mass of the target metal in leachate before and after precipitation as follows:

$$R_i \% = \frac{m_{i,prec}}{m_{i,leachate}} \times 100 = \left(1 - \frac{C_{i,prec}V_{prec}}{C_{i,leach}V_{leach}} \right) \times 100 \quad (5.1)$$

where $m_{i,leachate}$ and $m_{i,prec}$ are the mass of metal i in leachate (mg) and after precipitation at a specific pH level (mg). $C_{i,leach}$ and V_{leach} are assigned to the concentration of metal i in leachate (mg/L) and the volume of leachate solution (L). $C_{i,prec}$ and V_{prec} represent the concentration of metal i in leachate after precipitation (mg/L) and the volume of solution after precipitation (L). The purity of precipitated products (P_i) can also be defined based on the following equation:

$$P_i \% = \frac{m_{i,prec}}{\sum_{j=1}^n m_{j,prec}} \times 100 \quad (5.2)$$

In the above equation, $\sum_{j=1}^n m_{j,prec}$ is the summation of the mass of all metals precipitated at that specific pH.

The feasibility of CO₂ capturing and utilization was evaluated by exposure of NaOH-enriched effluent to a pure stream of CO₂ gas in a 500 mL Pyrex gas washing bottle equipped with a coarse frit disc. CO₂ was bubbled through the solution at a controlled flow rate of 20 mL/min for 4 h at 25 °C. Upon completion, NaHCO₃ precipitate was collected via vacuum filtration and dried at 70 °C. Along with the CO₂ capturing, calcium in the acid-leaching residue was selectively separated from quartz by dissolving gypsum in 300 mL of distilled water at 40 °C. The dissolved calcium solution was filtered to remove undissolved quartz and subsequently reacted with the synthesized NaHCO₃ to precipitate CaCO₃ solids. The resulting CaCO₃ was thoroughly rinsed with distilled water to ensure purity and dried at 80 °C. All the experiments in this research were repeated three times, and the results presented in the following sections are the average of these replications.

5.3.3 Thermodynamic simulation for selective precipitation

The thermodynamic simulations were performed using FactSage 8.3 software. The changes in enthalpy and Gibbs free energy during precipitation reactions were calculated by the Reaction Toolbox. The EpH toolbox of FactSage was employed to find the insolubility zone for selective precipitation. The mineral data for all thermodynamic simulations was extracted from the FToxid database. In addition, the thermodynamic data of ions and pure substances in solution were adopted

from the FThelg and FactPS databases, respectively. Species distribution diagrams for the Ca-S-O-H and Ca-S-O-H-Na-C systems as a function of pH were calculated using Medusa-Hydra software.

5.3.4 Characterization and analytical techniques

The mineralogy of dolomitic limestone waste rock was analyzed by the Quantitative Evaluation of Materials by Scanning Electron Microscopy (QEMSCAN; 650F, USA) equipped with a TESCAN Integrated Mineral Analyzer (TIMA, Tescan Vega TC x64, USA). The crystal structures of ores and solid products were characterized by X-ray diffraction measurement using Cu K α radiation (XRD; Bruker D8 ADVANCE; USA). The morphological characteristics of precipitates were analyzed by scanning electron microscopy (SEM, Hitachi TM3030 Plus, Japan). Also, the energy-dispersive X-ray spectroscope (EDS) linked to the SEM device was employed to determine the surface elemental composition and distribution. The changes in pH and redox potential (E) during the alkaline precipitation were recorded by pH meter (Thermo Scientific™ VSTAR13, Canada). The changes in metal concentration in the liquid phase were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent 5110, USA). To prepare the solid samples for ICP-OES analysis, a certain weight of each sample was digested by aqua regia solution at 100 °C for 24 h in a block digestion system (DigiPREP LS; SCP SCIENCE, Canada).

5.4 Results and discussion

5.4.1 Identification of dolomitic limestone leach liquor

The mineralogical composition of dolomitic limestone waste rocks was characterized by QEMSCAN analysis as presented in Figure A.1. More than eight distinct minerals were recognized in the dolomitic limestone waste rocks. The main minerals of which the mass distribution exceeded 4 wt.% include dolomite (about 78 wt.%), calcium silicate (about 14 wt.%), and quartz (about 4 wt.%). Approximately 6 wt.% of the dolomite mineral was completely liberated, while 92 wt.% remained associated with silicates. According to our previous work [275], 0.5 M H₂SO₄ with a temperature of 80 °C was the optimal condition for the digestion of 10 g/L dolomitic limestone waste rock with an average particle size of 45 μ m. The elemental compositions of dolomitic limestone leach liquor after this process were analyzed by ICP-OES, as presented in Table A.2.

The leach liquor predominantly contains 1187 ppm of Mg and 551 ppm of Ca. Other significant components include Si (22 ppm), P (7 ppm), Al (6.5 ppm), K (4 ppm), Fe (3 ppm), and Na (1.6 ppm). Additionally, the leach liquor contains 3 ppm of Mn and 2 ppm of Ti. Around 75% of the calcium and 82% of SiO₂ in dolomitic limestone were precipitated as the acid-leaching residue.

5.4.2 The insolubility region and selective precipitation reactions

The leach liquor of dolomitic limestone contained different metal cations, including Mg²⁺, Ca²⁺, Al³⁺, Na⁺, Fe³⁺, K⁺, Mn⁺, and Ti⁴⁺. The solubility of these metals inside the aqueous media was evaluated by the EpH toolbox of FactSage. This toolbox provides a diagram of redox potential (E) versus pH, which is renewed as a Pourbaix diagram. As presented in Figure 5.1, the Pourbaix diagram is a phase diagram that maps the regions where redox species are thermodynamically stable. These regions are a function of solution redox potential, pH, temperature, and redox species concentrations. The upper and lower dash lines in all figures indicate the redox potential for conversion of water to O₂ and H₂ at different pH, respectively. To prevent these side reactions during metal recovery, the leaching or precipitation processes need to happen between these dash lines, which is called the water stability zone.

As illustrated in Figure 5.1(a), seven regions existed for the Mg-Ca-H₂O system. At the temperature of 20 °C and pH below 10, magnesium and calcium are soluble in leachate and can be present in the form of Mg⁺² and Ca²⁺ in the water stability zone (region 1). By increasing the pH and decreasing the solution oxidative potential at room temperature, Mg and Ca will be precipitated in the form of Mg(OH)₂ and Ca(OH)₂ at pH above 10 (region 2) and 13 (region 3), respectively. Based on Figure 5.1(a), beyond the water stability zone, Mg²⁺ cations and CaO₂ solids are only stable phases at high oxidative potential and pH between 4 and 10 (region 4). At high oxidative potential and pH above 10, both Mg and Ca cations in the leachate will be oxidized to Mg(OH)₂ and CaO₂ solids (region 5). In addition, Mg and Ca cations in the leachate will be precipitated as Mg(OH)₂, MgH₂, and CaH₂ at high reductive potential for all pH ranges (regions 6 and 7).

Figures 5.1(b) to 5.1(e) indicate the solubility of other cations in dolomitic limestone leach liquor. Si, K, and Na are soluble cations at all pH ranges, while Ti will precipitate at low acidic pH (below 4). In addition, digested P is soluble at all pH and exists in the form of H₃PO₄, H₂PO₄⁻, HPO₄²⁻, and PO₄³⁻ in the water stability zone. At 20 °C, Al³⁺ is the dominant phase at a pH below 4, while it

exists in the form of Al_2O_3 above that pH. Regarding iron cations, Fe_2O_3 is insoluble at all pH in the water stability zone. However, Fe_3O_4 is a soluble compound that exists as Fe^{2+} in the leach liquor with a pH lower than 6 at 20 °C. Furthermore, Mn will precipitate as MnO_2 , Mn_2O_3 , and Mn_3O_4 at the oxidative leach liquor and pH above 8 at 20 °C. Based on these results, it can be concluded that selective recovery of Mg and Ca as the major elements in dolomitic limestone is feasible using the alkaline precipitation method. By adjusting the pH of the leach liquor below 8 at 20 °C, the Ti, Al, Fe, and Mn will be separated while Mg^{2+} and Ca^{2+} will remain in the dolomitic limestone leach liquor. Then, increasing the pH to 10 and 13 at 20 °C will lead to precipitation of Mg and Ca in the form of $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, respectively. It is worth mentioning that the temperature of precipitation plays a significant role in the solubility of metal cations. As depicted in Figures 5.1(a) to 5.1(e), the solubility regions of digested metals decrease, and precipitation can occur at a lower pH by increasing the temperature. In this regard, if the precipitation occurs at 80 °C, Ti, Al, Fe, and Mn in leach liquor can be precipitated at a pH of 3, 4, 6, and 7, respectively, while $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ can be recovered at a pH of 9 and 11, respectively (Figure 5.1(f)). The possible precipitation reactions and their thermodynamic parameters at 80 °C have been presented in Table 5.1. As presented in this table, the K_{eq} for all precipitation reactions is very high ($K_{\text{eq}} \gg 1$), indicating that the equilibrium mixture mainly consists of precipitates [276].

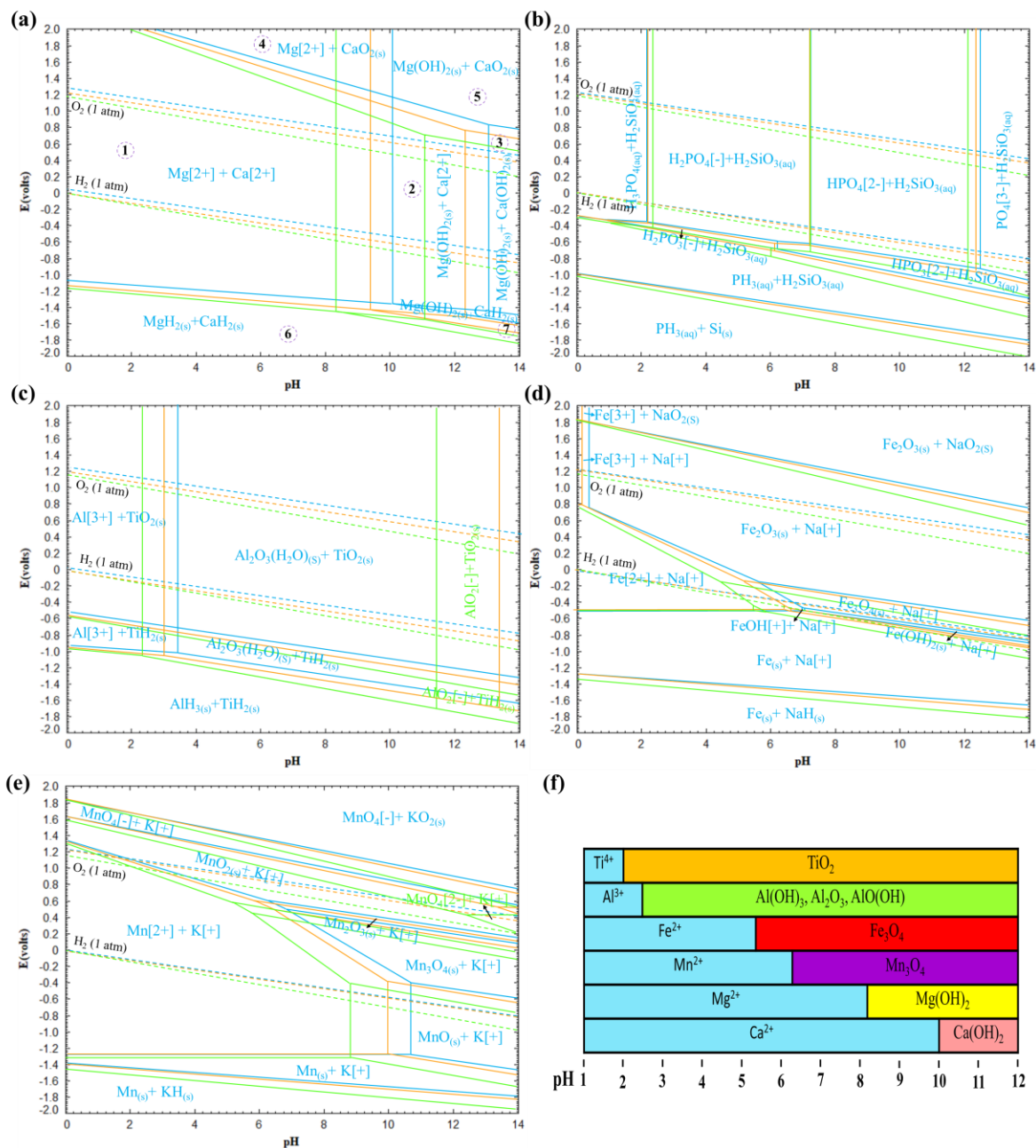


Figure 5.1 The Pourbaix diagrams at different temperatures (blue line: 20 °C, orange line: 40 °C, and green line: 80 °C) for the systems of (a) Mg-Ca-H₂O, (b) Si-P-H₂O, (c) Al-Ti-H₂O, (d) Fe-Na-H₂O, (e) Mn-K-H₂O; and (f) insolubility zones of metal cations adopted from the Pourbaix diagrams at 80 °C.

Table 5.1 The possible precipitation reactions and their related thermodynamic parameters.

NO.	Reaction	$\Delta H_{353.15}$ (kJ/mol)	$\Delta G_{353.15}$ (kJ/mol)	$K_{eq,353.15}$	S		
					1 M NaOH	0.5 M NaOH	0.1 M NaOH
(5.3)	$NaOH_{(s)} \leftrightarrow Na^+_{(aq)} + OH^-_{(aq)}$	-63	-43	2.2E+06			
(5.4)	$Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \leftrightarrow Mg(OH)_{2(s)}$	17	-78	3.4E+11	1.7E+10	4.2E+09	1.7E+08
(5.5)	$Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \leftrightarrow Ca(OH)_{2(s)}$	35	-41	1.1E+06	1.5E+04	3.8E+03	1.5E+02
(5.6)	$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \leftrightarrow Al(OH)_{3(s)}$	-32	-207	4.2E+30	1.0E+27	1.3E+26	1.0E+24
(5.7)	$2Al^{3+}_{(aq)} + 6OH^-_{(aq)} \leftrightarrow Al_2O_{3(s)} + 3H_2O_{(l)}$	-20	-419	9.7E+61	5.6E+54	8.8E+52	5.6E+48
(5.8)	$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \leftrightarrow Fe(OH)_{2(s)}$	-9	-114	6.5E+16	3.5E+12	8.7E+11	3.5E+10
(5.9)	$2Fe^{3+}_{(aq)} + 6OH^-_{(aq)} \leftrightarrow Fe_2O_{3(s)} + 3H_2O_{(l)}$	-153	-562	1.4E+83	4.2E+74	6.5E+72	4.2E+68
(5.10)	$Fe^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} + 8OH^-_{(aq)} \leftrightarrow Fe_3O_{4(s)} + 4H_2O_{(l)}$	-165	-694	3.9E+102	6.3E+89	2.5E+87	6.3E+81
(5.11)	$2Mn^{2+}_{(aq)} + 4OH^-_{(aq)} + \frac{1}{2}O_{2(l)} \leftrightarrow Mn_2O_{4(s)} + 2H_2O_{(l)}$	-125	-288	3.6E+42	1.1E+33	7.1E+31	1.1E+29
(5.12)	$3Mn^{2+}_{(aq)} + 6OH^-_{(aq)} + \frac{1}{2}O_{2(l)} \leftrightarrow Mn_3O_{4(s)} + 3H_2O_{(l)}$	-146	-401	2E+59	1.1E+45	1.7E+43	1.1E+39
(5.13)	$Mn^{2+}_{(aq)} + 2OH^-_{(aq)} \leftrightarrow MnO + H_2O_{(l)}$	-20	-419	9.7E+61	1.7E+57	4.3E+56	1.7E+55
(5.14)	$Ti_{(l)} + 2OH^-_{(aq)} + 2H^+_{(aq)} \leftrightarrow TiO_{2(s)} + H_{2(l)}$	-474	-562	1.4E+83	3.8E+77	9.6E+76	3.8E+75

5.4.3 Single-step precipitation by NaOH

For single-step precipitation, 1M NaOH was employed to recover digested metals from dolomitic limestone leach liquor at temperatures of 20 °C, 60 °C, and 80 °C. Figure 5.2 demonstrates the solubility of metals, precipitation percentage, and purity of recovered metals as a function of pH at various temperatures. According to Figure 5.2(a), the mass concentration of Mg^{2+} in leach liquor at 20 °C was constant until pH 9. Subsequently, a sharp decrease in Mg^{2+} mass concentration was

observed in the pH range of 9 to 10.5, indicating the precipitation of digested Mg from leach liquor. Considering the Ca, its mass concentration remained unchanged until a pH of 10. From this pH onward, Ca^{2+} mass concentration significantly declined up to a pH of 12. In addition, the slight co-precipitation of Mn was observed with Mg and Ca in the pH range of 8 to 12. The rest of the metal cations, including Al, Fe, Mn, and Ti, were precipitated from the leach liquor in the pH ranges of 4 to 8. Si, K, Na, and P also did not precipitate in the pH range of 2 to 12, implying their strong solubility in an aqueous solution.

As shown in Figures 5.2(b) to 5.2(i), the reaction temperature significantly contributed to achieving selective precipitation. Based on Figures 5.2(a) to 5.2(c), increasing the temperature from 20 °C to 80 °C could decrease the precipitation pH level of Mg and Ca from 10.5 to 9 and from 12 to 11, respectively. In addition, the pH gap between metals' solubility increased, leading to lower co-precipitation and higher purities of precipitates. The comparison of Figures 5.2(f) and 5.2(i) with Figures 5.2(d) and 5.2(g) indicated that 98 % of Mg^{2+} with a purity of 99.5 % could be recovered at a pH 9 and temperature of 80 °C. In contrast, 15% of Mg^{2+} with a purity of 88% was precipitated at the same pH with a reaction temperature of 20 °C. A similar trend was observed for other metal cations. Raising the reaction temperature from 20 °C to 80 °C improved the recovery efficiency of Ca^{2+} from 25% to 90% and enhanced its purity from 19% to 99.8 % at pH 11. According to Figures 5.2(f) and 5.2(i), more than 90% of Ti^{2+} , Al^{3+} , Fe^{3+} , and Mn^{2+} were recovered selectively at pH levels of 3, 4, 6, and 7, respectively.

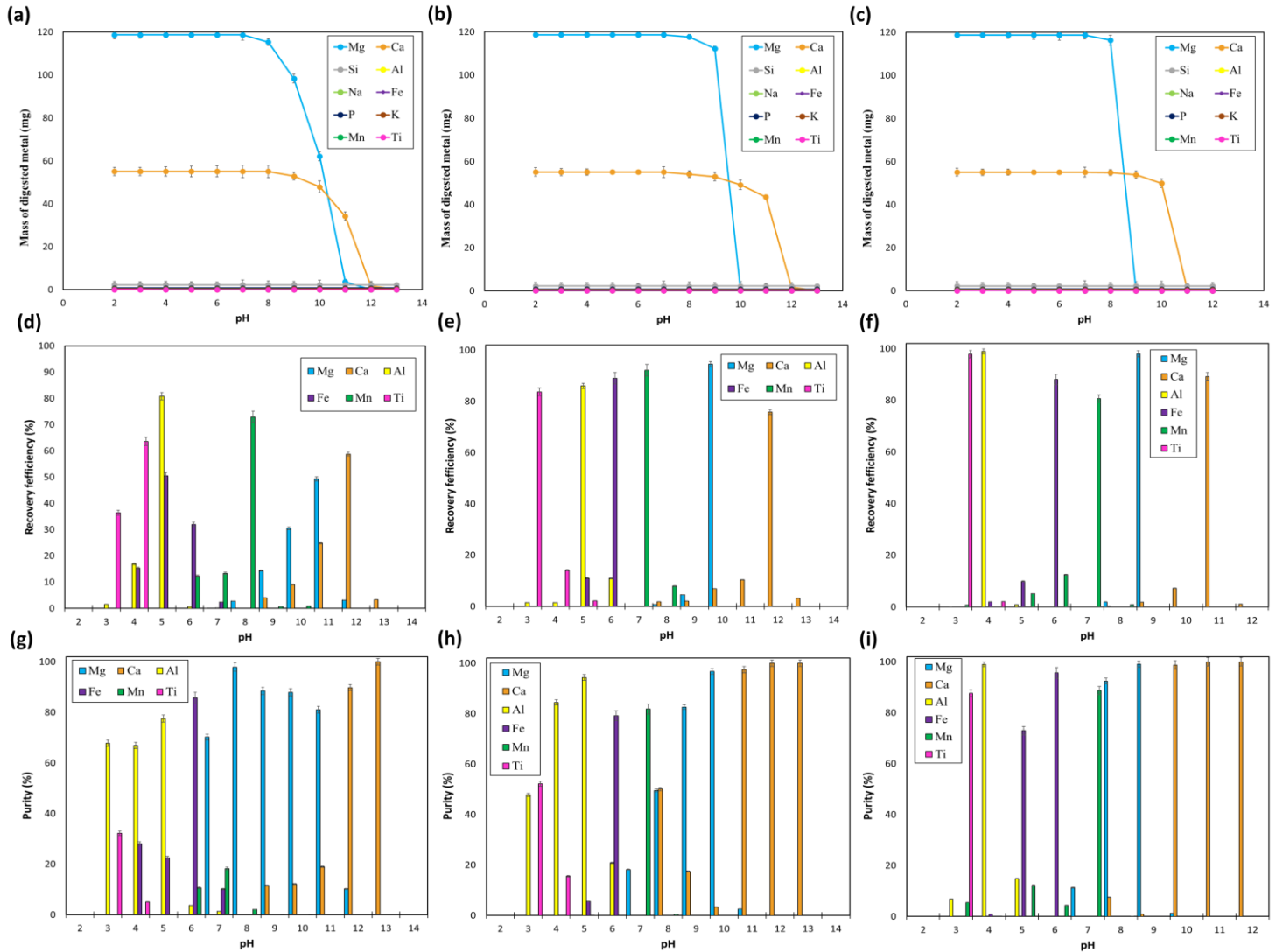


Figure 5.2 Precipitation of the leached metals from dolomitic limestone liquor at (a) 20 °C, (b) 60 °C, and (c) 80 °C with a single precipitant; recovery efficiency for selective precipitation from leachate liquor at (d) 20 °C, (e) 60 °C, and (f) 80 °C; and purity of selectively recovered metals from leachate liquor at (g) 20 °C, (h) 60 °C, and (i) 80 °C.

Two main reasons can explain the contribution of reaction temperature to selective precipitation. First, the solubility of metal cations depends on the precipitation reaction's equilibrium constant (K_{eq}). According to Van't Hoff equation (Equation (5.15)), the change in K_{eq} is related to the change in reaction temperature (T) in the given standard enthalpy change (ΔH_r°). In the following equation, R is the ideal gas constant.

$$\frac{d}{dT} \ln K_{eq} = \frac{\Delta H_r^\circ}{RT^2} \quad (5.15)$$

Regarding Table 5.1, the net ionic reactions for precipitation of metal cations with NaOH have negative enthalpy, suggesting the exothermic nature of precipitation reactions. Based on the Van't Hoff equation, the increase in temperature for an exothermic reaction leads to a decrease in the precipitation equilibrium constant. Therefore, the insolubility of metal cations is achieved at lower pH levels [252, 277].

The second reason is attributed to the kinetic energy of ions at elevated temperatures. According to the Arrhenius equation, increasing the temperature enhances the precipitation reaction's kinetic energy and fastens the precipitation rate at lower pH. Therefore, a wider pH gap is created between cations' insolubility regions, causing selective metals precipitation with higher purity [272].

The effects of reaction time and NaOH concentration on the recovery efficiency of Mg, Ca, Al, Fe, and Mn are exhibited in Figures 5.3(a) to 5.3(f). According to these figures, NaOH concentration significantly influences the stabilization time, and increasing the NaOH concentration could decrease the precipitation time. For Mg, Al, and Mn cations, increasing the NaOH from 0.1 M to 1M decreased the precipitation time from 80 min to 20 min. For Ca and Fe cations, the increase of NaOH concentration to 1 M made stabilization time around 40 min shorter than that for 0.1 M NaOH.

The changes in stabilization time as a function of NaOH concentration can be explained by the supersaturation (S) of metal cations. Supersaturation is a driving force for crystal nucleation and growth, established when the solute concentration exceeds its solubility value at equilibrium. The supersaturation of the leach liquor can be written as Equation (5.16), which is the ratio of the activity of metal cations (α_M) and precipitants (α_P) divided by the solubility product constant (K_{SP}) [278].

$$S = \frac{\alpha_M^a \alpha_P^b - K_{SP}}{K_{SP}} = \frac{\gamma_M^a [M]^a \gamma_{OH}^b [OH]^b - K_{SP}}{K_{SP}} \quad (5.16)$$

where γ is the activity coefficient for an ion that can be calculated using the extended Debye Hückel equation [279]. $[M]$ and $[NaOH]$ also represent the molar concentrations of Metal cations in leach liquor and NaOH precipitant. The calculated S values for the Reactions (5.4) to (5.14) at different NaOH concentrations are presented in Table 5.1. According to this table, the supersaturation values

for 1 M NaOH are 10^2 – 10^8 orders greater than that for 0.1 M NaOH. Consequently, due to higher supersaturation values, the instantaneous contact between metal cations and OH^- anions at higher NaOH concentrations leads to faster metals' precipitation from leach liquor. Conversely, the water dilution of leach liquor with 0.1 M NaOH leads to lower supersaturation values, making the precipitation condition milder and slower.

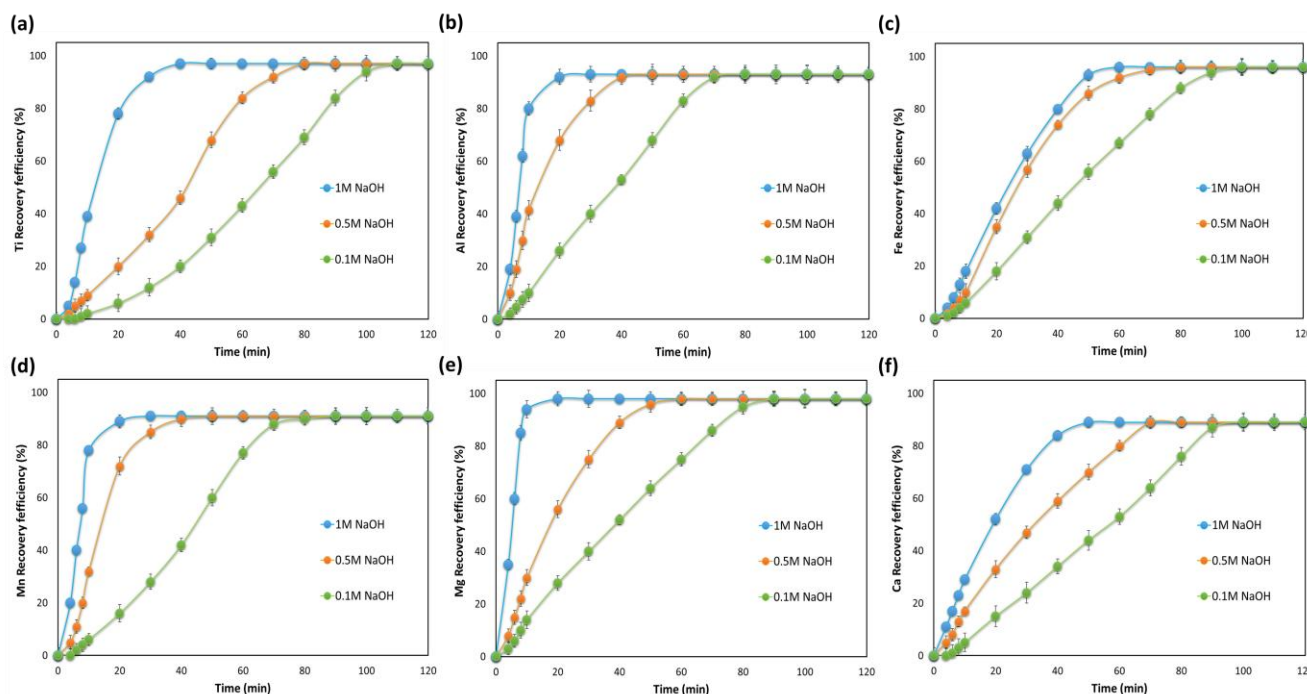


Figure 5.3 The effect of NaOH concentration and stabilization time on recovery efficiency of (a) Ti at pH 3, (b) Al at pH 4, (c) Fe at pH 6, (d) Mn at pH 7, (e) Mg at pH 9, and (f) Ca at pH 11.

5.4.4 Multi-step selective precipitation and precipitate characterization

According to the impact of key parameters in single-step precipitation, a reaction temperature of 80 °C, NaOH concentration of 1M, and stabilization time of 60 min were selected for the selective precipitation of metal cations from dolomitic limestone leach liquor. The multi-step precipitation was performed at the pH levels of 3, 4, 6, 7, 9, and 11 under optimum conditions to selectively recover Ti, Al, Fe, Mn, Mg, and Ca. The crystal phase structure and normalized oxide/hydroxide-equivalent mass compositions of obtained solid products in the multi-step precipitation are presented in Figures 5.4(a) and 5.4(b). The mass percentage of metal components in Figure 5.4(b) was calculated by incorporating XRD analysis with ICP-OES. In this context, the obtained solid products were redigested in aqua regia solution, and the mass balance was conducted in accordance

with crystal phases detected by XRD analysis. The morphology and elemental compositions of precipitates in the multi-step process are depicted in Figure 5.5.

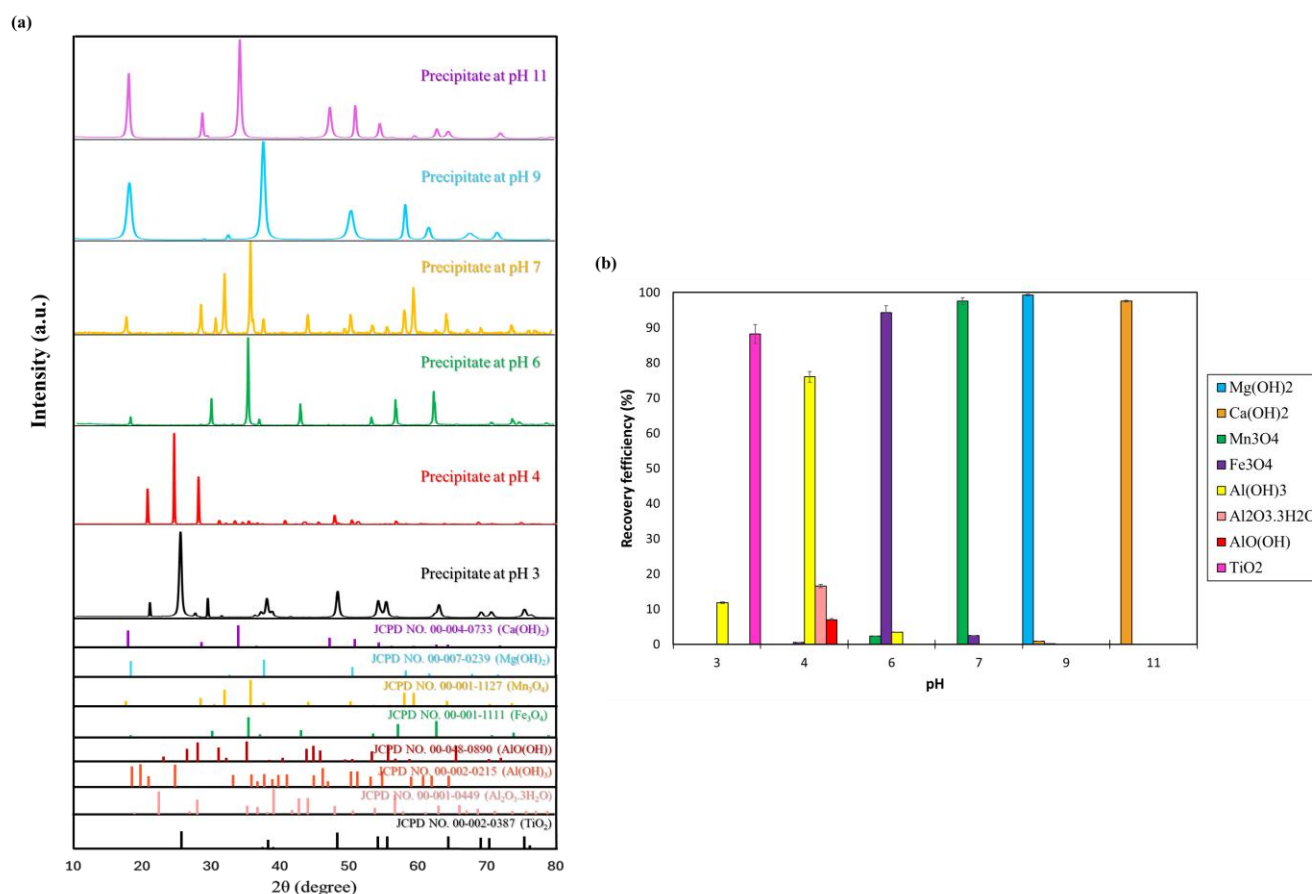


Figure 5.4 (a) The XRD pattern and (b) normalized oxide/hydroxide-equivalent mass compositions of obtained solid products in the multi-step precipitation.

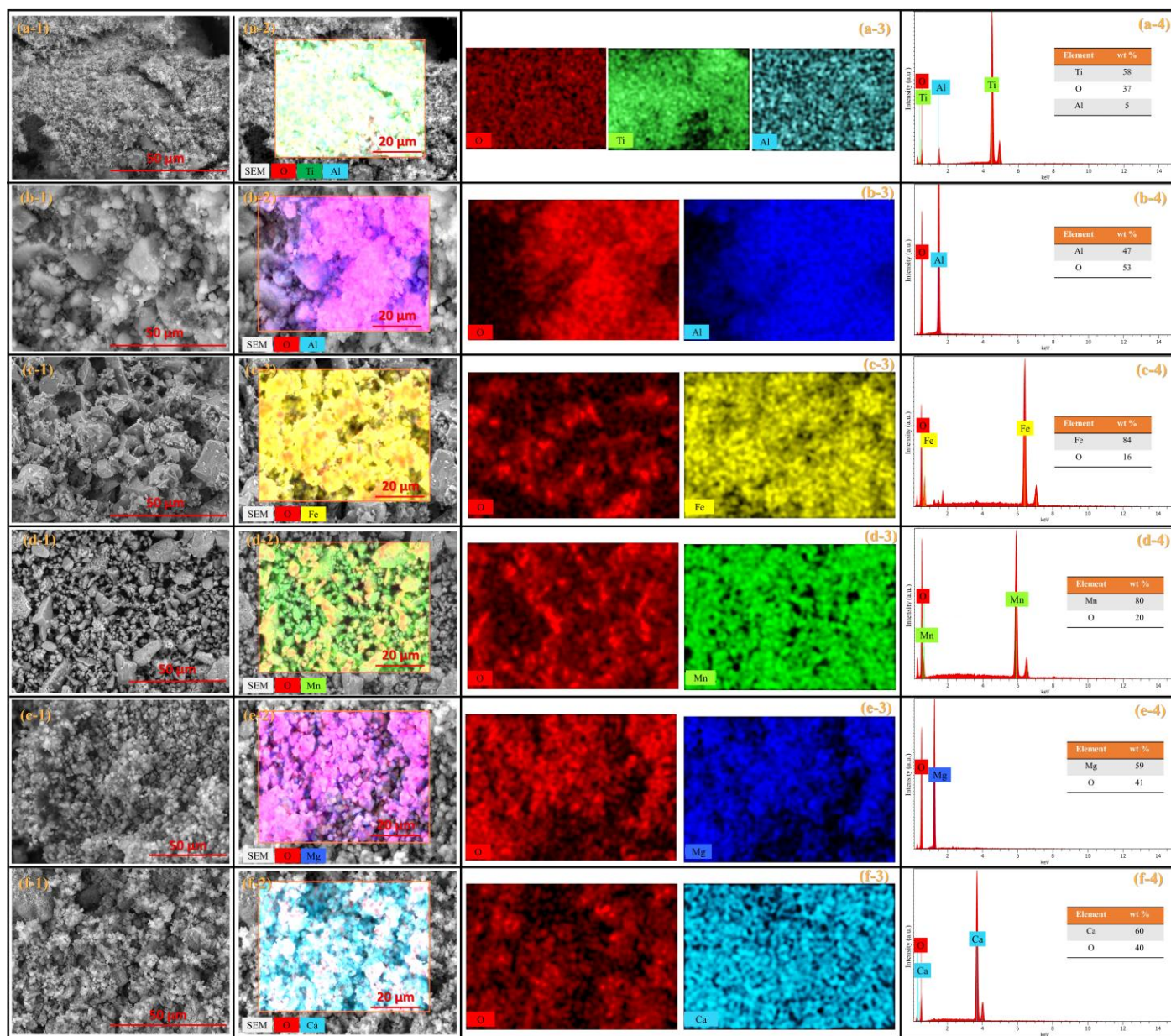


Figure 5.5 SEM images and EDs-mappings of (a) precipitates at pH 3, (b) precipitates at pH 4, (c) precipitates at pH 6, (d) precipitated at pH 7, (e) precipitated at pH 9, and (f) precipitated at pH 11.

As illustrated in Figure 5.4, 88 wt% of the solids obtained at pH 3 were TiO_2 with 12 wt% $\text{Al}(\text{OH})_3$. According to Figure 5.5(a), spherical $\text{Al}(\text{OH})_3$ particles were encompassed with nanoscale TiO_2 particles in the size of 500 nm. Based on Figure 5.4, 99 wt% of precipitates at pH 4 mainly consist of $\text{Al}(\text{OH})_3$, $\text{AlO}(\text{OH})$, and Al_2O_3 , in which $\text{Al}(\text{OH})_3$ is the dominant Al phase. Semi-quantitative XRD analysis using DIFFRAC.EVA software indicated that the aluminum precipitate comprises approximately 76 wt% $\text{Al}(\text{OH})_3$, 7 wt% $\text{AlO}(\text{OH})$, and 17 wt% $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. As shown in Figure 5.5(b), $\text{Al}(\text{OH})_3$ had spherical geometry with an average diameter of 5 μm. Considering Figures

5.4 and 5.5(c), around 95 wt% of solids precipitated at pH 6 consisted of cube-like Fe_3O_4 with an average particle size of 10 μm . Negligible Al and Mn were co-precipitated with Fe_3O_4 , including 5 wt% of precipitates. According to Figure 5.4, the precipitates achieved at pH 7 comprised 98 wt% Mn_3O_4 and 2 wt% Fe_3O_4 . Based on Figure 5.5(d), Mn_3O_4 had an irregular tetragonal shape with a micrometric size ranging from 2 to 6 μm . Regarding Figure 5.4, $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, with mass percentages around 99%, could be achieved by precipitation at pH 9 and 11. As demonstrated in Figures 5.5(e) and 5.5(f), $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ had microsphere morphology with average diameters of 4 μm and 2 μm , respectively.

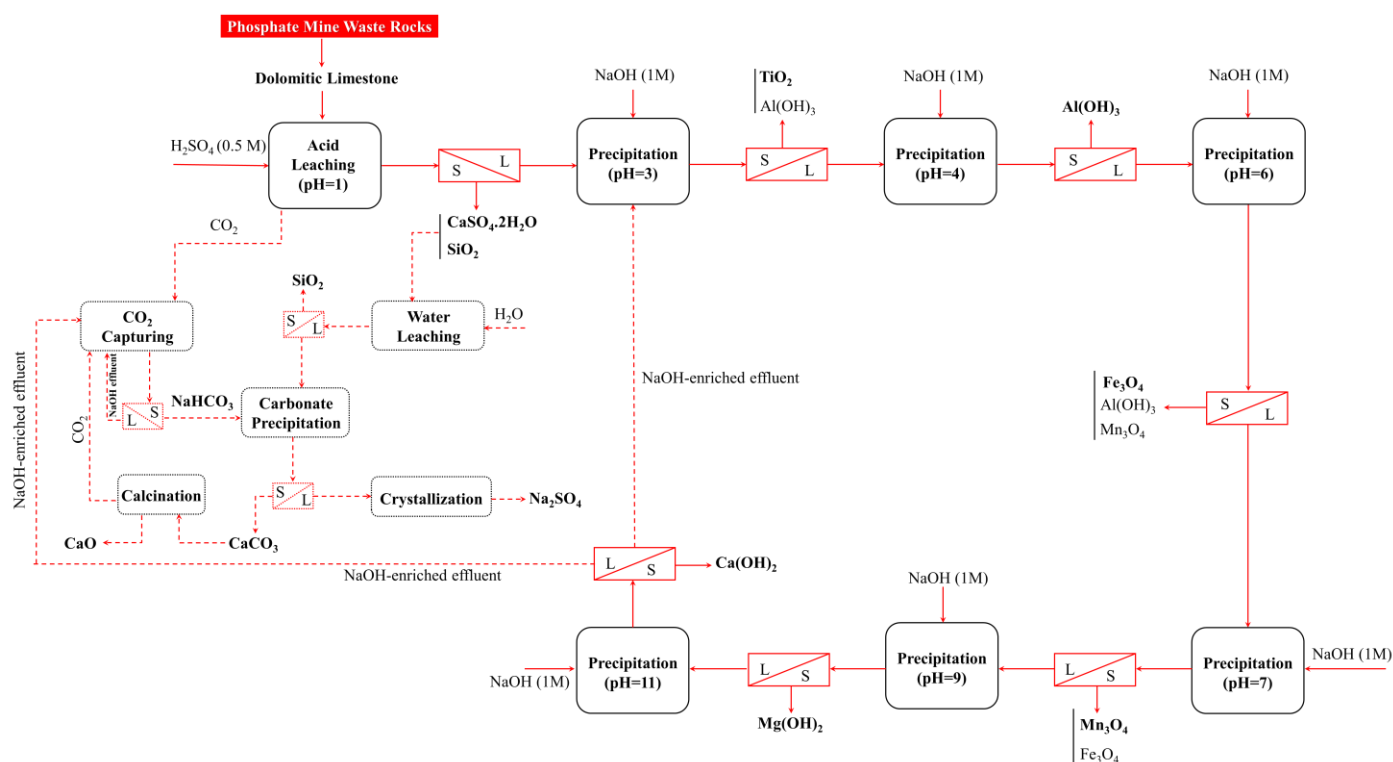


Figure 5.6 Block flow diagram for selective recycling of valuable metals from dolomitic limestone waste.

5.4.5 Kinetic of stepwise alkaline precipitation and corresponding activation energy

The Avrami kinetic model, also referred to as the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model, is a widely adopted approach for analyzing the kinetics of precipitation and crystallization processes. This model enables the evaluation of phase transformation rates by accounting for four

fundamental mechanisms, including nucleation, growth, soft impingement, and coarsening [269]. Under isothermal conditions, the Avrami model is expressed as Equation (5.17):

$$\alpha(t) = 1 - \exp(-kt^n) \quad (5.17)$$

where $\alpha(t)$ represents the fraction of the precipitated phase at time t (min). k is the apparent rate constant, and n is the Avrami exponent, often called the precipitation mechanism coefficient. The exponent n incorporates both the spatial and temporal dimensions of the transformation process. For homogeneous nucleation, the temporal dimension is unity, whereas it is zero for heterogeneous nucleation. To facilitate the extraction of kinetic parameters, Equation (5.17) can be linearized by taking the double logarithm of both sides, as follows:

$$\ln\left(\ln\left(\frac{1}{1-\alpha(t)}\right)\right) = n \ln(t) + n \ln(k) \quad (5.18)$$

The precipitation rate constant and exponent n can be determined from t the slope of the linear regression line in the plot of $\ln\left(\ln\left(\frac{1}{1-\alpha(t)}\right)\right)$ versus $\ln(t)$, which is shown in Figure A.2. The corresponding values for various metals are presented in Table A.3. Among the precipitated elements, Ti exhibited the highest precipitation rate, with a k value of 0.86 min^{-1} at 80°C . Mg, Al, and Mn followed, with rate constants ranging from 0.09 to 0.12 min^{-1} . Ca and Fe showed the lowest precipitation rates, at 0.04 min^{-1} and 0.03 min^{-1} , respectively. For all elements, decreasing the temperature from 80°C to 20°C caused a decrease in precipitation rates. The Avrami exponent for all metals ranged between 1 and 2, suggesting that the precipitation of metals such as Mg, Mn, Fe, Al, Ti, and Ca by NaOH is governed by an instantaneous nucleation mechanism followed by diffusion-controlled growth.

The activation energy (E_a) of the precipitation process can be estimated using the Arrhenius equation in its logarithmic form, as written in Equation (5.19).

$$\ln(k) = \ln(A_0) - \frac{E_a}{RT} \quad (5.19)$$

where k is the apparent rate constant, A_0 is the Arrhenius pre-exponential factor or frequency factor (min^{-1}), E_a is the apparent activation energy (kJ/mol), T is the leaching temperature (K), and R is the universal gas constant ($8.314 \text{ J}/(\text{mol}\cdot\text{K})$). According to Equation (5.19), the E_a and A_0 can be obtained from the slope and intercept of the plot of $\ln(k)$ versus $\frac{1}{T}$. As shown in Figure A.3, $\ln(k)$ is linearly dependent on $\frac{1}{T}$ with a correlation coefficient of 0.91. As illustrated in Table A.3, the activation energies for precipitation of Mg, Fe, and Al were approximately 19 kJ/mole, 16 kJ/mole, and 15 kJ/mole, respectively. The activation energies for precipitation of Mn, Ti, and Ca were also around 10 kJ/mole. The activation energy values below 20 kJ/mole further reveal that the rate-limiting step is the mass diffusion of ions through the fixed layer of the solution around the nucleates and precipitates.

5.4.6 Carbon-neutral process for valorization of dolomitic limestone waste rocks

Based on the experimental results, a novel closed-loop process for the valorization of dolomitic limestone waste rock is proposed, as illustrated in Figure 5.6. In the first step, dolomitic limestone waste is subjected to dilute acid leaching using 0.5 M H_2SO_4 . Our previous work systematically evaluated the effect of leaching parameters such as acid concentration, temperature, particle size, and solid-to-liquid ratio [275]. The dilute acid required for this process can be sustainably sourced from the effluent recovery stream generated during phosphoric acid production via wet chemical methods. Following leaching, solid residues primarily composed of gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$) and SiO_2 are obtained. Gypsum has established applications in construction materials (e.g., plasterboards, cement production) and soil conditioning [68] while SiO_2 is used across industries from food manufacturing to electronics and biomedicine [280, 281].

The leachate is then subjected to stepwise pH adjustment to selectively recover critical metals. TiO_2 precipitates at pH 3 and finds applications in solar cells, photocatalysis, and self-cleaning surfaces [282-284]. In addition, the co-precipitated $\text{Al}(\text{OH})_3$ with TiO_2 at pH 3 can be separated by physical or chemical methods or be utilized to produce Ti-Al alloy. For the perspective of separation, either physical separation based on density difference (4.23 g/cm^3 for TiO_2 vs. 2.42 g/cm^3 for $\text{Al}(\text{OH})_3$) or chemical separation based on solubility difference (at pH 3, Al is soluble while Ti is insoluble) can be employed. In the case of direct processing into Ti-Al alloys,

the mixture can be electrochemically reduced in a molten salt medium such as KCl-LiCl-MgCl_2 at elevated temperatures, enabling the co-production of Ti-Al metallic phases. Ti-Al alloys are valued for their high-temperature resistance and lightweight properties, making them highly attractive for automotive and aerospace applications [285]. At pH 4, Al(OH)_3 , Al_2O_3 , and AlO(OH) are recovered, with broad applications in ceramics, flame retardants, and biomedical materials [286, 287]. Further pH adjustments yield Fe_3O_4 at pH 6, Mn_3O_4 at pH 7, and high-purity Mg(OH)_2 and Ca(OH)_2 at pH 9 and 11, respectively. These materials have versatile uses in environmental remediation, construction, catalytic processes, healthcare industries, and energy storage and conversion [288-291].

Despite the successful recovery of critical metals, two main environmental challenges are associated with the process, including (I) the generation of CO_2 gas during acid leaching and (II) the production of NaOH-enriched effluent after precipitation. To address these issues, we developed a carbon-neutral strategy by utilizing the NaOH-enriched effluent to capture CO_2 , forming NaHCO_3 , which can then be used for further material recovery.

Calcium cations' dissolution and precipitation behavior in the presence of sulfate anions were analyzed thermodynamically. As shown in Figure 5.7(a), calcium cations and sulfate anions can coexist as aqueous CaSO_4 and solid $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) at neutral pH. Thus, from a thermodynamic perspective, gypsum is moderately soluble in water, while SiO_2 is insoluble. Given this distinction, water leaching can be a practical route to separate calcium from the leachate residue. To validate these predictions, water-leaching experiments were conducted at 40 °C with 300 mL of distilled water, resulting in the complete dissolution of gypsum. The experimentally measured solubility of 2.4 g/L aligns well with literature-reported values [292, 293].

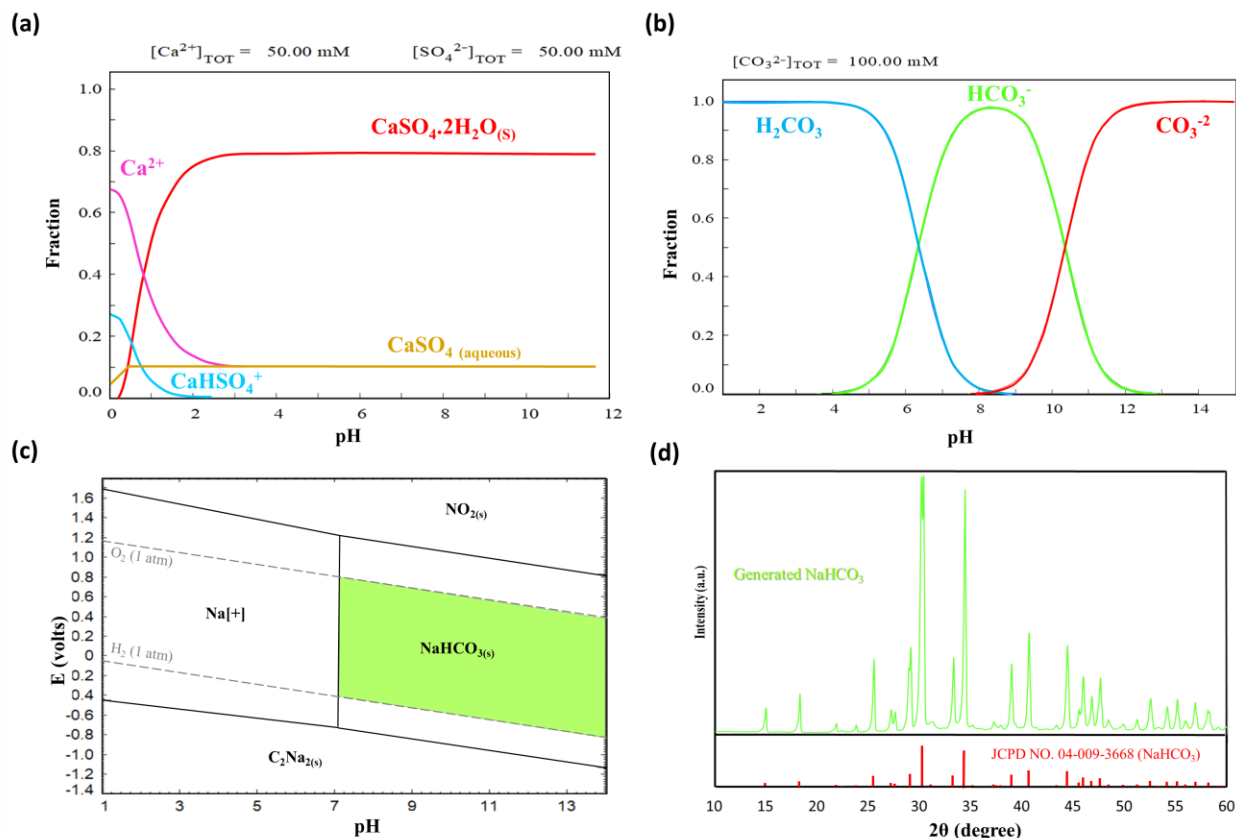


Figure 5.7 (a) Distribution fraction for Ca in Ca-S-O-H system at different pH, (b) distribution fraction for CO_2 in C-O-H system at different pH, (c) Pourbaix diagram for Na-O-H-C system at atmospheric pressure and 25 °C, and (d) XRD pattern of solids obtained by CO_2 bubbling NaOH-enriched effluent.

Thermodynamic simulation further elucidated the absorption of CO_2 in aqueous solutions under varying pH conditions. According to Figure 5.7(b), CO_2 can exist in three distinct forms in water depending on the pH, including carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), or carbonate ions (CO_3^{2-}). As illustrated in Figure 5.7(c), When CO_2 is absorbed in NaOH-enriched effluent, it reacts to form carbonate ions, which subsequently combine with NaOH to precipitate as $NaHCO_3$. To validate this mechanism, the NaOH-enriched effluent was subjected to a pure CO_2 stream at a flow rate of 20 mL/min at 25 °C. After 4 h, the solution transformed into a white slurry, indicating the formation of $NaHCO_3$. The as-prepared white powder was separated by vacuum filtration, and then the crystal phase was characterized by XRD analysis. As shown in Figure 5.7(d), the diffraction peaks at all 2θ are attributed to the $NaHCO_3$ with a Monoclinic crystal shape based on JCPD NO. 04-009-3668. Following the precipitation of $NaHCO_3$, we can utilize it to extract Ca in the form of $CaCO_3$ from dissolved gypsum solution, as shown in Figure 5.6.

Thermodynamic analysis of the Ca-S-O-H-C-Na system presented in Figures A.4(a) to A.4(d) revealed the pH-dependent speciation of calcium, sulfate, sodium, and carbonate ions. Based on Figure A.4(a), the sulfate anion will react with Ca cations and form gypsum in a solid phase at pH below 6. However, above this pH, sulfur will present in the aqueous phase in the form of SO_4^{2-} and NaSO_4^- . Considering Figure A.4(b), Na cations will react with CO_3^{2-} and SO_4^{2-} anions at a pH range of 4 to 11, forming NaHCO_3 and NaSO_4^- . At a more basic pH above 9, Na will attend as NaCO_3^- . With respect to Figure A.4(c), at pH above 5, carbonate and bicarbonate anions can react with sodium and calcium, resulting in the formation of NaHCO_3 and CaCO_3 . Consequently, as depicted in Figure A.4(d), CaSO_4 in the aqueous phase can thermodynamically react with NaHCO_3 and cause the formation of solid CaCO_3 and aqueous NaSO_4^- . This thermodynamic analysis was experimentally assessed by the addition of as-produced NaHCO_3 into dissolved gypsum in water. After 5h stirring under 500 rpm at 25 °C, the white powder was precipitated. Based on the XRD result presented in Figure 5.8(a), CaCO_3 with a Rhombohedral crystal structure was the main phase of white precipitate. According to Figure 5.8(b), precipitated CaCO_3 has a quasi-cubed shape with an average particle size of 3 μm . Regarding the ICP-OES analysis, the recovery efficiency of CaCO_3 was 100% with purity of 98%. The CaCO_3 can be directly employed as a primary raw material for producing Portland cement and building construction or be calcined at 800 °C to produce CaO . CaO has broad applications in cement and mortar construction, water treatment, flue gas desulfurization, soil amendment, thermochemical energy storage systems, and food and health industries [294, 295]. If the production of CaO is the main aim, liberated CO_2 during calcination can be captured by NaOH -rich effluent and be reused for NaHCO_3 generation. Eventually, the effluent after CaCO_3 precipitation is aqueous Na_2SO_4 that can be separated in solid form through crystallization. Na_2SO_4 has diverse applications and can be used as a detergent, glass manufacturing, energy storage system, and impregnating agent in the kraft pulping process [296, 297].

Based on the above results, it can be observed that our developed process can be a novel approach to valorized dolomitic limestone waste rock via a carbon-neutral hydrometallurgical process. This novel process not only mitigates environmental emissions but also offers a sustainable solution for industrial waste management.

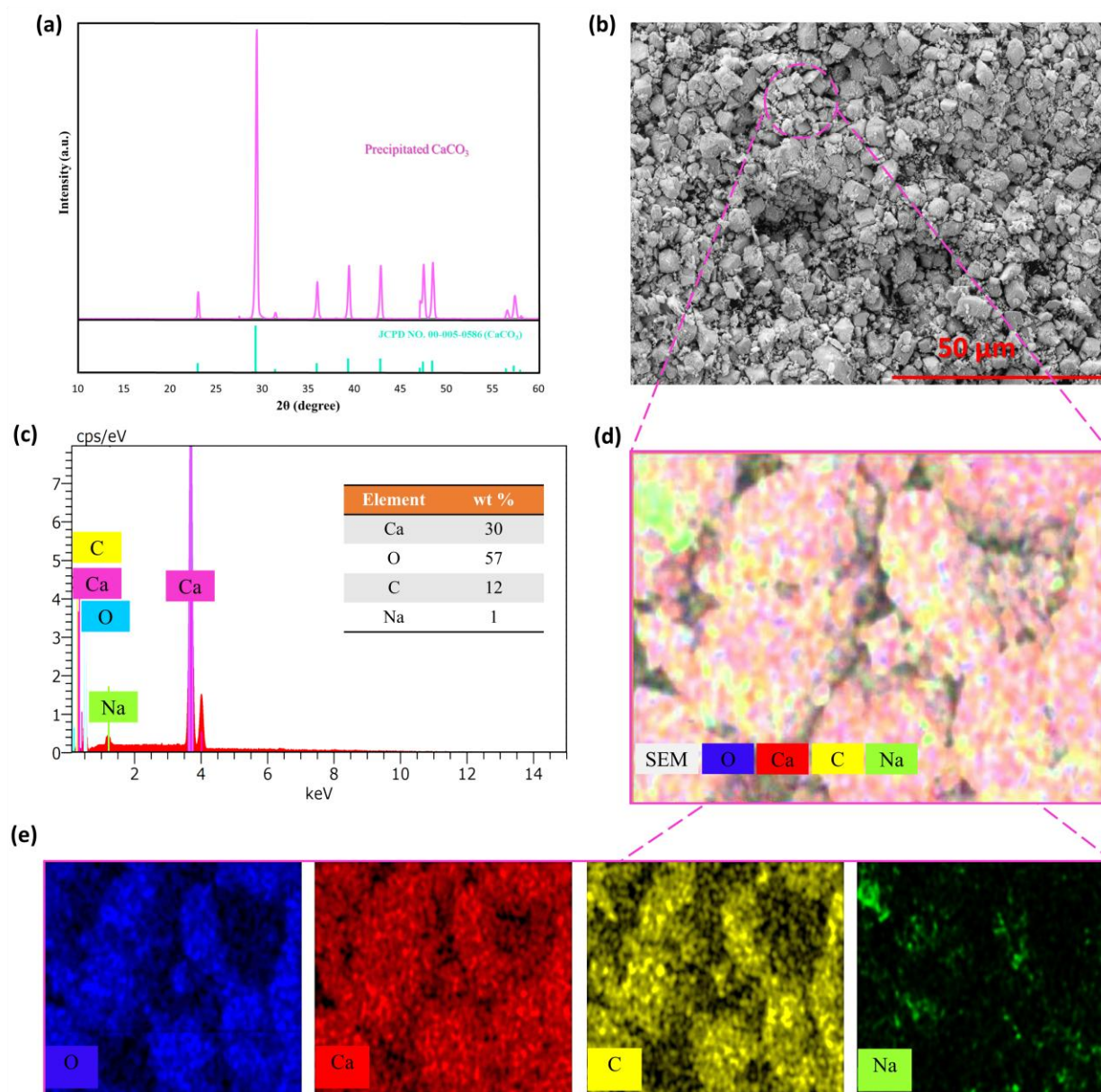


Figure 5.8 (a) XRD pattern, (b) SEM image, (c) EDS, and (d)-(e) Mapping of precipitated CaCO_3 using synthesized NaHCO_3 .

5.4.7 Comparison of precipitation approaches for critical metals recovery

A detailed comparison between our developed process and previously reported precipitation-based metal recovery processes is summarized in Table A.1. Various studies have employed different alkaline precipitants such as ammonia solution, $\text{Ca}(\text{OH})_2$, and NaOH to separate critical metals from leachates derived from dolomitic rocks, laterite ores, synthetic seawater, and steelmaking

slags. While some studies successfully achieved high recovery rates for target metals, significant co-precipitation of undesired elements such as Ca, Fe, Mn, Al, and trace elements frequently occurred [23, 232, 268-271, 298]. For instance, the use of NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ often required oxidizing agents like H_2O_2 to remove iron and aluminum impurities, adding complexity and reagent cost [23, 268]. Moreover, the relatively low alkalinity of ammonia necessitated higher pH thresholds, longer precipitation times, and led to lower selectivity. Other approaches using $\text{Ca}(\text{OH})_2$ [270] or Na_2CO_3 [269] were associated with substantial co-precipitation of multiple metal ions, particularly at overlapping pH ranges, reducing product purity. Even when NaOH was employed in steelmaking slag leachate treatment [272], selectivity remained limited, with co-precipitation of Mg, Al, Ca, Mn, and Fe at different pH thresholds.

In contrast, the process developed in our study integrated thermodynamic modeling with systematic experimental validation to establish a selective, stepwise precipitation route using only NaOH as the precipitant. By carefully tuning the pH and ORP at each stage, selective recovery of Ti, Al, Fe, Mn, Mg, and Ca was achieved with recovery efficiencies of 90%-99% and product purities exceeding 90%-99%, depending on the metal. Co-precipitation of other elements was minimized, as confirmed by ICP-OES, ICP-MS, XRD, and EDS analyses. Furthermore, our process has offered an environmentally sustainable advantage by recycling the NaOH-rich effluent to capture CO_2 released during the acid leaching stage, producing NaHCO_3 and contributing to carbon neutrality. This closed-loop integration of critical metal recovery with CO_2 sequestration has not been previously reported in the hydrometallurgical processing of carbonate-rich mining wastes. Therefore, compared to conventional hydrometallurgical methods, our proposed strategy demonstrates superior metal selectivity, higher product purity, greater operational simplicity (using a single, widely available precipitant without complexing agents or oxidants), and improved environmental compatibility, providing a robust pathway toward industrial implementation of sustainable resource recovery from dolomitic limestone waste rock.

5.4.8 Preliminary economic evaluation

A preliminary economic analysis was performed to evaluate the feasibility and profitability of the proposed hydrometallurgical process for the recovery of valuable metals, including Mg, Ca, Si, Al, Fe, Mn, and Ti from dolomitic limestone obtained from phosphate mine waste rocks. As illustrated in Figure A.5, the industrial-scale model of the proposed process comprises a stirred tank for dilute

H₂SO₄ acid leaching, six stirred tanks for selective alkaline precipitation at six different pH, and seven gravity filter tanks for passive solid-liquid separation. The cost of raw materials, energy consumption, and final product was estimated by employing the approximate market value of metals and metal compounds (i.e., Oxides, hydroxides, and sulfates) and data achieved from experimental results. The capital and auxiliary operating costs were calculated in accordance with the methodology suggested by Turton et al. [299].

Based on the preliminary economic evaluation shown in Figure A.6, 322 kg of dolomitic limestone/h is the minimum breakeven processing rate at which gross revenue exceeds the total operating cost. Therefore, this flow rate of dolomitic limestone is essentially required to obtain positive cash flow. The proposed hydrometallurgical process possesses a fixed capital investment on the order of US\$ 4.5 million, of which approximately half (US\$ 2.6 million) belongs to seven stirred tanks for leaching and precipitation reactions. As the precipitation process is conducted under mildly alkaline conditions, with the NaOH concentrations in the precipitation tanks ranging between 0.1 M and 0.3 M at 80 °C based on the target pH from 3 to 11, stainless steel 304 or 316 tanks are recommended due to their proven long-term corrosion resistance under such conditions [300]. Regarding the annual operating cost for a dolomitic limestone feeding rate of 400 kg/h, the major contributing parameters are raw material costs (US\$ 1.7 million/year for H₂SO₄, NaOH, and water), operating labor (US\$ 360,000/year) and utility costs (US\$ 261,000/year), that cause a total cost of US\$ 2.3 million/year. It should be emphasized that the conducted economic analysis is an approximate calculation considering a plant launching at the breakeven capacity. In other words, the payback period (PBP) to recover the fixed capital investment after the project's start-up is ignored at this stage. Since the proposed hydrometallurgical process engages two conventional equipment (i.e., stirred tank reactor and gravity filter separator) and generates around US\$ 387,000/year profit for a dolomitic limestone feeding rate of 400 kg/h, it has great potential for scale-up. Therefore, phosphate mine industries can establish this new unit to valorize the dolomitic limestone waste.

The main issues associated with the proposed hydrometallurgical process at an industrial scale can be related to applying an H₂SO₄ leaching agent and dealing with alkaline leach liquor (pH of 12) collected at the project's final step. Because of employing a diluted H₂SO₄ solution (0.5 M), the proposed process is not only compatible with the environment but also contributes to safer

industrial operations. In addition, H_2SO_4 is the common raw material in phosphate industries used to produce acid phosphoric from phosphate rock by wet chemical reaction. The recovery of H_2SO_4 waste collected from the phosphoric acid production line and applying it for leaching dolomitic limestone can increase the sustainability and profitability of the proposed hydrometallurgical process. Regarding the final effluent after precipitation at pH 12, alkaline leach liquor can be recycled and reused for selective precipitation of metals from the dolomitic limestone leach liquor. In this way, the consumption of NaOH in the inlet of the precipitation stage will be decreased. In addition, it can be employed to capture CO_2 from the acid leaching step and produce NaHCO_3 precipitant. Less than 0.7% of total P and Si in the leachate co-precipitated during the stepwise alkaline precipitation process from pH 9 to 11. The majority of Si and P remained in the NaOH-enriched effluent in the forms of H_2SiO_3 and HPO_4^{2-} . Recovery of these elements could be achieved through silica polymerization under high acidity (2-8 M with mineral acid) to form silica gel nanoparticles, followed by phosphorus precipitation as dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) via Na_2EDTA chelation and CaO addition, as reported in previous studies [301, 302].

More details about the preliminary economic evaluation are described in the supplementary file. It should be emphasized that all the above calculations were a rough preliminary economic analysis and should be evaluated more qualitatively than strictly quantitative. To gain a reliable cost evaluation for an industrial-scale operation, further investigations are required in terms of process flowsheet optimization, equipment sizing, and equipment materials selection. An iterative scale-up approach is crucial for ensuring operational stability, process robustness, and economic viability. Instead of direct extrapolation, a stepwise scale-up strategy that includes successive pilot-scale evaluations will progressively address challenges related to homogeneous mixing efficiency, precise pH control, solid-liquid separation, and heat transfer management at higher throughputs. In the proposed process, the mildly alkaline operating conditions at temperatures below 80°C allow the use of standard industrial materials, such as stainless steel grades 304 and 316, which minimizes corrosion risks. However, factors such as maintaining uniform supersaturation levels and preventing localized co-precipitation in larger volumes must be carefully optimized at each stage of scale-up. To further enhance process control and separation efficiency, implementing automated pH control systems, baffled reactor designs, and advanced filtration techniques suitable for continuous or semi-continuous operations will be essential. Future work will prioritize pilot-scale

validation under semi-continuous and continuous flow regimes, enabling iterative refinement of reactor design and process parameters. This stepwise scale-up approach will reinforce the technological readiness of the developed method for full-scale industrial adoption in waste valorization and resource recovery sectors.

5.5 Conclusion

This study successfully developed a method for the selective alkaline precipitation of Mg, Ca, Al, Fe, Mn, and Ti. The process was validated through thermodynamic simulations, lab-scale experiments, and characterization of both liquids and solids. Our thermodynamic simulations revealed that increasing the temperature of the pregnant leach solution from 20 °C to 80 °C within the water stability zone reduces the precipitation equilibrium constant and enhances the pH separation of metal insolubility. Consequently, selective separation of leached metals is feasible at 80 °C and ORP of -1 V to 1.2 V using a single hydroxide precipitant without the need for additional oxidizing, reducing, or stabilizing agents. The supersaturation factor analysis confirmed that 1M NaOH is sufficient for immediate metal precipitation at the specified pH levels. Experimental results were consistent with thermodynamic predictions. Optimal conditions for high-purity metal precipitation were achieved through a six-step sequential precipitation with 1M NaOH at 80 °C for 60 min. At pH 3, TiO₂ nanoparticles were the predominant solids, while at pH 4, Al(OH)₃ was the main phase among aluminum compounds. At pH 6 and 7, cubic Fe₃O₄ and tetragonal Mn₃O₄ were the primary precipitates, respectively. Microspherical Mg(OH)₂ and Ca(OH)₂ were the main products at pH 9 and 11, respectively. The NaOH-enriched effluent facilitated CO₂ sequestration and NaHCO₃ production, enabling further separation of calcium from leach residues as CaCO₃. Preliminary economic evaluations indicate that the proposed hydrometallurgical process is feasible and profitable for sustainably valorizing dolomitic limestone from phosphate mine waste, with a minimum breakeven processing rate of 322 kg of solid waste per hour. Although the payback period was not included in this analysis, the process shows substantial potential for scale-up, projecting an estimated profit of US\$ 387,000 per year at a processing rate of 400 kg of dolomitic limestone per hour.

5.6 Supporting Information

Additional information on preliminary economic analysis, detailed assumptions, calculations and supporting results (Appendix A).

5.7 Acknowledgments

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CHAPTER 6 ARTICLE 3 - EXTRACTION OF HIGH-PURITY MAGNESIUM AND CALCIUM FROM PHOSPHATE MINE WASTE ROCKS BY A CARBON-NEUTRAL AND CIRCULAR HYDROMETALLURGY

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6.1 Abstract

Dolomitic limestone waste rock (DLWR), generated during phosphate ore extraction, represents a high-potential source of magnesium and calcium. However, its valorization is hindered by CO₂ emissions from carbonate ore leaching, the co-dissolution of impurities, and the difficulty of separating leached Mg and Ca due to their similar aqueous chemistries. In this study, a simplified and carbon-neutral hydrometallurgical process was developed to recover high-purity Mg(OH)₂ and CaCO₃ microspheres from DLWR. Thermodynamic simulations, combined with experimental validation, were used to identify insolubility domains for Mg, Ca, and impurities, as well as optimal recovery conditions. Using 0.5M H₂SO₄ enabled the separation of over 50% of Ca from Mg during leaching, forming needle-shaped CaSO₄·2H₂O particles. Adding 1M NaOH to the acid-leaching liquor and adjusting the pH to 7 separated all impurities, including Ti, Al, Fe, and Mn. Subsequent pH adjustment to 9 caused Mg(OH)₂ precipitation, with 98% recovery and 99.5% purity. The residual CaSO₄·2H₂O was solubilized by water leaching and mixed with the remaining precipitation liquor containing Ca ions. When exposed to CO₂ released during acid leaching, this mixture promoted CaCO₃ precipitation, achieving a recovery of 98.6% and a purity of 99.7%. This developed process demonstrates a carbon-neutral and circular approach to valorizing DLWR.

Keywords: Lightweight metals; Waste recycling; Acid leaching; Alkaline precipitation; CO₂ mineralization

6.2 Introduction

Magnesium (Mg) and calcium (Ca) are two common alkaline-earth metals that play vital roles in modern materials, environmental, and metallurgical industries. Specifically, the oxide, hydroxide, and carbonate forms of these lightweight metals have a wide range of applications, from engineering to healthcare. These include CO₂ capture, flame-retardant additives, cement, steelmaking, fertilizer, hydrogen production, ammonia synthesis, rechargeable batteries, wastewater treatment, pharmaceuticals, tissue engineering, and acting as essential cofactors for hundreds of enzymes [303-309]. Today, there is growing interest in investing in recycling Mg and Ca from secondary sources, such as industrial waste and end-of-life products, rather than traditional mining, because of the considerable environmental, economic, and sustainability benefits. Environmentally, recycling consumes less energy and greatly lowers the carbon footprint [310]. It also mitigates land degradation, habitat destruction, and water/soil pollution associated with mining operations and the disposal of industrial waste [311]. Economically, recycling is usually more affordable than processing virgin ore and boosts domestic resource security by decreasing dependence on unstable primary extraction markets [312]. Ultimately, focusing on secondary resources supports circular economy principles, turning waste into useful materials and encouraging long-term sustainable industrial practices [313].

Among current technologies, hydrometallurgy is the most common approach for recycling valuable metals from secondary resources [314]. It offers higher recovery efficiency than biometallurgy and consumes less energy than pyrometallurgy [315]. A bibliometric analysis of Mg and Ca recovery from secondary resources via hydrometallurgical processes is presented in Figure 6.1 to identify leading research trends and remaining gaps. The analysis highlights acid leaching as the central and most interconnected research theme and confirms its role as the foundational step for extracting Mg and Ca from complex waste matrices such as phosphate tailings, steelmaking slags, fly ash, and municipal solid waste residues. Inorganic acids, primarily HCl and H₂SO₄, dominate the literature due to their effectiveness in dissolving carbonate- and oxide-bound alkaline-earth metals [224, 225]. However, the bibliometric map also reveals that most studies emphasize extraction efficiency rather than downstream selectivity, process integration, or carbon management. They give limited attention to impurity control and CO₂ utilization within a unified flowsheet.

Although both HCl and H₂SO₄ leaching systems are widely reported, the implications of acid selection on separation selectivity and downstream process complexity are rarely addressed in prior studies. Chloride-based systems often promote extensive co-leaching of Ca and impurity metals with Mg, complicating subsequent separation because of the similar physicochemical behavior of Mg²⁺ and Ca²⁺ [99, 316]. In contrast, sulfate-based systems offer an intrinsic advantage by selectively precipitating Ca as gypsum (CaSO₄·2H₂O), thereby suppressing calcium dissolution and enabling the generation of Mg-enriched liquors [317]. Additionally, H₂SO₄ is widely available in industry and environmentally significant because it is generated as a by-product of phosphate ore processing and various metallurgical operations, which makes it especially appropriate for large-scale waste valorization [318-320]. Despite these advantages, systematic exploitation of sulfate chemistry to simultaneously enhance selectivity, simplify downstream separation, and enable carbon-neutral processing remains largely unexplored.

Following leaching, Figure 6.1 further indicates that the literature primarily focuses on alkaline precipitation and carbonation as isolated downstream separation to recover Mg and Ca from leachate as Mg(OH)₂ or CaCO₃ [321-323]. These steps are generally investigated independently, without integration into a single process capable of managing impurities, minimizing reagent consumption, and reutilizing CO₂ generated during carbonate ore leaching. Consequently, many reported hydrometallurgical flowsheets rely on energy-intensive pretreatments (e.g., calcination), multiple precipitants, external CO₂ sources, or strongly alkaline effluents, which increase operational complexity and environmental impact [23, 99].

In our previous studies, we addressed several of these challenges by demonstrating that direct leaching of dolomitic limestone waste rock can suppress impurity dissolution through an intrinsic carbonate-buffering effect, thereby eliminating the need for high-temperature calcination [275]. We further developed a stepwise alkaline precipitation strategy enabling the sequential recovery of multiple metal products and demonstrated the feasibility of internal CO₂ capture and reuse [324]. Although this earlier flowsheet established a carbon-neutral process, it required multiple leaching and precipitation stages (i.e., two for leaching, six for alkaline precipitation, and two for CO₂ capture and utilization) and extended processing times, resulting in operational complexity that limits industrial scalability.

The present study built upon these foundations by addressing process simplicity and integration rather than extraction feasibility alone. Here, we proposed a simplified, closed-loop hydrometallurgical flowsheet that strategically combines sulfate-based selective leaching, impurity-controlled alkaline precipitation, and internal CO₂ utilization to recover high-purity Mg(OH)₂ and CaCO₃ from dolomitic limestone waste rock. By reducing the number of unit operations, avoiding high-pH effluent generation, and consolidating CO₂ capture and utilization into a single carbonation step, this work advanced a process-concept-level carbon-neutral hydrometallurgical strategy that is more compact and industrially relevant than previously reported approaches. To the best of our knowledge, such an integrated and simplified carbon-neutral process for the valorization of carbonate-rich phosphate mining wastes has not been reported previously.

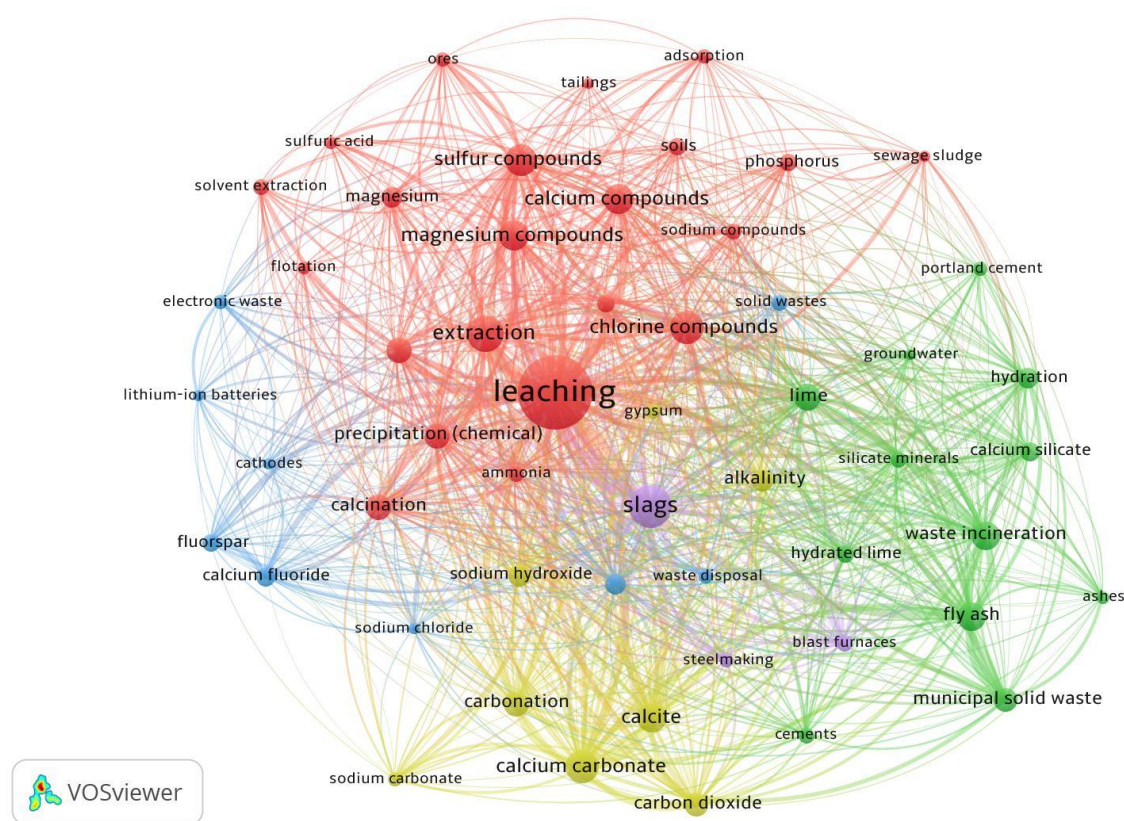


Figure 6.1 Bibliometric map of keywords created with VOSviewer software, featuring 54 frequently used keywords related to recycling Mg and Ca from secondary resources, grouped into 5 clusters. The data were collected from 901 articles indexed in Engineering Village from 2010 to 2025. The sizes of the labels and circles on the map reflect the importance of keyword co-occurrence in the articles.

6.3 Experimental procedure

The DLWR was collected from phosphate interlayers in the Gantour Basin at the Benguerir mine site, located in central Morocco. It was ground and sieved into particles of 45 μm , 63 μm , 90 μm , and 150 μm , corresponding to ASTM mesh sizes 325, 230, 170, and 100. These size ranges were selected to balance mineral liberation and leaching kinetics against the energy demand associated with fine grinding, while maintaining relevance to industrial hydrometallurgical practice. Leaching experiments were conducted in a 250 mL three-neck flask equipped with an electromagnetic stirrer, with two necks holding a thermocouple and a pH meter probe, and the central neck connected to an Allihn condenser to maintain a constant solid-to-liquid ratio (S/L). The solution temperature was set before adding the weighed ore. All experiments were performed under atmospheric pressure at a constant stirring speed of 500 rpm. The effects of temperature (20 -80 $^{\circ}\text{C}$), acid concentration (0.2-0.5 M), S/L ratio (10-80 g/L), and particle size (45-150 μm) on metal dissolution were systematically investigated. The selected acid concentration range was determined based on stoichiometric calculations, ore composition, and previous kinetic studies [275], which indicated that concentrations above 0.5 M increase impurity co-leaching without significantly improving Mg recovery. The temperature range was chosen to enhance acidolysis kinetics while avoiding pressurized operation, whereas the S/L ratio range was selected to capture both kinetically favorable and mass-transfer-limited regimes. Leaching time was set to 120 min to ensure near-equilibrium dissolution under all operating conditions. Upon completion of leaching, solids and liquids were separated by vacuum filtration. The leachate was passed through 0.45 μm nylon syringe filters and diluted with 5 wt.% HNO_3 to prevent supersaturation prior to ICP-OES analysis. Solids were rinsed and dried at 80 $^{\circ}\text{C}$ for 15 h, and liquid samples were analyzed for metal concentrations. The leaching efficiency (E_i) of metals was calculated using Equation (6.1):

$$E_i(\%) = \frac{m_{i,\text{leachate}}}{m_{i,\text{ore}}} \times 100 = \frac{C_{i,\text{leach}} V_{\text{leach}}}{f_{i,\text{ore}} m_{\text{ore}}} \times 100 \quad (6.1)$$

where $m_{i,\text{leachate}}$ and $m_{i,\text{ore}}$ represent the mass of metal i in leachate (mg) and in initial ore (mg), respectively. $C_{i,\text{leach}}$ and V_{leach} are ascribed to the concentration of metal i in leachate measured by ICP-OES (mg/L) and the volume of leachate solution (L). In addition, m_{ore} and $f_{i,\text{ore}}$ are signs of the total mass of initial ore (mg) and mass fraction of metal i in initial ore.

The precipitation experiments were carried out in a four-neck round-bottom flask connected to an Allihn condenser, a J-type thermocouple, a pH meter probe, and a 100 mL burette containing 1 M NaOH. The leachate temperature and agitation speed were initially set to 80 °C and 500 rpm, respectively, and maintained throughout the experiments. The pH of the DLWR leach liquor was adjusted to 7 and 9 to remove impurities and separate Mg compounds. Each precipitation step involved stirring the mixture for 120 min at 80 °C, followed by vacuum filtration to separate the solid and liquid phases. The solid was then rinsed multiple times with distilled water, dried at 80 °C for 10 h, and subsequently characterized using various analytical techniques. For all precipitation experiments, the recovery efficiency (R_i) was calculated based on the mass of the target metal in leachate before and after precipitation as follows:

$$R_i \% = \frac{m_{i,prec}}{m_{i,leachate}} \times 100 = \left(1 - \frac{C_{i,prec}V_{prec}}{C_{i,leach}V_{leach}} \right) \times 100 \quad (6.2)$$

where $m_{i,leachate}$ and $m_{i,prec}$ are the mass of metal i in leachate (mg) and after precipitation at a specific pH level (mg). The $m_{i,prec}$ is determined from the difference between the mass of metal i dissolved in the solution before and after precipitation. Since ICP-OES provides the dissolved metal concentration (C_i , (mg/L)), the corresponding m_i was calculated as $m_i = C_i \times V$. In Equation (6.2), $C_{i,leach}$ and V_{leach} are assigned to the concentration of metal i in leachate (mg/L) and the volume of leachate solution (L). $C_{i,prec}$ and V_{prec} represent the concentration of metal i in leachate after precipitation (mg/L) and the volume of solution after precipitation (L).

The purity of precipitated products (P_i) can also be defined based on the mass fraction of the target metal relative to the total mass of all metals present in the precipitate, as expressed in Equation (6.3):

$$P_i \% = \frac{m_{i,prec}}{\sum_{j=1}^n m_{j,prec}} \times 100 \quad (6.3)$$

In the above equation, $\sum_{j=1}^n m_{j,prec}$ is the summation of the mass of all metals precipitated at that specific pH. To quantify these elemental masses, all precipitated solids were again completely dissolved in aqua regia prior to ICP-OES analysis. This approach ensures that all metal-bearing phases present in the precipitate, regardless of their crystallographic phase, are fully digested and accurately accounted for in the mass balance.

The calcium in the acid-leaching residue was selectively separated from quartz (SiO_2) by dissolving in 300 mL of distilled water at 40 °C. The dissolved calcium solution was filtered to remove undissolved quartz and then mixed with the liquor obtained after precipitation at pH 9. For CO_2 capture and utilization (CCUS), the enriched calcium in the mixed liquor was exposed to a pure CO_2 stream in a 500 mL Pyrex gas-washing bottle equipped with a coarse frit disc. CO_2 was bubbled through the solution at a controlled flow rate of 20 mL/min for 4 h at 25 °C. Afterward, the CaCO_3 precipitate was collected via vacuum filtration and dried at 80 °C. All leaching and precipitation experiments were performed in triplicate or quadruplicate under identical conditions, and the reported values represent the average of these repetitions.

The mineralogy of dolomitic limestone waste rock was analyzed using the Quantitative Evaluation of Materials by Scanning Electron Microscopy (QEMSCAN; 650F, USA), equipped with a TESCAN Integrated Mineral Analyzer (TIMA; Tescan Vega TC x64, USA). The crystal structures of the ores, solid residues, and recovered products were characterized by X-ray diffraction (XRD; Bruker D8 ADVANCE, USA) using $\text{Cu K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$), operated at 40 kV and 40 mA. Diffraction patterns were collected over a 2θ range of 10-80° with a step size of 0.04° in continuous scan mode. Morphological features were examined using scanning electron microscopy (SEM; Hitachi TM3030 Plus, Japan) operated at 15 kV under low vacuum, with a backscattered electron detector. Samples were analyzed without a conductive coating. Changes in metal concentrations in the liquid phase were measured with inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent 5110, USA). For ICP-OES sample preparation, a known weight of each solid sample was digested with aqua regia at 100 °C for 24 h in a DigiPREP LS digestion system (SCP Science, Canada).

The thermodynamic simulations were performed using FactSage 8.3 software. The EpH toolbox in FactSage was used to determine the insolubility zone for selective precipitation and CO_2 carbonation. The mineral data for all thermodynamic simulations were extracted from the FToxid database. In addition, thermodynamic data for ions and pure substances in solution were obtained from the FThelg and FactPS databases, respectively. Species distribution diagrams for the C-O-H, Ca-Si-S-O-H, and Ca-Si-S-O-H systems as a function of pH were calculated using Medusa-Hydra software. It is worth noting that Pourbaix diagrams in this work outline thermodynamic stability zones and serve as qualitative aids in understanding phase behavior. Nonetheless, they do not

account for reaction kinetics, dissolution and precipitation rates, or mass-transfer limitations, which can affect the extent of phase transformation during the experimental residence time.

6.4 Results and discussion

6.4.1 Mineralogy of dolomitic limestone

The mineralogy of DLWR is shown in Figures 6.2(a) and 6.2(b). This waste rock contains more than eight different minerals, of which the dominant phases with mass distribution above 4 wt% are dolomite (about 78 wt%), calcium silicate (about 14 wt%), and quartz (about 4 wt%). Around 6 wt% of the dolomite mineral was liberated entirely, while 92 wt% remained bonded with silicates. As summarized in Table 6.1, the DLWR is dominated by CaO- and MgO-rich phases, reflecting its dolomitic nature, with silica present as the primary gangue component. Phosphorus and aluminum occur at low concentrations, while other metal oxides are present only as trace impurities.

Table 6.1 The composition of DLWR analyzed by XRF analysis.

Component	MgO	CaO	SiO ₂	P ₂ O ₅	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO	Na ₂ O	K ₂ O	LOI
Mass (wt.%)	16	35	8	1	1	0.1	0.1	0.1	0.2	0.01	38-47

6.4.2 Acid leaching experiment

The acid leaching efficiencies of elements present in DLWR at different temperatures, H₂SO₄ concentrations, S/L ratios, and ore initial particle sizes are presented in Figures 6.2(c) to 6.2(f). According to Figure 6.2(c), increasing the temperature increased the leaching efficiency of all elements. For Mg and Ca, increasing the temperature from 20 °C to 80 °C with 0.3 M H₂SO₄ and an S/L ratio of 10 g/L increased leaching efficiency from 42% to 78% and from 13% to 26%, respectively. Raising the temperature can increase ion activity and enhance the solubility of metal cations. The ionization of H₂SO₄ increases at elevated temperatures, leading to faster H⁺ production [249]. In addition, the diffusion of ions and the solubility of metal cations are higher at elevated temperatures [252]. Consequently, elevated temperatures accelerated acidolysis reactions and improved the leaching efficiency of elements. Regarding Figure 6.2(d), H₂SO₄ concentration had

the same effect as temperature, with higher concentrations increasing the leaching efficiency of all elements. At 80 °C and an S/L ratio of 10 g/L, the leaching efficiencies of Mg (99.4%) and Ca (49%) with 0.5 M H₂SO₄ were 1.7 and 2.6 times higher than those with 0.2 M H₂SO₄. This improvement is due to increased H⁺ generation, improved diffusion of the leaching agent, and a higher probability of H⁺ collision with DLWR particles [275].

As illustrated in Figure 6.2(e) and 6.2(f), both the S/L ratio and the initial DLWR particle size had negative effects on the leaching efficiency of all elements, unlike the effects of temperature and H₂SO₄ concentration. With 0.5 M H₂SO₄ at 80 °C, raising the S/L ratio from 10 g/L to 80 g/L decreased the leaching efficiency of Mg and Ca from 100% to 63% and from 49% to 12%, respectively. Enlarging the initial DLWR particle size from 45 µm to 150 µm resulted in 43% and 22% reductions in the leaching efficiencies of Mg and Ca, respectively. Four main reasons explain this negative effect. First, increasing the S/L ratio lowers the H⁺ concentration relative to the DLWR particle, reducing the probability of acidolysis and resulting in lower leaching efficiency [256]. Second, increasing the S/L ratio increases the diffusion resistance of the leaching agent, making it more difficult for H⁺ to reach and collide with the surface of DLWR particles, thereby reducing leaching efficiency [253]. Third, fine particles have a higher specific surface area per unit mass than coarse particles in DLWR [250]. Therefore, smaller particles offer more reactive sites accessible to leaching agents, thereby boosting acidolysis and leaching efficiency. Lastly, fine particles are less prone to agglomeration during leaching than coarse particles, allowing leaching agents to more readily access suspended fine particles and thereby further enhancing leaching efficiency [275].

Although finer particle sizes enhance leaching efficiency by increasing the reactive surface area and improving mass transfer, excessive grinding significantly increases comminution energy consumption, which raises operational costs. Therefore, an optimal particle size must balance leaching performance with the energy demand of grinding, particularly in large-scale industrial applications [325].

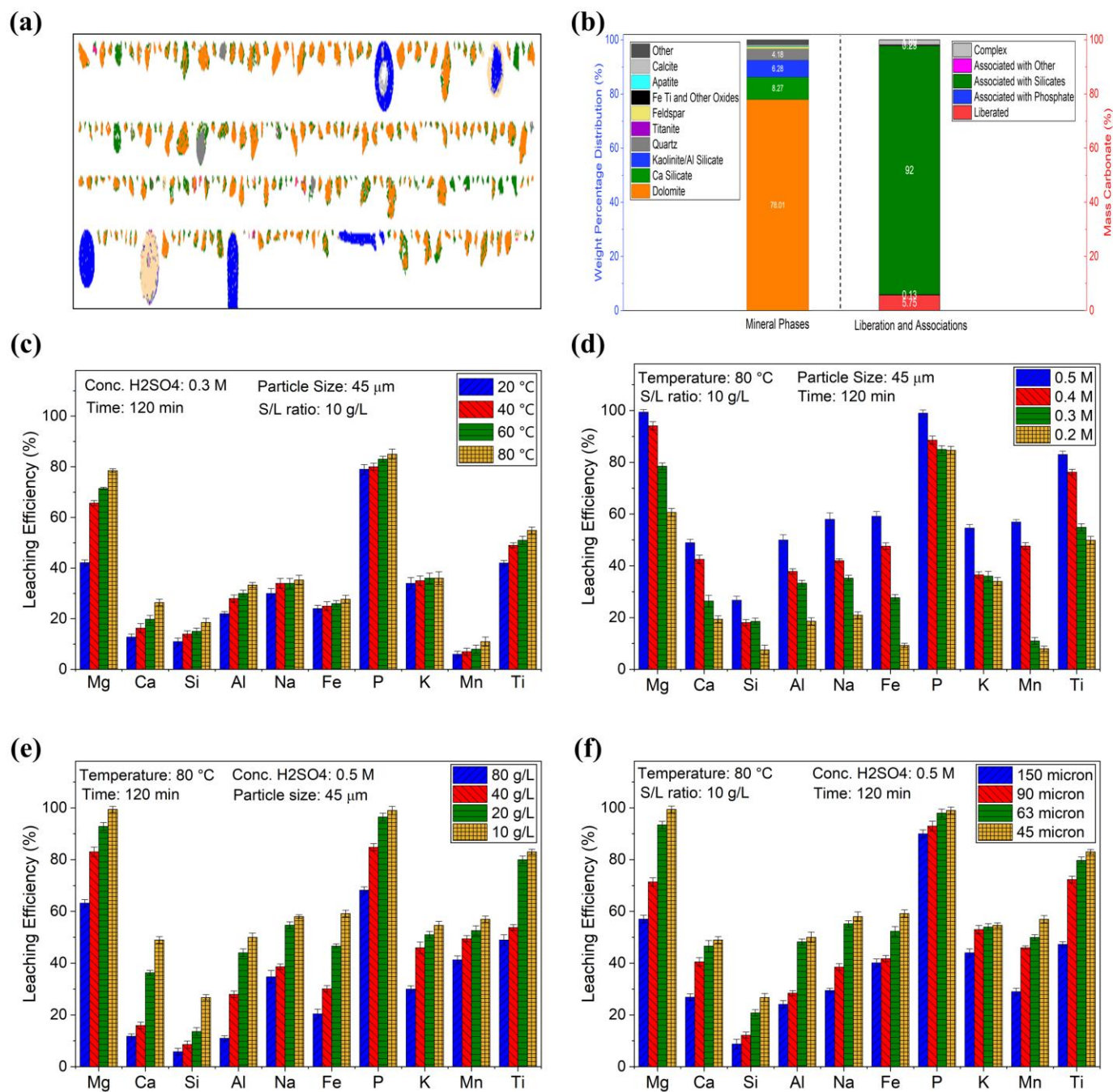


Figure 6.2 (a,b) Mineralogy of dolomitic limestone waste rock, (c) effect of temperature on leaching, (d) effect of acid concentration on leaching, (e) effect of S/L ratio on leaching, and (f) effect of initial particle size on leaching.

6.4.3 Pourbaix diagram for insolubility plus Closed-loop and carbon-neutral process

Understanding the insolubility of dissolved elements in DLWR leachate is a critical step toward obtaining highly pure Mg and Ca by precipitation. The insolubility of these metals in aqueous media at 80 °C was evaluated using the EPH toolbox in FactSage 8.3, as presented in Figure 6.3. The Pourbaix diagram maps regions where redox species are stable, based on solution redox potential, pH, temperature, and concentrations. The dashed lines in these figures indicate the redox potentials of water for O₂ and H₂ at different pH levels. To avoid side reactions during metal recovery, precipitation should occur within the water stability zone, which lies between the dashed lines.

As illustrated in Figure 6.3(a), at 80 °C and pH below 8.5, Mg and Ca in the Mg-Ca-H₂O system are soluble in the leachate, existing as Mg²⁺ and Ca²⁺ in the water stability zone. Increasing the pH and decreasing the oxidative potential at the same temperature result in the precipitation of Mg as Mg(OH)₂ and Ca as Ca(OH)₂, occurring at pH values above 8.5 and 11.5, respectively (yellow and pink areas). Figures 6.3(b) to 6.3(e) show the solubility of other cations in dolomitic limestone leachate. Under identical conditions, aqueous Al³⁺ dominates at pH below 2.5, while it transitions to Al₂O₃ solid at higher pH (green area). Iron species exhibit distinct thermodynamic behaviors depending on pH and redox potential. Based on Figure 6.3(c), Fe₂O₃, which contains Fe³⁺, is predicted to remain predominantly stable as a solid oxide over a broad pH range within the water-stability domain. However, under sufficiently acidic conditions (approximately pH < 4 at Eh ≈ 100-300 mV), dissolved iron species become thermodynamically favored, indicating that Fe-bearing oxides may partially dissolve. With respect to Fe₃O₄, which contains both Fe²⁺ and Fe³⁺, iron remains predominantly in the aqueous Fe²⁺ form at pH < 6, while precipitation of Fe₃O₄ becomes thermodynamically favorable at higher pH values (red region). Mn precipitates as MnO₂, Mn₂O₃, and Mn₃O₄ depending on the oxidation state of the leachate at pH above 3 and 80 °C (violet area). Si, K, and Na are soluble across all pH values, while Ti precipitates at low acidic pH (orange area). Dissolved P remains soluble at all pH levels, existing as H₃PO₄, H₂PO₄⁻, HPO₄²⁻, and PO₄³⁻ within the water stability zone. These findings suggest that the selective recovery of Mg and Ca from acidic leachate of DLWR is feasible through alkaline precipitation. Adjusting pH to 7 can separate Ti, Al, Fe, and Mn impurities, while Mg and Ca can be recovered at pH 9 and 11, respectively.

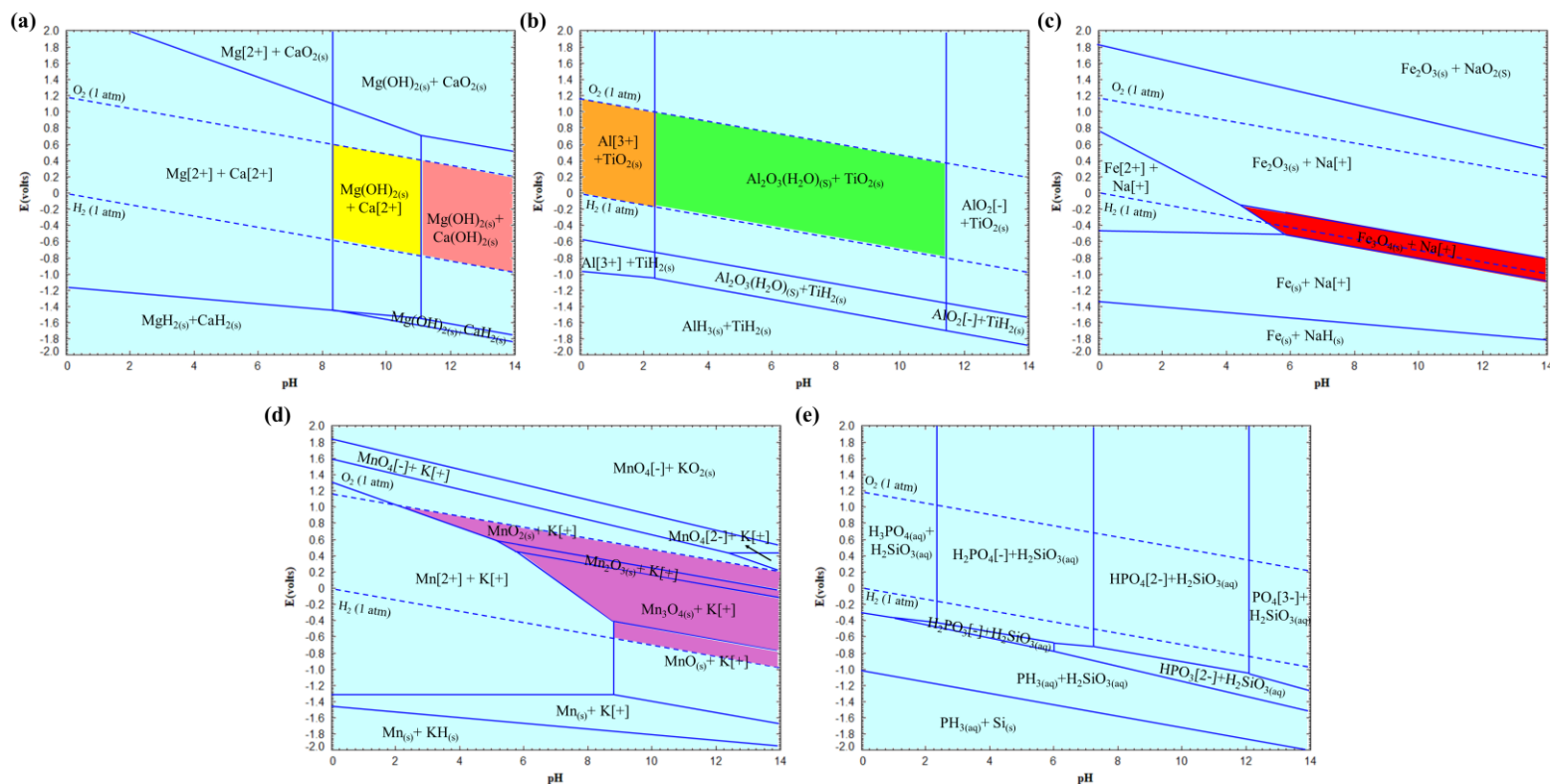


Figure 6.3 The Pourbaix diagrams at 80 °C for the systems of (a) Mg-Ca-H₂O (0.667 < Ca/Ca+Mg < 1, m = 0.001), (b) Al-Ti-H₂O H₂O (0.5 < Al/Ti+Al < 1, m = 0.001), (c) Fe-Na-H₂O H₂O (0.5 < Fe/Fe+Na < 1, m = 0.001), and (e) Si-P-H₂O (0.5 < Si/Si+P < 1, m = 0.001) systems.

Despite the potential for high recovery of pure Mg and Ca, some key environmental challenges remain. First, CO₂ gas is released during the acid leaching of DLWR, which impacts the environment. Second, if Ca is precipitated at pH 11, handling the strong caustic effluent will pose a significant challenge. Lastly, the residue from acid leaching of DLWR is a mixture of gypsum and quartz. To make use of it, an efficient separation process is needed. According to Figure 6.4(a), CO₂ can exist in three distinct forms in water depending on the pH, including carbonic acid (H₂CO₃), bicarbonate (HCO₃⁻), or carbonate ions (CO₃²⁻). Additionally, if a Ca cation is present in a basic solution (pH above 7), the absorbed CO₂ can react with it and result in CaCO₃ precipitation, as shown in the green area in Figure 6.4(b). According to Figures 6.4(c) and 6.4(d), calcium cations and sulfate anions can coexist as the aqueous CaSO₄ and the solid gypsum at pH 2 to 10, while SiO₂ exists only in solid form. Therefore, from a thermodynamic perspective, gypsum is moderately soluble in water, while SiO₂ is insoluble.

It is important to note that although the Pourbaix and speciation diagrams were created using typical concentrations of dissolved metal species, they do not explicitly account for ionic strength effects or activity coefficient corrections. As a result, they are used as qualitative thermodynamic references to interpret phase stability domains and reaction pathways rather than as exact predictors of multicomponent experimental behaviour.

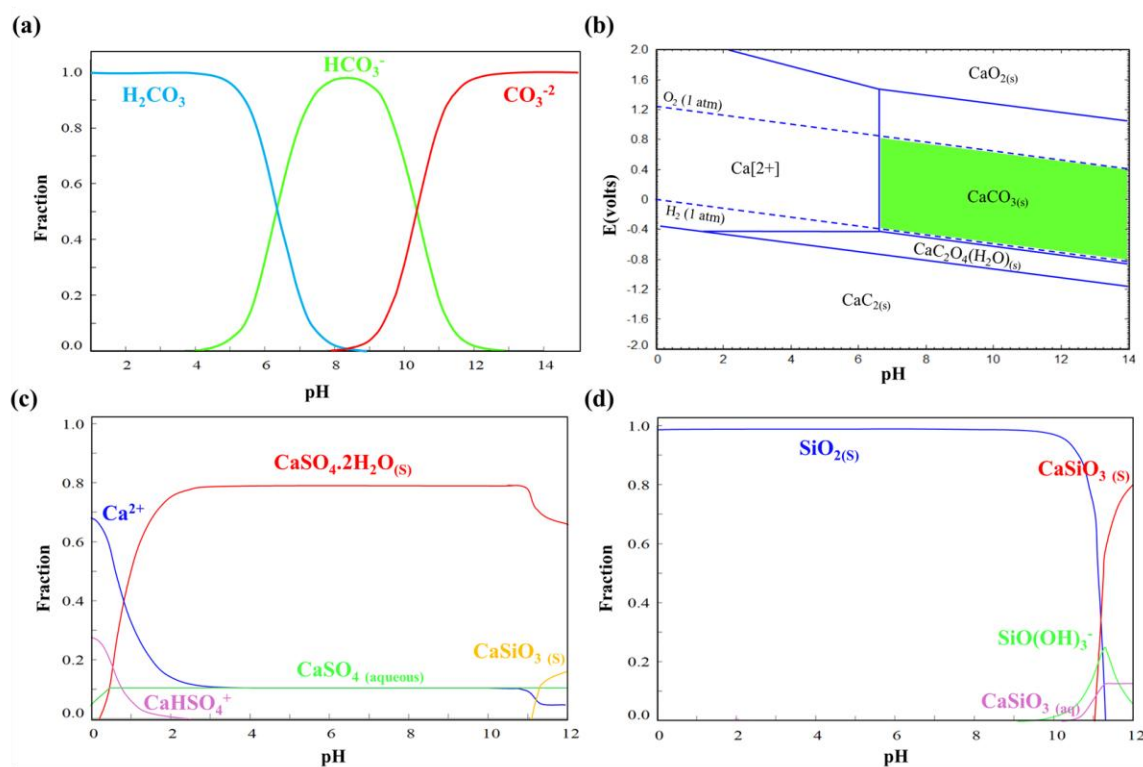


Figure 6.4 (a) distribution fraction for CO_2 in C-O-H system at different pH ($[\text{CO}_3^{2-}]_{\text{TOT}}=100\text{mM}$), (b) Pourbaix diagram for Ca-O-H-C system at atmospheric pressure and 25°C ($\text{Log}_{10}P(\text{CO}_2)=0$, $m=0.001$), (c) distribution fraction for Ca in Ca-Si-S-O-H system at different pH ($[\text{Ca}^{2+}]_{\text{TOT}}=50\text{mM}$, $[\text{SO}_4^{2-}]_{\text{TOT}}=50\text{mM}$, $[\text{Si}(\text{OH})_4]_{\text{TOT}}=10\text{mM}$), and (d) distribution fraction for Si in Ca-Si-S-O-H system at different pH ($[\text{Ca}^{2+}]_{\text{TOT}}=50\text{mM}$, $[\text{SO}_4^{2-}]_{\text{TOT}}=50\text{mM}$, $[\text{Si}(\text{OH})_4]_{\text{TOT}}=10\text{mM}$).

Based on these findings, we developed a carbon-neutral hydrometallurgical method to extract high-purity Mg and Ca from DLWR, as illustrated in Figure 6.5. Following DLWR acid leaching, gypsum and quartz can be separated by water leaching at a neutral pH (approximately 6-7). In this step, Ca dissolves in water, while SiO_2 remains as a residue. Next, a two-step precipitation at pH 7 and 9 is employed to remove impurities and recover $\text{Mg}(\text{OH})_2$. After precipitation at pH 9, the calcium-containing liquor at basic pH can be combined with the water leachate and exposed to CO_2 released from DLWR acidolysis, as depicted by the CO_2 capture and utilization (CCUS) unit in

Figure 6.5. In this stage, CO_2 gas is absorbed as HCO_3^- and reacts with Ca cations, forming CaCO_3 solid. Ultimately, this process allows for the recovery of high-purity $\text{Mg}(\text{OH})_2$ and CaCO_3 in a carbon-neutral manner.

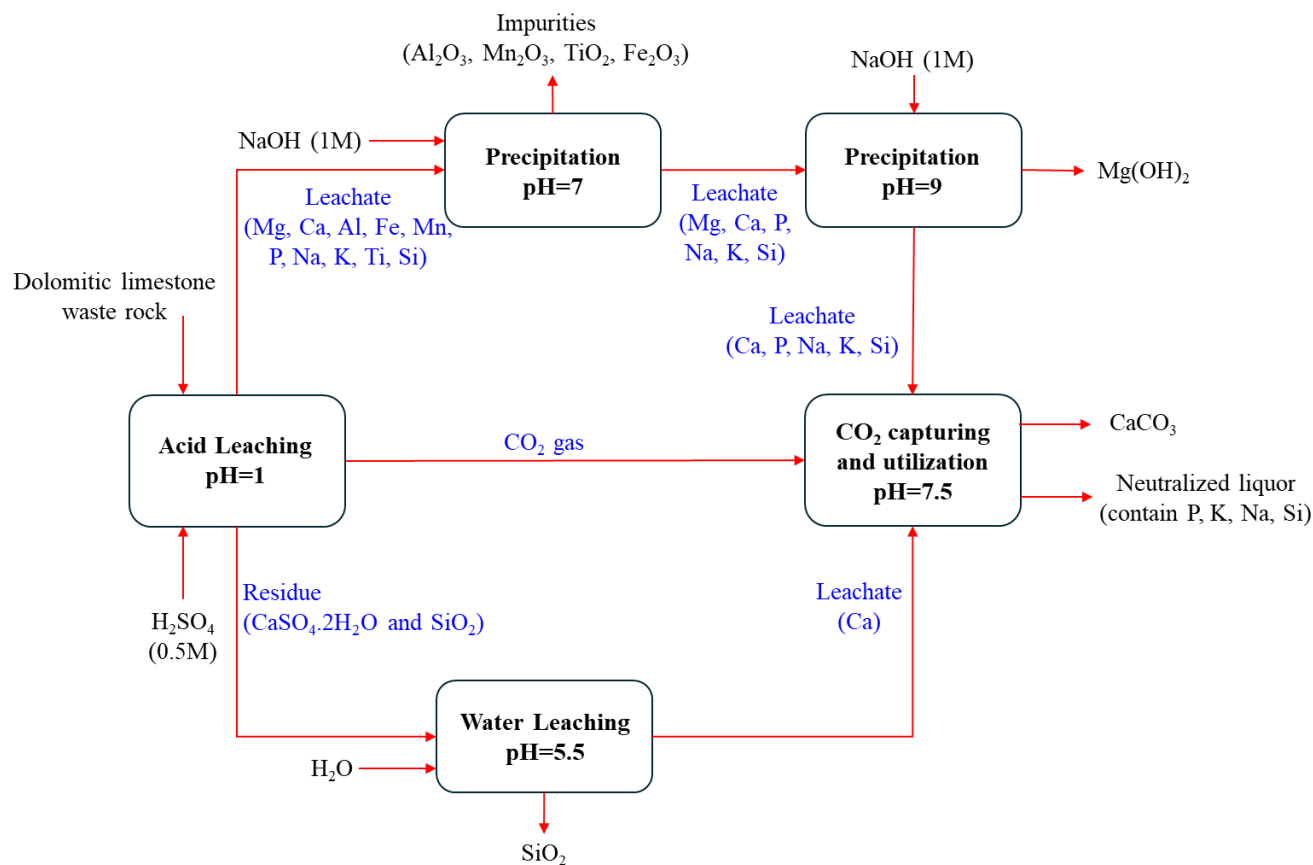


Figure 6.5 Block flow diagram for carbon-neutral recycling of magnesium and calcium from dolomitic limestone waste.

6.4.4 Multisite precipitation

The removal of impurities and the recovery of $\text{Mg}(\text{OH})_2$ from the liquor obtained through acid leaching of DLWR were accomplished by stepwise pH adjustments at pH 7 and 9, respectively. The recovery efficiency and precipitate purity are shown in Figures 6.6(a) and 6.6(b). At 80 °C, all Ti, Al, Fe, and Mn precipitated at pH 7 with purities of 2%, 61%, 28%, and 9%, respectively. Under the same conditions, 98% of Mg with a purity of 99.5% precipitated at pH 9. Negligible amounts of Mn and Ca caused 0.5% impurity in the Mg precipitate at pH 9. During water-leaching, 100% of Ca dissolved in water at an S/L of 2.4 g/L at 40 °C and was completely separated from SiO_2

solids. It is worth noting that less than 0.5% of the total P and Si in the leachate were co-precipitated during the alkaline precipitation process at pH 9. Most of the Si and P remained in the NaOH-enriched effluent as H_2SiO_3 and HPO_4^{2-} . These elements could be recovered by polymerizing silica under highly acidic conditions (2-8 M with mineral acid) to form silica gel nanoparticles, followed by phosphorus precipitation as dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) through Na_2EDTA chelation and CaO addition, as described in previous studies [301, 302].

According to Figure 6.6, 98.6% of Ca, with a purity of 99.7%, was precipitated during the CCUS stage by CO_2 bubbling at ambient temperature. The 0.3% impurity in this stage is due to slight residual Mg in the liquor that co-precipitated with Ca. Although pure CO_2 was employed in laboratory carbonation experiments to decouple carbonation chemistry from gas-phase mass-transfer limitations, comprehensive quantification of capture efficiency across a range of CO_2 concentrations and partial pressures will be required for process scale-up. In this study, carbon neutrality is defined at the process-concept level, referring to a closed-loop hydrometallurgical system (as shown in Figure 6.5) in which CO_2 generated during DLWR acid leaching is internally reused for CaCO_3 precipitation rather than vented to the atmosphere. From the thermodynamic and stoichiometric perspectives presented in Section 6.4.3, the molar quantity of CO_2 released during carbonate ore acidolysis is sufficient to precipitate the dissolved Ca species. In an industrial implementation, the evolved CO_2 would be temporarily collected in a buffer tank and subsequently circulated through the carbonation reactor, thereby separating gas generation from utilization. While carbonation efficiency is influenced by CO_2 partial pressure, temperature, and gas-liquid contact conditions, the present study demonstrates the intrinsic feasibility and selectivity of CaCO_3 formation under relevant solution chemistry. Quantitative assessment of CO_2 capture efficiency under various operating conditions will be addressed in future scale-up and process-integration studies.

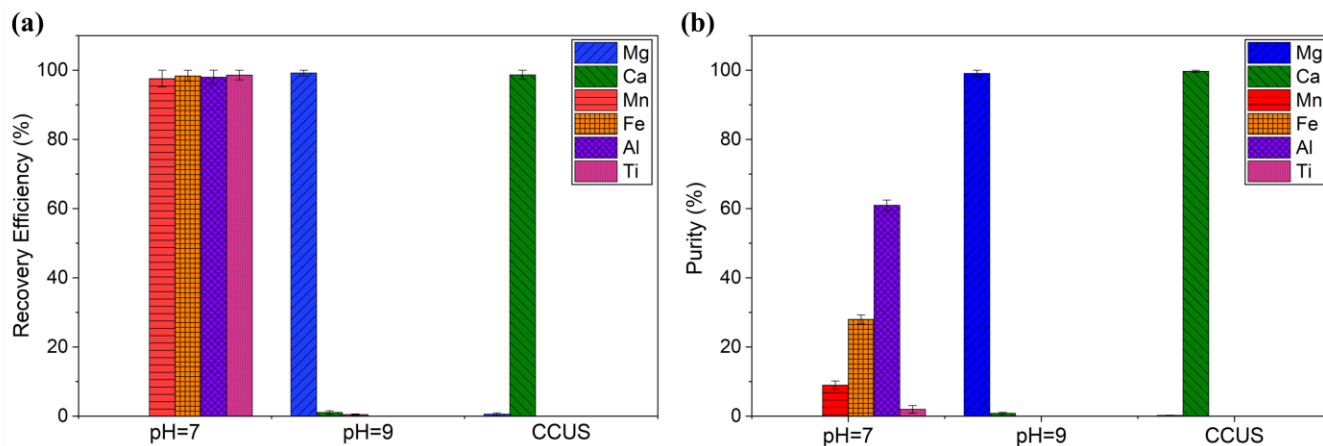


Figure 6.6 (a) Recovery efficiency and (b) purity of metals precipitated by carbon-neutral recycling of dolomitic limestone waste rock.

Experimentally, the redox potential of the leachate was measured to be approximately +315 mV under acidic conditions and decreased to around -40 mV after alkalization to pH 9 and carbonation at pH 7. These values fall within the aqueous stability region shown in the Pourbaix diagrams of Figure 6.3 and Figure 6.4 and indicate that the system operates under moderately oxidizing conditions, where strong redox reactions do not occur. Accordingly, metal dissolution and precipitation in the present study are governed primarily by acid-base equilibria and carbonate chemistry rather than redox transformations.

6.4.5 Characterization of ore, solid residues, and precipitates

The morphology and crystal phases of DLWR, a residue from acid leaching, precipitate at pH 9, and precipitate by CCUS are shown in Figure 6.7. According to Figure 6.7(a), DLWR has a cubic structure with an average side length of 43 μm . Based on the XRD pattern, the DLWR is dominated by the rhombohedral structure of $\text{MgCa}(\text{CO}_3)_2$ (JCPDS card No. 00-011-0078). As shown in Figure 6.7(b), needle-shaped particles with an average length of 30 μm and a width of 5 μm precipitated as the acid leaching residue. Regarding the XRD, this residue corresponds to a monoclinic structure of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (JCPDS card No. 00-003-0053).

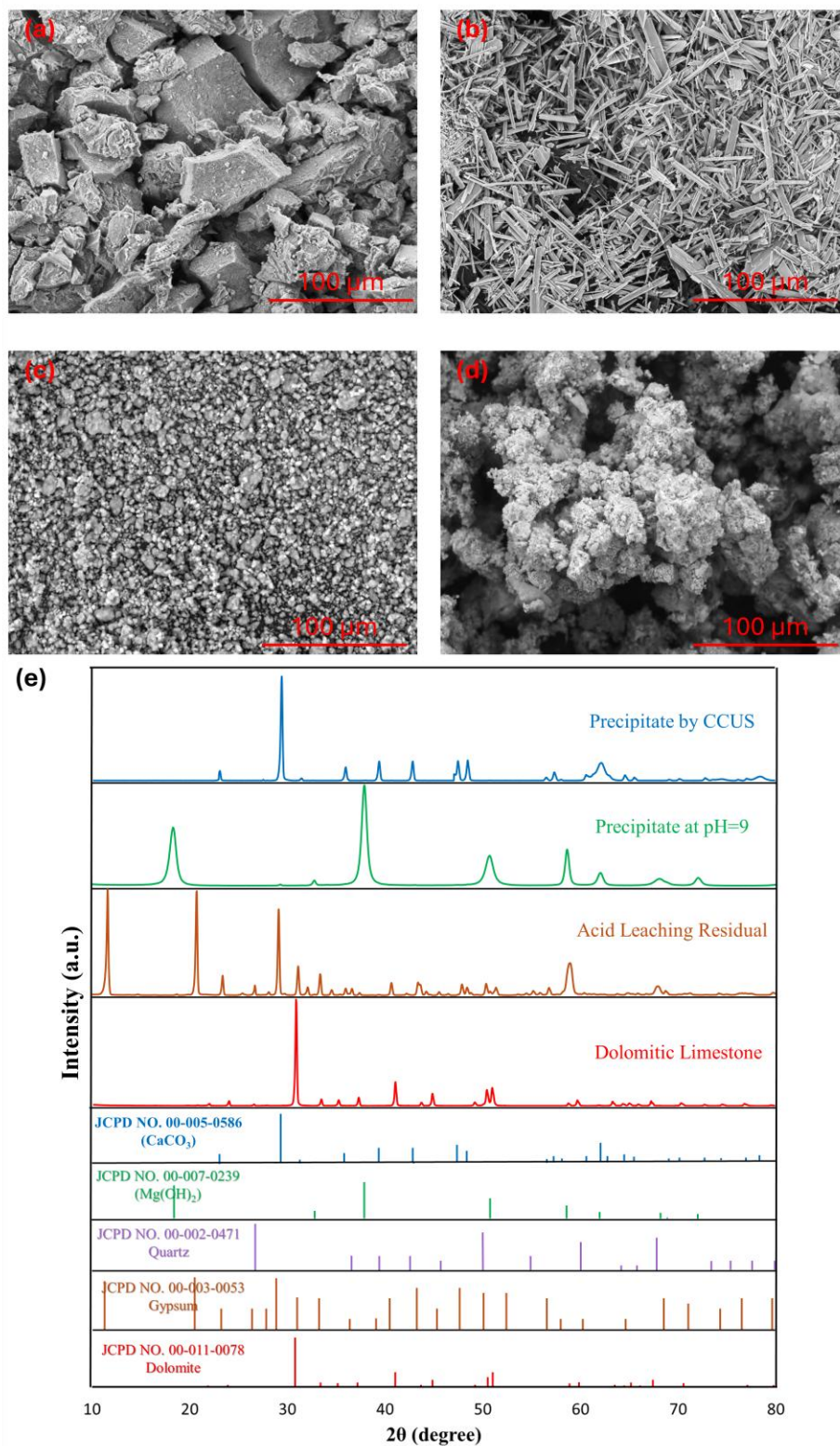


Figure 6.7 SEM images of (a) dolomitic limestone waste rock, (b) residuals from acid leaching, (c) precipitate at pH=9, (d) precipitate generated by CCUS, and (e) XRD patterns of these solids.

As shown in Figure 6.7(c), microsphere particles with an average diameter of 4 μm precipitated at pH 9. According to the XRD pattern, this precipitate has a hexagonal $\text{Mg}(\text{OH})_2$ crystal structure (JCPDS card No. 00-007-0239). As shown in Figure 6.7(d), CCUS caused the precipitation of microsphere CaCO_3 particles with an average diameter of 3 μm and a rhombohedral crystal structure (JCPDS card No. 00-005-0586).

6.5 Conclusion

In this study, we demonstrated that dolomitic limestone waste rock can serve as an efficient feedstock for the carbon-neutral recovery of high-purity Mg and Ca compounds. By coupling thermodynamic simulation with experimental validation, we developed a simplified five-step hydrometallurgical flowsheet that integrates selective leaching, impurity removal, $\text{Mg}(\text{OH})_2$ precipitation, gypsum water leaching, and CO_2 -driven carbonation of Ca. A key finding was utilizing the natural chemistry of DLWR reacting with H_2SO_4 , which produced insoluble gypsum and enabled the selective leaching of Mg. The subsequent pH-controlled precipitation and CO_2 carbonation steps yielded $\text{Mg}(\text{OH})_2$ and CaCO_3 with purities above 99.5%, demonstrating the effectiveness and selectivity of the method. Beyond recovering products, this process closed the CO_2 loop by using the gas released during acidolysis for in situ carbonation. This innovation shows how hydrometallurgy can align with carbon-neutral industrial practices. The five-step process outlined here simplifies previous multi-step methods, offering a more practical and scalable way to valorize carbonate-rich mining waste. This research provided a pathway for circular metallurgical processing and identified DLWR as a strategic resource for sustainable Mg and Ca production.

6.6 Acknowledgment

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CHAPTER 7 ARTICLE 4 - RAPID NON-VACUUM MAGNESIUM AND SYNGAS PRODUCTION VIA MICROWAVE-ASSISTED CARBOTHERMIC REDUCTION OF WASTE-RECYCLED BRUCITE

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Yassine Taha: Conceptualization, Methodology, Investigation, Writing - review & editing, Co-supervision.

Jamal Chaouki: Conceptualization, Resources, Writing - review & editing, Funding acquisition, Supervision.

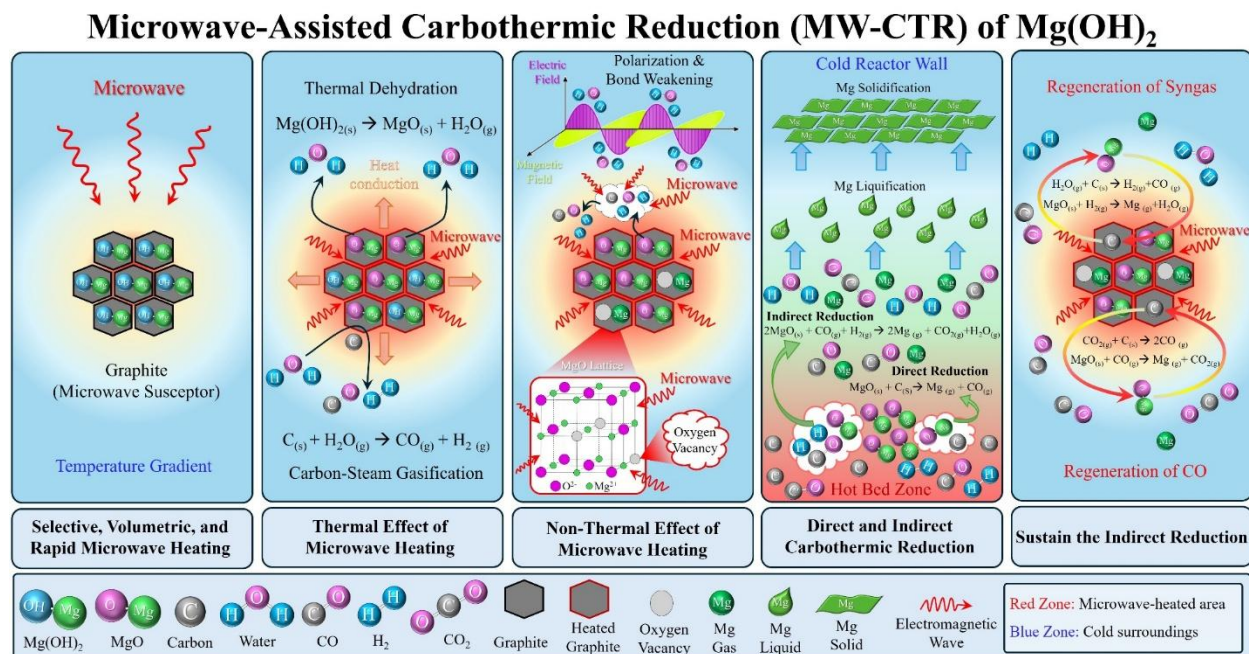
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7.1 Abstract

Magnesium (Mg) is a lightweight critical metal essential to advanced technologies and clean energy. However, its conventional production technologies, the Pidgeon process, are energy-intensive and environmentally unsustainable. Here, we present an electrified pyrometallurgical route for atmospheric Mg production via microwave-assisted carbothermic reduction (MW-CTR) of brucite ($\text{Mg}(\text{OH})_2$) recycled from phosphate mining waste. Replacing MgO with $\text{Mg}(\text{OH})_2$ fundamentally altered the reaction pathway and enabled atmospheric Mg metal production via CTR. In-situ H_2O release during $\text{Mg}(\text{OH})_2$ dehydration triggered steam-graphite gasification above 600°C , generating syngas (CO and H_2) as a valuable co-product. This syngas is more reductive than CO or graphite, shifting the process from a solid-solid to a gas-solid reaction, suppressing Mg reoxidation, and lowering the onset atmospheric CTR temperature from 1900°C to 1200°C . Microwave irradiation caused a dual synergistic effect. The thermal effect enabled rapid, volumetric, and selective heating of the $\text{Mg}(\text{OH})_2$ -graphite mixture ($> 990^\circ\text{C}/\text{min}$), which minimized sintering and facilitated rapid quenching of Mg vapor. Non-thermal microwave effects arising from localized electric-field interactions could promote water splitting, electron excitation, and oxygen-vacancy formation in the MgO lattice. These combined microwave phenomena accelerate thermal reduction and Mg vapor generation. Under optimized conditions (2.45 GHz, 880 W, 20 min, graphite: $\text{Mg}(\text{OH})_2$ ratio of 2:1), MW-CTR achieved 87% reduction efficiency and 94% Mg purity at 1280°C and 1 atm, producing syngas with a $\text{CO}:\text{H}_2$ molar ratio of 1.86 in a fixed-bed reactor with argon cross-flow. Our MW-CTR process advances low-carbon, circular magnesium metallurgy and offers potential for recovering other volatile metals.

Keyword: Critical elements; Process electrification; Recycling; Hydrogen production; Thermal reduction; Waste valorization

Graphical Abstract



7.2 Introduction

Magnesium (Mg) has emerged as one of the most strategic metals of the coming decades. The U.S. Department of Energy has designated Mg as a critical metal for the period 2025-2035 because of its indispensable role in energy applications and its high-risk supply [326]. Similarly, Canada has classified Mg as a strategic material because of its relevance to lightweight transportation, aerospace, defence, and emerging clean-energy technologies such as hydrogen storage and CO_2 sequestration [327]. Therefore, ensuring a secure and sustainable domestic Mg supply chain is crucial not only for economic competitiveness but also for national security and the transition to net-zero-emission industrialization.

Mg metal is currently produced from several primary resources, including dolomite ($\text{MgCa}(\text{CO}_3)_2$), magnesite (MgCO_3), seawater, brines, and magnesia (MgO), as well as secondary resources such as ferronickel slag and refractory brick waste [47]. Production technologies rely on either molten-salt electrolysis or thermal reduction processes. Lower capital costs and reduced technical barriers have made the thermal reduction process more advantageous than molten-salt electrolysis for large-scale applications [328]. At present, 85% of global Mg supply originates from China via the silicothermic reduction of calcined dolomite ($\text{MgO} \cdot \text{CaO}$), widely known as the Pidgeon process.

As illustrated in Figure 7.1, the Pidgeon process involves calcining dolomite above 1000 °C, producing ferrosilicon (FeSi) as a reductant at around 1600 °C, and reducing MgO under vacuum pressure (1-13 Pa) at temperatures above 1200 °C. These three thermal steps demand 8.68 tce per ton of Mg, of which more than half (4.51 tce per ton of Mg) is associated with the vacuum reduction step, and produce 21-26 t CO_{2eq} emissions [128, 329]. The process also generates 5-6 t of solid waste per ton of Mg due to residual oxides and silicates [330].

To decrease the environmental impact and save energy, carbon can be directly substituted for ferrosilicon reductant to produce Mg metal in one-step carbothermic reduction (CTR), as shown in Figure 7.1. CTR consumes only 2.6-4 tce per ton of Mg energy, reduces emissions to 8.8-14.8 t CO_{2eq}, and decreases solid-waste formation to 0.5-1 t of solid waste per ton of Mg [128]. Furthermore, CTR benefits from CO generation as a secondary product, which can be captured and utilized as a chemical feedstock or energy source. Despite these advantages, CTR encounters significant practical challenges. Thermodynamically, MgO requires around 1900 °C for reduction at atmospheric pressure, which necessitates vacuum conditions (10-100 Pa) to lower the operating temperature to around 1200 °C [331]. The vacuum CTR increases energy consumption, limits reactor design to batch operation, and raises labor and maintenance costs. Under vacuum conditions, heat transfer primarily occurs by radiation, resulting in slow heating rates and extended reaction times. Prolonged high-temperature exposure causes particle sintering, thereby reducing interfacial contact between MgO and carbon. Moreover, Mg vapor is vulnerable to reoxidation during condensation below 600 °C, where CO gas is converted to oxidative CO₂ via the Boudouard reaction.

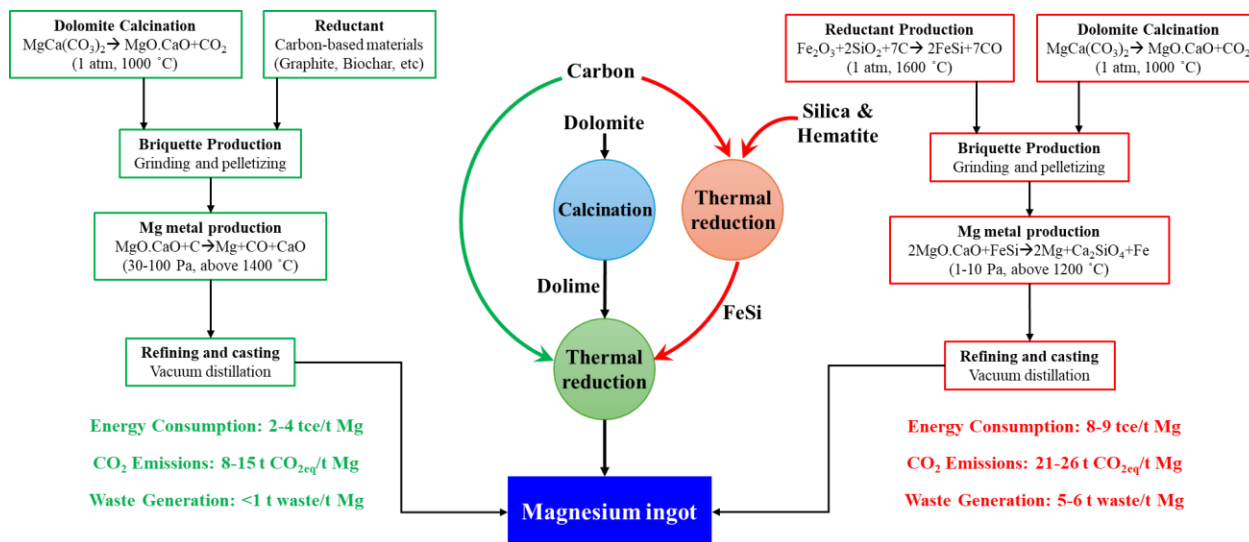


Figure 7.1 Comparison of Pidgeon and CTR processes for magnesium metal production.

Several strategies have been explored over the last decade to overcome these limitations. Some studies have shown that flowing argon can reduce Mg vapor partial pressure and enable both the Pidgeon and CTR reactions under atmospheric conditions [205, 332-334]. Nonetheless, without fluxing agents like CaF_2 , the atmospheric CTR of MgO or calcined dolomite still requires a temperature above 1600 °C. Furthermore, heating with a conventional furnace, which transfers heat from the wall inward, remains problematic. This surface heating results in a non-uniform temperature distribution within the fixed-bed particles, and consequently, the process takes 1-4 h, which hinders reduction efficiency due to sintering. Therefore, it is necessary to improve thermal reduction efficiency by developing new heating technologies that significantly increase heating rates and enhance temperature distribution uniformity.

Alongside these challenges, Mg condensation also requires reconsideration. Technologies such as Laval nozzles and moving-bed condensers have been used for rapid quenching under vacuum CTR, where Mg vapor transitions directly to solid [132, 335]. At atmospheric pressure, however, Mg vapor first condenses to liquid before becoming solid particles. Therefore, new methods are required to prevent Mg reoxidation by CO during atmospheric CTR.

Recently, non-conventional heating methods, such as Joule heating, microwave heating, and induction heating, have emerged as promising technologies in pyrometallurgy due to their rapid, efficient heating capabilities [336-338]. Among them, microwave heating is more suitable because it relies on electromagnetic penetration into a microwave absorber, such as carbon, and produces a

uniform temperature distribution from the particle's center to its periphery. This unique feature enables rapid, selective, and volumetric heating, which can benefit atmospheric CTR. Over the past 22 years, Yoshikawa and Morita have been the only researchers to have performed CTR of MgO under atmospheric pressure using a microwave-heating furnace [204]. Although they demonstrated the potential for rapid atmospheric CTR through microwave heating and achieved a 46% reduction efficiency at 1600 °C, many uncertainties remained about their research. The limited access of argon gas for purging reaction products due to the isolation of the reaction zone by firebrick, the lack of comprehensive characterization of products and residues, the possibility of thermal and non-thermal effects caused by microwave radiation, the condensation behavior of Mg vapor under atmospheric pressure, the impact of bulk temperature differences on reduction efficiency, and the influence of the initial Mg resource crystal phase are some examples of uncertainty that were not addressed in their study. These gaps highlight the need for a comprehensive investigation to establish the mechanistic foundation and operational conditions necessary for rapid atmospheric CTR with high Mg metal yield.

In this work, for the first time, we aim to produce Mg metal and syngas (CO and H₂) via rapid, non-vacuum CTR derived from microwave heating. The main originality of this research lies in the microwave-assisted carbothermic reduction (MW-CTR) of brucite (Mg(OH)₂), which simultaneously generates syngas and Mg metal. It is worth mentioning that Mg(OH)₂ used in this process was recovered from phosphate ore mining waste rock via a carbon-neutral hydrometallurgical process. Upcycling waste rock to produce Mg metal and syngas is a unique aspect of this research that has not been reported in the literature so far. To achieve this main goal, we will follow four specific objectives. First, the microwave absorption and heat generation capabilities of a mixture of graphite and Mg(OH)₂ will be analyzed in detail and compared with those of a mixture of graphite and MgO. Next, a fixed-bed pyrometallurgical reactor equipped with argon cross-flow for rapid MW-CTR of Mg(OH)₂ and MgO will be developed. The effects of contributing parameters, including the graphite ratio in the mixture and microwave input power, will be studied with respect to reduction efficiency and gas-phase product output. The third objective involves thermodynamic simulations to interpret experimental results and clarify the mechanism by which CTR of Mg(OH)₂ produces Mg metal and syngas. Finally, a comprehensive characterization of the feedstock, solid residue, condensed Mg, and gas products will be conducted

to evaluate the influence of microwave radiation on reduction efficiency and to examine thermal and non-thermal effects during atmospheric MW-CTR.

7.3 Experimental procedures

7.3.1 Materials and reagents

The $\text{Mg}(\text{OH})_2$ was recovered from dolomitic limestone waste rock by a carbon-neutral hydrometallurgical process [275, 324, 339]. As schematically described in Figure 7.2(a), the dolomitic limestone waste rock was first leached with a diluted H_2SO_4 solution (0.5 M). The impurities in the leachate were then separated by adjusting the pH to 7 with 1 M NaOH. Finally, high-purity $\text{Mg}(\text{OH})_2$ (>99.5%) was precipitated by adjusting the liquor pH to 9 with 1 M NaOH. The MgO was also prepared from the obtained $\text{Mg}(\text{OH})_2$ by calcination at 800 °C under an air atmosphere for 120 min. The calcination was performed in a muffle furnace with a heating rate of 5 °C/min and a reaction time of 2h. For the CTR, natural graphite flakes (99% carbon basis and - 325 mesh particle size) were purchased from Sigma-Aldrich and used as the reductant.

7.3.2 Microwave heating reactor

The non-conventional CTR was performed in a home-made microwave heating reactor, with the process flow diagram (PFD) and reactor schematic illustration shown in Figures 7.2(b) and 7.2(c). The Panasonic Genius Multimode Microwave Oven (model NN-SU64LB) with an interior cavity size of 353 mm × 261.5 mm × 387.8 mm (W × H × D) and a 1100W magnetron was used to perform thermal reduction at 2.45 GHz. Maintaining high-power conditions for thermal reactions generates immense heat in the microwave magnetron. Therefore, a compressed air flow was created on the magnetron sides to dissipate the generated heat and prevent permanent damage to the magnetron. We also modified the cavity to assemble a fused quartz reactor, pyrometer, and circulating cooling water. The reaction vessel was a fused quartz tube with an outer diameter of 3.2 cm, an inner diameter of 2.8 cm, and a length of 40 cm. A quartz fritted disc with a 3 cm diameter, 0.5 cm thickness, and porosity of 1 (100-160 µm nominal maximum pore size) was welded at the middle of the fused quartz tube to hold the particle bed at the centre of the cavity and distribute carrier gas through it. Circulating cooling water was incorporated into the cavity to absorb excess electromagnetic radiation and prevent spark formation. The temperatures of the particles and the reactor were measured using two non-contact and invasive methods. In the non-contact method, an

infrared pyrometer (Micro Epsilon, CTM-3SF75H2-C3) was placed at the back of the cavity, with a spectral range of 2.3 μm and a measurement range of 200-1500 $^{\circ}\text{C}$. In this spectral range, fused quartz has very low internal absorption, making it transparent to the pyrometer. Therefore, the temperature recorded by the pyrometer is assigned to the temperature of the bed's particles. In the invasive method, a type S thermocouple (Platinum-10% Rhodium, DwyerOmega) with a probe diameter of 1/8 inch and a measurement range of 0-1540 $^{\circ}\text{C}$ is placed 1 cm into the solid particle bed. The reactor wall was also measured using a grounded type K thermocouple (316 stainless steel, McMaster-Carr) with a 1/16 inch probe diameter.

At all drilled and open-cavity locations, 316 stainless steel cylinders were embedded as microwave chokes to prevent electromagnetic wave leakage from the cavities during the experiment. In addition, a radio frequency monitor (Radman 2LT) was used to ensure the cavity remained sealed against MW leakage during the experiment. Argon and N_2 as carrier gases were connected to the bottom of the cavity, and the flow rate was controlled through a mass flow controller (MFC Bronkhorst F-201CV). The MFC was communicated with a LabVIEW program, and the gas flow rate was automated precisely through it. The temperature of pyrometers and thermocouples was monitored and recorded by the LabVIEW program. The inlet and outlet gas lines were connected to the quartz reactor using 1¼ inch high-vacuum quick-connect fittings. At the reactor outlet, a pressure relief valve was first installed to prevent sudden overpressurization. Next, two sequential 27 μm and 7 μm in-line gas filters (Swagelok F Series) were placed to capture the particles that escaped from the bed. At the end, the filtered gas was connected to a gas chromatograph and then to the central ventilation line. It is worth noting that the MFC and microwave oven were connected to an emergency control box that shut down the experiment in the event of unsafe conditions, such as gas or microwave leakage, over-pressurization, and fire/explosion.

Figure 7.2 (a) The block flow diagram for carbon-neutral recycling of $\text{Mg}(\text{OH})_2$ from dolomitic limestone waste rocks, (b) the process flow diagram for the atmospheric CTR of $\text{Mg}(\text{OH})_2$ (V: valve, P: pressure gauge, R: pressure regulator, 3WV: three-way valve, CV: check valve; RV: relief valve, FT: particles filter, NV: needle valve, MC: microcontroller, and ESB: emergency safety box), (c) the schematic illustration of conventional and microwave heating reactors for CTR process.

7.3.3 Carbothermic reduction experiments

For the carbothermic reduction, the theoretical molar ratios of 2:1 graphite:Mg(OH)₂ and 1:1 graphite:MgO were well mixed mechanically using a mortar and pestle. For MW-CTR, 5 g of the mixture was placed inside the quartz tube on top of the fritted disc. The height of the bed was approximately 3 cm. Before starting the experiment, the bed was purged with argon gas at 0.4 L/min for 30 min to remove any air or oxygen molecules. The CTR experiments were performed with 880 W of microwave input power for 20 min under continuous argon flow (0.4 L/min). After cooling the bed to ambient temperature, the condensed particles on the reactor wall and inside the bed were separated from the bed residue using sieving and dense separation methods. The effects of input power (550-880 W) and the graphite:Mg(OH)₂ molar ratio (0.5-3) were also investigated as contributing parameters. To evaluate the impact of MW-CTR, comparative experiments were conducted by using a conventional heating method. In this regard, the mixtures of graphite with Mg(OH)₂ and MgO based on the mentioned theoretical molar ratio were placed in an alumina crucible and transferred to the center of a single-zone tubular furnace equipped with an alumina tube with an outer diameter of 9 cm (Carbolite Gero STF 16/450). The process flow diagram and schematic illustration of the reactor for this conventional CTR are presented in Figures 7.2(b) and 7.2(c). The system assembly and process operation were the same as those of the non-conventional heating approach, with the only difference being the use of a tubular furnace instead of a home-made microwave reactor.

7.3.4 Characterization and analytical techniques

The crystal phases of feed, residue, and condensates were analyzed by X-ray diffraction measurement using Cu K α radiation (XRD; Bruker D8 ADVANCE, USA). Raman spectra of the feed and residues were recorded using a 532 nm excitation laser (inVia Reflex confocal Raman microscope, Renishaw, UK), and each spectrum represents the average of five measurements. The morphology of the samples, both before and after the reaction, was characterized using scanning electron microscopy (SEM; Hitachi TM3030 Plus, Japan). The microstructure, lattice fringes, and selected-area electron diffraction (SAED) patterns were examined using high-resolution transmission electron microscopy (HRTEM; JEM-2100F, JEOL, Japan), while elemental distributions were obtained by STEM-EDS mapping. The particle size distribution was measured using a laser diffraction particle size analyzer (PSD; Malvern Mastersizer 3000+ Ultra, UK).

equipped with an automated dry powder dispersion unit (Aero S). The elemental composition and chemical state of residues and condensates were evaluated by using X-ray photoelectron spectroscopy microprobe (XPS; Thermo Scientific ESCALAB 250Xi, USA). The formation of oxygen vacancies was detected by an Electron Paramagnetic Resonance Spectrometer (EPR; Bruker-Magnettech ESR5000, Germany). The composition of the gases produced during CTR and MW-CTR was analyzed by gas chromatography (GC; Agilent 8890 Series, USA) equipped with a single-filament thermal conductivity detector (TCD) and an autoranging flame ionization detector (FID). The reduction efficiency (R_T) and magnesium purity (P_{Mg}) were calculated using the following equations, respectively.

$$R_T (\%) = \left[1 - \left(\frac{m_{MgO,f}}{m_{MgO,i}} \right) \right] * 100 \quad (7.1)$$

$$P (\%) = \left[\left(\frac{m_{Mg,Condens}}{m_{t,Condens}} \right) \right] * 100 \quad (7.2)$$

where $m_{MgO,i}$ and $m_{MgO,f}$ represent the mass of MgO before and after carbothermic reduction (g). For the CTR of $Mg(OH)_2$ experiments, $m_{MgO,i}$ was calculated as the theoretical MgO-equivalent mass derived from the stoichiometric dehydration of the initial $Mg(OH)_2$, while $m_{MgO,f}$ represents the remaining MgO mass in the residue after reduction. $m_{t,Condens}$ and $m_{Mg,Condens}$ are the total mass of condensate and mass of produced Mg metal (g). These weights were determined by the XRD semi-quantitative analysis using the RIR method and the inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent 5110, USA). Additionally, HCl leaching was employed as a third method for quantifying the produced Mg. In this analytical method, the reaction of Mg metal with 1 M HCl solution produces aqueous $MgCl_2$ and H_2 gas, which can be quantified by ICP-OES and the water displacement method, respectively. Then, conducting a mass balance between the dissolved Mg concentration and evolved H_2 volume allowed for determining the weight of Mg metal present in the condensates.

It is worth noting that all thermal reduction experiments were performed in triplicate under identical conditions, and the reported values represent the average of these repetitions. The overall mass balance was verified by comparing the total mass of recovered solid products and collected condensates with the initial feed mass. The mass balance closure was within $\pm 3\%$, indicating good

agreement between the input and recovered materials and confirming the reliability of the experimental measurements.

7.3.5 Thermodynamic simulation

Thermodynamic simulations were performed using FactSage 8.3. The possible reaction pathways for CTR of $\text{Mg}(\text{OH})_2$ were determined by multiphase-multicomponent equilibrium computations. The magnesium-dominant phase as a function of pressure and temperature was simulated using the Phase Diagram toolbox with the classical phase method. Changes of Gibbs free energy during CTR at various pressures and temperatures were calculated using the Reaction Toolbox. Materials data were extracted from the FToxid and FactPS databases.

All simulations were conducted under the assumption of global thermodynamic equilibrium at the specified temperature and pressure. Gas-phase species were treated as ideal gases, while condensed phases were described using the thermodynamic models available in the selected databases. For equilibrium-composition calculations, the systems were initialized using the stoichiometric feed compositions of the MgO-C and $\text{Mg}(\text{OH})_2\text{-C}$ mixtures. The system was treated as a closed system, allowing all stable gas and condensed phases available in the databases to form during Gibbs free-energy minimization. These calculations neglect kinetic limitations, mass-transfer resistance, microwave-specific effects, and gas sweeping by the carrier gas, and therefore represent the thermodynamic limit of the system rather than the exact experimental reaction pathway.

7.4 Results and discussion

7.4.1 Microwave absorption capability and non-conventional heat generation

In microwave heating, the interaction between the bed materials and the electromagnetic waves is crucial for determining the setpoint temperature and heating rate. As illustrated in Figure 7.3(a), the graphite demonstrated excellent microwave absorption capability, reaching an average temperature of about 1400 °C within 1 min under an input power of 880 W, and maintaining this temperature afterward. The strong interaction of graphite with electromagnetic waves arises from its high dielectric and conduction losses. Generally, microwave heating occurs due to the interaction of the electric (E-field) or magnetic (H-field) fields of microwaves with materials that exhibit dielectric loss, Joule (conduction) loss, or magnetic loss [20]. In the case of graphite, oscillation of the E-field in the electromagnetic wave causes electrons to move in this highly

conductive material. The movement of electrons and their collisions with the graphite lattice generate resistive heat. [340]. According to the literature, a loss tangent ($\tan\delta$) greater than 0.05 or a penetration depth of the order of centimeters indicates that the material is a good microwave absorber, capable of converting the absorbed electromagnetic wave into heat [165, 172]. Regarding graphite, the $\tan\delta$ and penetration depth in a 2.45 GHz multimode microwave cavity range from 0.36 to 0.67 and from 1.34 to 2.09 cm, respectively, indicating that it is a strong microwave absorber and susceptor.

Unlike graphite, MgO could not be heated by electromagnetic waves, and its temperature remained around 26 °C after 6 min of microwave radiation. The very low dielectric loss and $\tan\delta$ in the range of 2.5×10^{-7} to 9×10^{-3} are the main reasons why MgO behaves as a transparent material and cannot absorb or dissipate electromagnetic waves to generate heat [341, 342]. Regarding $\text{Mg}(\text{OH})_2$, although it is a weak microwave absorber and cannot generate as much heat as graphite, it demonstrated better interaction with electromagnetic waves than MgO, mainly due to bound water and dipolar relaxation. [343]. The temperature of $\text{Mg}(\text{OH})_2$ rose slightly from 25 °C to 80 °C within 6 min of microwave radiation. The mixture of MgO and graphite exhibited good microwave absorption ability, and the temperature increased gradually to 1240 °C within 2 min. The mixture of $\text{Mg}(\text{OH})_2$ and graphite also absorbed microwaves more effectively and reached 1280 °C in 1 min, mainly because of the dehydration of $\text{Mg}(\text{OH})_2$ and improved dielectric synergy with graphite.

In addition to the temperature of the solid inventories, the quartz reactor wall temperature was monitored under microwave radiation with different beds at an input power of 880W, as shown in Figure 7.3(b). In comparison with solid inventories, there is a 770-860 °C temperature difference between beds of graphite, graphite-MgO, and graphite- $\text{Mg}(\text{OH})_2$ with the reactor walls. For a pure graphite bed, the wall temperature increased gradually from 24 °C to 540 °C over 6 min of microwave radiation. For the graphite-MgO and graphite $\text{Mg}(\text{OH})_2$ mixtures, the wall temperatures also reached 430 °C and 450 °C at the same time of radiation, respectively. The significant temperature difference between the reactor's bed and its wall results from the nature of microwave heating, which depends on wave penetration. In conventional heating at atmospheric pressure, the reactor wall is first heated by a heat source, such as a flame or an electric element. Then, heat is transferred from the wall to the bed's surroundings through convection. Eventually, the bed absorbs this heat, transferring it from the particles' surfaces to their core via conduction. Therefore, in conventional heating, the bed's temperature is close to that of the surrounding environment and

reactor wall. Conversely, in our microwave heating reactor, the electromagnetic wave first directly penetrates the microwave absorbent (in this study, graphite), and its energy is dissipated as heat. In this type of selective heating, the temperature quickly transfers from the core to the surface of the graphite, creating a uniform temperature distribution within the bed. Then, over time, heat moves from the bed to the surrounding environment and finally to the reactor wall through convection. Therefore, during a short exposure to microwave radiation, a significant temperature difference will exist between the reactor wall and the bed. It is worth noting that a primary challenge in CTR is the gradual condensation of Mg gas alongside CO gas in the conventional heating furnace, which reoxidizes Mg with CO₂ produced through the Boudouard reaction. The significant temperature difference between the reactor bed and the wall in microwave heating can enable rapid quenching and prevent Mg metal from reoxidizing during condensation. This advantage is explained further in the following sections.

As mentioned earlier, the microwave heating of graphite mainly occurs through the Joule loss mechanism. Therefore, the input power significantly affects the bed temperature. To assess this effect, beds made of graphite and mixtures of graphite with MgO or Mg(OH)₂ were subjected to microwave irradiation at input power levels ranging from 550 W to 880 W. As shown in Figure 7.3(c), lowering the input power resulted in both a slower heating rate and a lower maximum bed temperature. Specifically, lowering the input power from 880 W to 550 W reduced the bed temperature from 1400 °C to 1190 °C for graphite, from 1280 °C to 1110 °C for Mg(OH)₂-graphite, and from 1240 °C to 1020 °C for MgO-graphite. In addition, the corresponding heating rate for the graphite bed was significantly decreased fourfold, from 1770 °C/min to 450 °C/min, over the same decrease in input power. The bed mixture of Mg(OH)₂-graphite and MgO-graphite showed similar trends, with heating rates reducing 3 times (from 990 °C/min to 328 °C/min) and 2.5 times (from 760 °C/min to 305 °C/min), respectively. The decrease in the heating rate and bed temperature is due to reduced electron mobility in graphite, which slows down the dissipation of electromagnetic waves and, as a result, heat generation. According to Figure 7.3(d), lowering the input power to 550 W decreased the reactor wall temperature to about 400-450 °C, with corresponding heating rates of 66-75 °C/min for both graphite and its mixtures with MgO and Mg(OH)₂. This decline happened because, at lower input power, the falling bed temperature reduces the temperature gradient between the bed and the reactor wall. As a result, the conductive heat transfer rate drops and leads to a lower wall temperature.

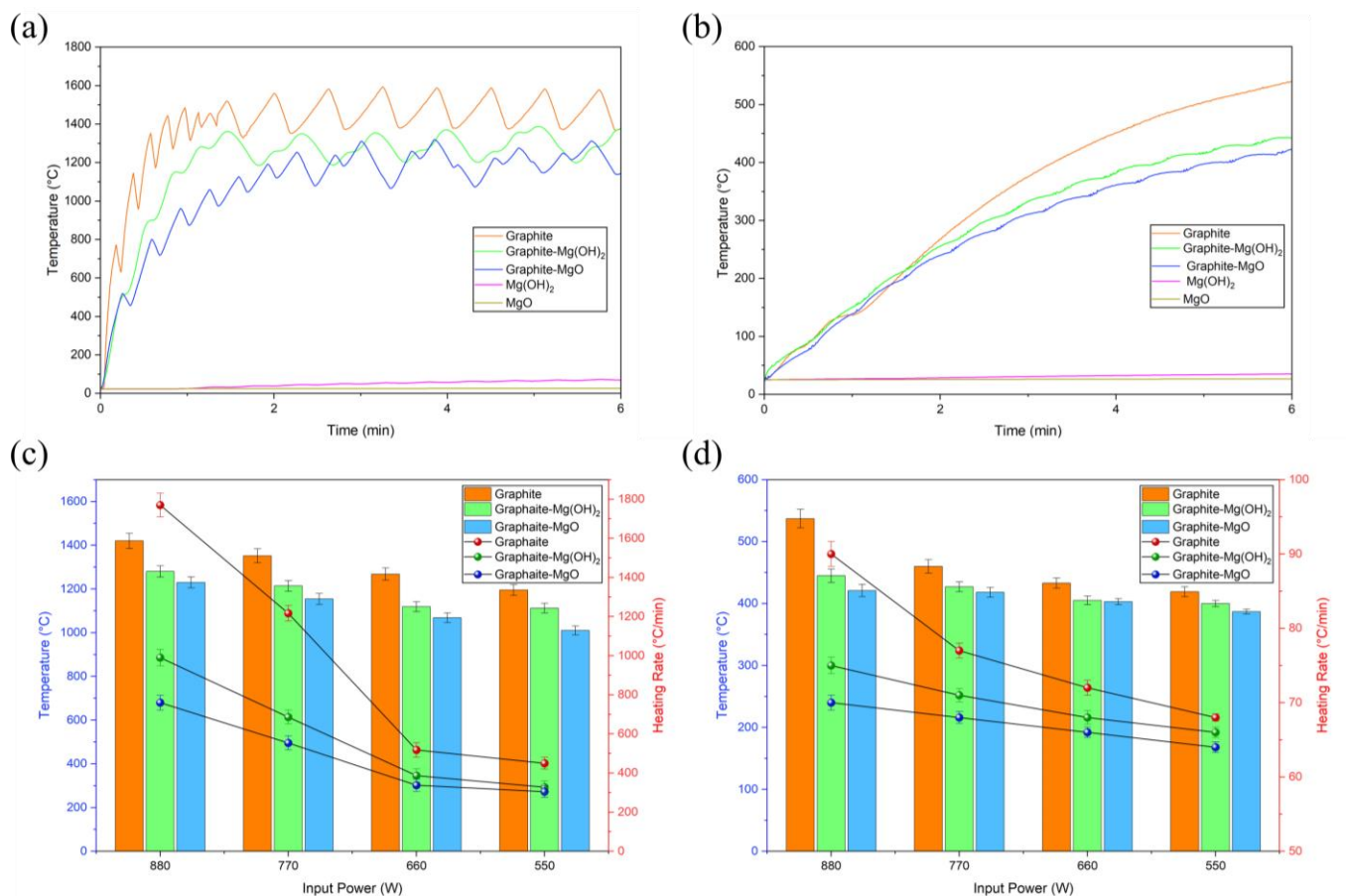


Figure 7.3 (a) Bed temperature for different feeds at 880 W, (b) wall temperature for different feeds at 880 W, (c) effect of input power on bed temperature (bar chart) and its heating rate (line and symbols), and (d) effect of power on wall temperature (bar chart) and its heating rate (line and symbols).

7.4.2 Carbothermic reduction of Mg(OH)_2 and MgO

7.4.2.1 Conventional carbothermic reduction

The conventional CTR of MgO and Mg(OH)_2 under atmospheric pressure, using argon as the carrier gas, was evaluated in a fixed-bed tubular furnace reactor. The reduction efficiency, evolved reaction gases, and the composition of condensed products are shown in Figures 7.4(a) to 7.4(c). As illustrated in Figure 7.4(a), even though our experiments were performed at atmospheric pressure, 12% of MgO was reduced by carbon at 1300 °C. According to Figure 7.4(b), the gas produced from the MgO -graphite reaction contained approximately 77 vol% CO and 23 vol% CO_2 . The CO_2 in the gas results from the Boudouard reaction. Based on Figure 7.5(a), two moles of CO

gas can react at temperatures below 700 °C to produce one mole of CO₂ and one mole of solid carbon. In a typical heating process within a tubular furnace reactor, the temperature peaks at about 1300 °C at the center of the tube and gradually decreases toward the inlet and outlet, reaching around 200-300 °C. Therefore, due to the temperature profile in the conventional tubular furnace, the CO evolved from the CTR of MgO can be slowly converted into CO₂. The CO₂, with its oxidative properties, reacts with Mg vapor during condensation at the reactor outlet, leading to Mg reoxidation. As illustrated in Figure 7.4(c), the solid condensate consists of 68 wt% Mg, 20 wt% MgO, and 12 wt% carbon, which is consistent with the reoxidation process theory.

According to Figure 7.4(a), using Mg(OH)₂ instead of MgO can decrease the reoxidation rate and thus improve the reduction efficiency. In this context, 46% of Mg(OH)₂ was reduced at 1300 °C for 240 min in a conventional heating reactor. The gas produced from this reaction contained 44 vol% CO, 31 vol% H₂, 6 vol% CO₂, and 19 vol% steam. Additionally, the condensed solid consisted of 73 wt% Mg, 18 wt% MgO, and 12 wt% C. The higher CTR efficiency of Mg(OH)₂ compared to MgO is attributed to its weaker oxygen-bonding energy and the synergistic effects of H₂ and CO, as discussed in the following section through thermodynamic calculations.

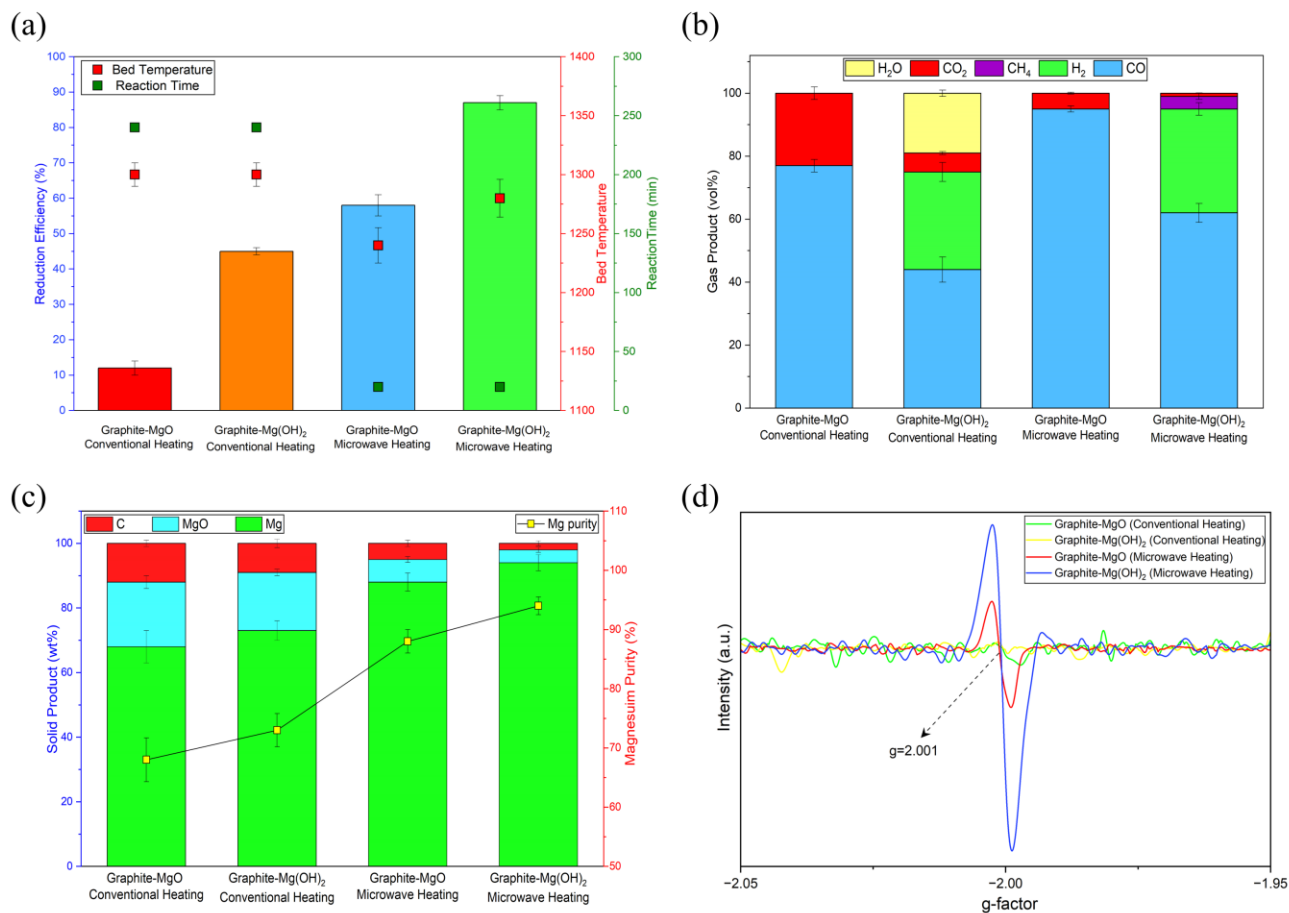
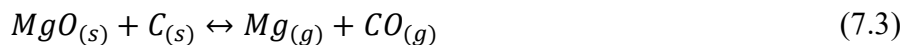


Figure 7.4 Comparing the CTR of MgO and Mg(OH)₂ in both conventional and microwave heating reactors (a) reduction efficiency, (b) evolved gases, and (c) condensed solid products; and (d) EPR patterns of Mg(OH)₂ and MgO partially reduced by conventional CTR and MW-CTR.

7.4.2.2 Thermodynamic interpretation

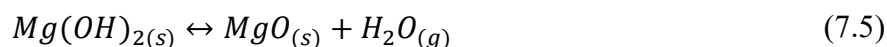
To better understand the advantage of the CTR of Mg(OH)₂ over MgO, the possible reactions in these processes were thermodynamically evaluated using multiphase-multicomponent equilibrium calculations based on Gibbs free energy minimization. According to Figure 7.5(c), the CTR of MgO (Reaction (7.3)) becomes thermodynamically favorable only above 1200 °C at 100 Pa, with complete reduction occurring around 1300 °C, yielding a gas mixture of 50% Mg metal and 50% CO.

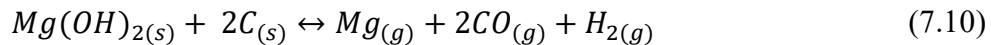
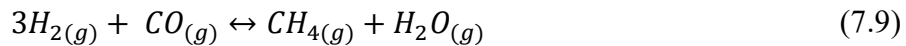
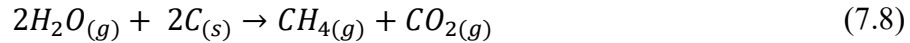
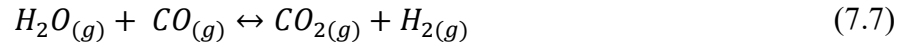
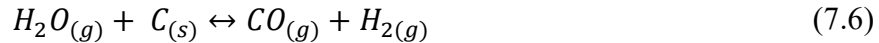


Two mechanistic scenarios for CTR of MgO have been proposed by Komarek et al. [344] and Rongti et al [345]. In the first scenario, MgO thermally dissociates into Mg vapor and atomic oxygen, after which the oxygen diffuses to the carbon surface and desorbs as CO. Because both oxygen diffusion and CO desorption are slow, this pathway is kinetically limited. The second and more widely accepted scenario involves two sequential steps: (I) a direct solid-solid reduction of MgO by carbon, driven by the high electron affinity of oxygen, which results in partial MgO conversion (less than 25%) and CO formation; and (II) an indirect gas-solid reduction in which the evolved CO reduces the remaining MgO to Mg and CO₂. The CO₂ produced in this step is continually converted back to CO via the reverse Boudouard reaction (Reaction (7.4)), sustaining the indirect reduction. In this scenario, the overall reaction rate follows solid-phase boundary kinetics, and indirect reduction via evolved CO gas is the rate-limiting step. Most experimental work on MgO and calcined dolomite supports this two-stage mechanism as the dominant pathway [29, 346, 347].



In contrast to MgO, the CTR of Mg(OH)₂ follows a distinct sequence as shown in Figure 7.5(d). Mg(OH)₂ first dehydrates below 500 °C, generating H₂O vapor (Reaction (7.5)), which then reacts with carbon above 500 °C to produce syngas via steam-carbon gasification (Reaction (7.6)). Transient CO₂ and CH₄ formed at lower temperatures (Reactions (7.7-7.9)) are converted to CO and H₂ as the temperature increases, establishing a strongly reducing gas atmosphere. Reduction to Mg begins near 1000 °C and reaches completion at 1200 °C, producing a gas mixture of 25% Mg, 50% CO, and 25% H₂ (Reaction (7.10)). The superior reducibility of Mg(OH)₂ compared to MgO results from the formation of H₂-containing syngas, rather than CO alone. According to Ellingham diagrams, H₂ is a stronger reductant than CO within the 600-1000 °C range, and its smaller molecular size enables faster diffusion through the MgO-C matrix [134, 348]. As a result, H₂ acts synergistically with CO to accelerate the indirect gas-solid reduction step, enabling Mg(OH)₂ to reduce at temperatures around 700 °C, lower than those needed for MgO under 100 Pa.





The pressure-dependent thermodynamic trends in Figures 7.5(e) and 7.5(f) further clarify the contrasting behaviors of MgO and Mg(OH)₂. At a total pressure of 1 atm, the Gibbs free energy change (ΔG) for CTR of MgO remains positive up to 1800 °C, indicating that Reaction (7.3) is thermodynamically non-spontaneous at this temperature and pressure. In contrast, the reduction of Mg(OH)₂ becomes spontaneous at 1200 °C, which is in excellent agreement with the 46% reduction efficiency observed experimentally in the conventional furnace at 1300 °C.

The small but measurable 10% reduction of MgO at 1300 °C does not contradict the thermodynamic calculation, because MgO reduction under atmospheric pressure is strongly influenced by kinetic factors and gas-sweeping effects. As Yoshikawa and Morita reported [204], continuously purging the reactor with argon helps remove the produced CO from the reaction interface. This gas-sweeping effect lowers the local CO partial pressure and shifts the reaction away from equilibrium, and allows a limited extent of MgO reduction even when ΔG remains positive. In other words, the reaction proceeds because the system is kept far from equilibrium, not because the reaction is thermodynamically favorable. In total, while MgO reduction at 1 atm is fundamentally limited by thermodynamics, Mg(OH)₂ benefits from more favorable thermodynamics and a stronger gas-phase reducing environment (H₂ and CO), which explains its markedly higher reduction efficiency under the same experimental conditions.

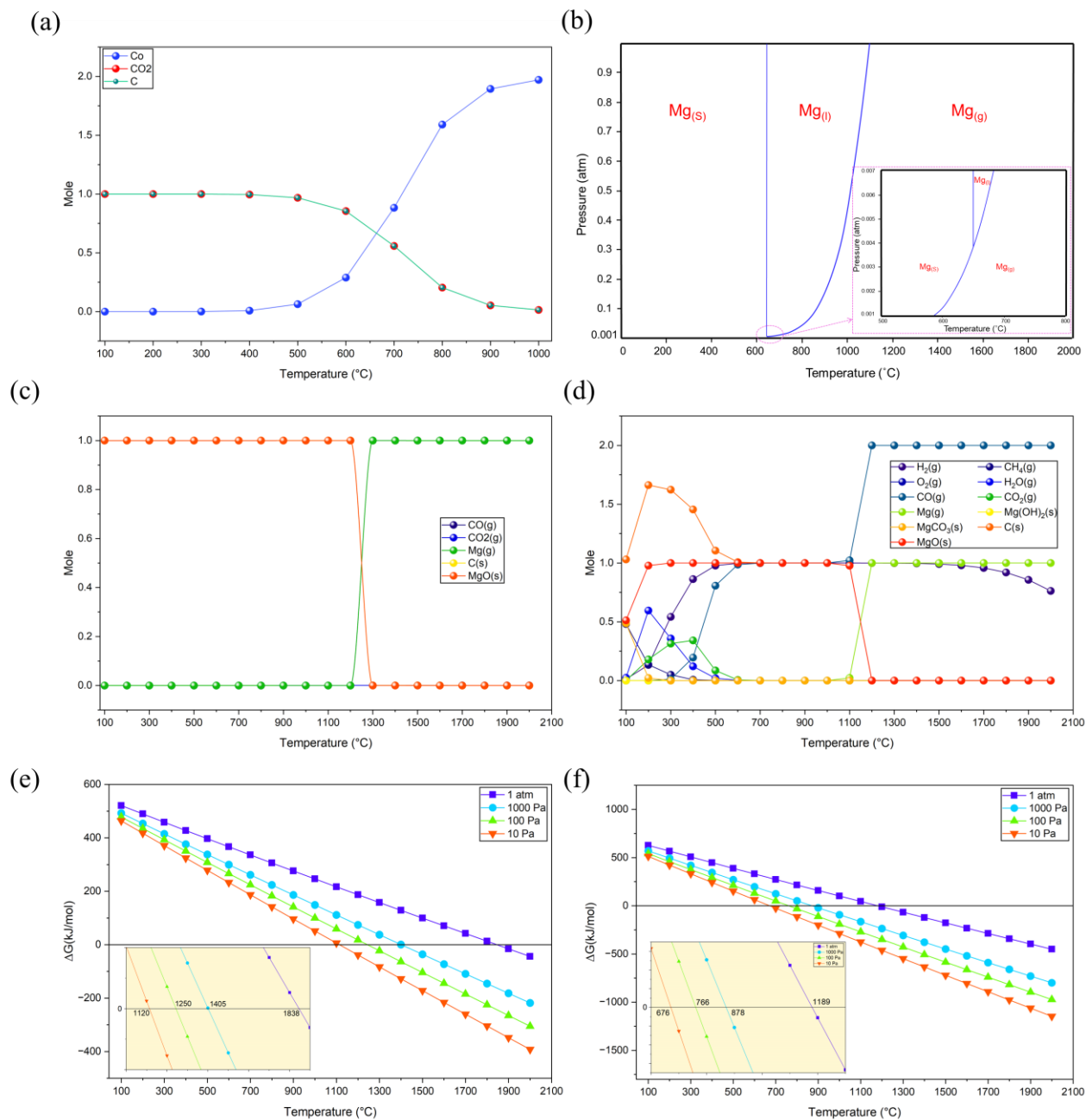


Figure 7.5 Thermochemical simulations (a) Boudouard reaction equilibrium diagram, (b) magnesium phase diagram, (c) equilibrium compositions for MgO-C system at 100 Pa, (d) equilibrium compositions for Mg(OH)₂-C system at 100 Pa, (e) favourability domain at various temperatures and pressures for MgO-C system and (f) favourability domain at various temperatures and pressures for Mg(OH)₂-C system.

7.4.2.3 Microwave-assisted carbothermic reduction

Although the CTR of $\text{Mg}(\text{OH})_2$ enabled atmospheric-pressure Mg metal production, its reduction efficiency in a conventional furnace remains limited because heating was slow and non-uniform, and the temperature drops sharply near the reactor outlet. This temperature profile led to the formation of H_2O and CO_2 and caused the reoxidation of Mg vapor, thereby reducing the overall Mg production yield. To address these challenges, the CTR of both MgO and $\text{Mg}(\text{OH})_2$ was assessed in a microwave-heated fixed-bed reactor.

According to Figures 7.4(a) to 7.4(c), microwave irradiation dramatically improved CTR performance. At 1240-1280 °C and within only 20 min, the reduction efficiencies increased to 58% for MgO and 87% for $\text{Mg}(\text{OH})_2$, roughly three times higher than in the conventional furnace. For MgO , the CO_2 fraction in the outlet gas decreased from 23 vol% to 5 vol%, indicating a suppression of the Boudouard reaction. The purity of condensed Mg also increased from 68 wt% to 88 wt%. A similar trend was observed for $\text{Mg}(\text{OH})_2$. The CO_2 fraction decreased from 6 vol% to 1 vol%, all hydroxyl groups were fully converted to H_2 , and approximately 4 vol% CH_4 appeared in the gas. The condensed Mg metal improved from 73 wt% to 94 wt%, containing only 4 wt% MgO and 2 wt% C.

These substantial enhancements arise from the combined thermal and non-thermal effects of microwave heating. Microwave radiation heats the reaction bed rapidly, selectively, and volumetrically, producing a temperature difference of nearly 800 °C between the hot bed and the cold reactor wall (Section 7.4.1). In contrast, conventional heating warms the reactor from the reactor wall, producing a much smaller temperature gradient and a long cold zone near the outlet. As shown in Figure 7.5(b), unlike the vacuum CTR, where Mg vapor can be condensed directly into Mg metal below 700 °C, under atmospheric pressure, Mg vapor condenses in two steps. First to liquid Mg at a temperature range of 1000-650 °C, then to solid Mg below 650 °C. In the conventional furnace, this slow-cooling zone overlaps regions where CO_2 forms, leading to Mg reoxidation. Microwave heating prevents this by creating a steep thermal gradient where Mg vapor generated in the hot bed is quenched rapidly on the cold wall, suppressing reoxidation and increasing the final Mg purity.

In addition to the global thermal gradient, microwave irradiation can generate localized hotspots at carbon-metal oxide or hydroxide interfaces due to the strong microwave absorption of graphite

compared with the weak dielectric response of MgO and $\text{Mg}(\text{OH})_2$. These hotspots arise from local electric-field concentration and interfacial dielectric mismatch, which produce uneven energy deposition within the reaction bed [349]. As a result, the temperature at the graphite-oxide interface can locally exceed the bulk temperature, accelerating interfacial carbothermic reduction reactions and enhancing mass transfer at the reaction interface [350, 351]. However, the magnitude of microwave-induced hotspot temperature differences is typically limited to approximately 200 °C above the bulk temperature [352].

Beyond thermal effects, microwaves also influence reaction pathways through non-thermal electromagnetic interactions. Non-thermal microwave effects arise from direct coupling between the oscillating electromagnetic field and polarizable lattice species, which can induce electron excitation, bond polarization, and defect formation without requiring a macroscopic temperature increase [155]. In both MgO and $\text{Mg}(\text{OH})_2$, such electromagnetic interactions can destabilize lattice oxygen and promote the formation of oxygen vacancies, thereby lowering the activation energy for oxygen removal during carbothermic reduction [215, 353]. It is important to note that the formation energy of oxygen vacancies in MgO is relatively high (typically around 5-7 eV depending on the defect environment), corresponding to temperatures far exceeding those reached in the present experiments under purely thermal conditions [354, 355]. Therefore, the modest temperature increase associated with microwave hotspots cannot account for the generation of oxygen vacancies in MgO.

Direct experimental evidence supporting this interpretation is provided by the EPR analysis. The g-factor of approximately 2.001 is a well-known signature of oxygen vacancies or lattice defects in a treated material [356]. As shown in Figure 7.4(d), no EPR signal was detected for partially reduced MgO and $\text{Mg}(\text{OH})_2$ obtained from conventional CTR, indicating the absence of vacancy defects under purely thermal heating. In contrast, clear signals at a g-factor of about 2.001 appeared in samples obtained from MW-CTR, confirming the formation of oxygen vacancies only after microwave irradiation. These results strongly indicate that vacancy formation originates from non-thermal microwave heating interactions rather than localized thermal overheating.

For $\text{Mg}(\text{OH})_2$, microwave fields may additionally modify the decomposition mechanism. Instead of proceeding by sequential dehydration and secondary water-gas reactions, the oscillating electromagnetic field directly interacts with polar O-H bonds in both $\text{Mg}(\text{OH})_2$ and the released

H₂O vapor. This interaction weakens the O-H bond through polarization and promotes the formation of reactive radical species ($\cdot\text{H}$ and $\cdot\text{OH}$) [357, 358]. These radicals rapidly react with carbon to produce H₂ and CO, resulting in nearly complete conversion of water vapor and suppressing the accumulation of H₂O in the gas phase.

Overall, the superior performance of MW-CTR results from the synergistic contribution of microwave thermal and non-thermal effects. Rapid volumetric heating and steep thermal gradients enable fast Mg vapor generation and immediate quenching, preventing reoxidation. At the same time, non-thermal microwave-matter interactions with metal oxides and hydroxides promote oxygen-vacancy formation and radical pathways, lowering kinetic barriers and enabling reaction routes that are not accessible under conventional heating. These combined phenomena create a fundamentally different reaction environment, allowing high reduction efficiency and high-purity Mg production at atmospheric pressure within minutes.

7.4.3 Characterization of feed, residues, and products

7.4.3.1 XRD analysis

The crystalline patterns of initial beds, reaction residues, and condensed particles are presented in Figures 7.6 to 7.8. Regarding Figure 7.6, diffraction peaks at 2θ of 26.5° and 54° with Miller index of (002) and (004) are attributed to the hexagonal crystal structure of graphite (JCPD card No. 04-016-0554). The XRD pattern at 2θ of 32.5° , 37.9° , 50.8° , 58.7° , 62.1° , 68.8° , and 72° corresponding to the Miller index of (100), (101), (102), (110), (111), (200), (201), demonstrate the hexagonal crystal structure of Mg(OH)₂ with $P\bar{3}m1$ space group (JCPD card No. 00-044-1482). The calcined Mg(OH)₂ at 800°C also showed diffraction peaks at 2θ of 37.1° , 42.9° , 62.3° , 74.6° and 78.6° with Miller index of (111), (200), (220), (311), and (222) which is ascribed to the cubic crystal structure of MgO with $Fm\bar{3}m$ space group (JCPD card No. 04-009-5447). The mixture of MgO-graphite and Mg(OH)₂-graphite demonstrated the presence of the mentioned phases together without any shift in the corresponding 2θ .

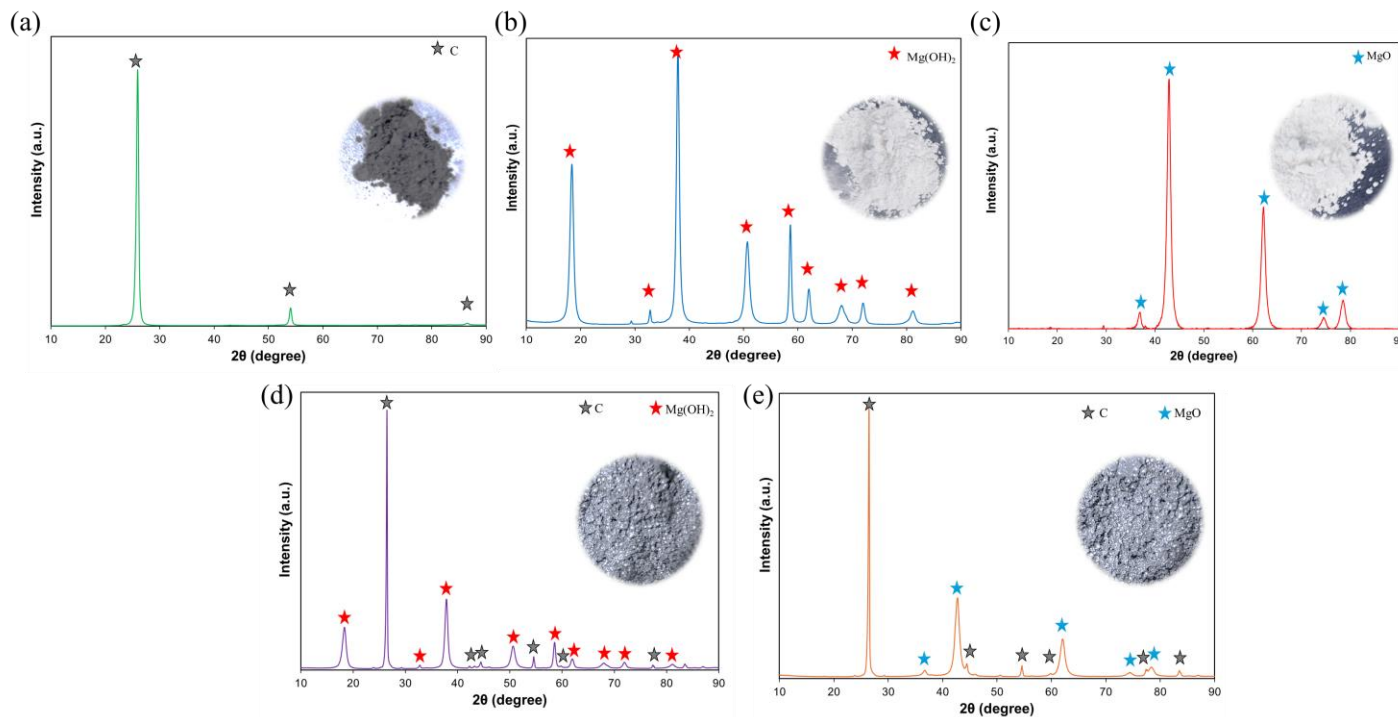


Figure 7.6 XRD patterns of (a) graphite, (b) $\text{Mg}(\text{OH})_2$, (c) MgO , (d) graphite- $\text{Mg}(\text{OH})_2$ mixture, and (e) graphite- MgO mixture.

According to Figure 7.7, the residue of $\text{Mg}(\text{OH})_2$ -graphite produced from both conventional and microwave heating reactors showed the presence of graphite and MgO phases after CTR. This result indicates that in both heating methods, $\text{Mg}(\text{OH})_2$ was fully dehydrated during the reaction. The MgO -graphite mixture also displayed the same crystal phase as the $\text{Mg}(\text{OH})_2$ -graphite mixture following CTR. Regarding the residues from the conventional heating method, the intensity of the MgO phases increased after the reaction in both MgO -graphite and $\text{Mg}(\text{OH})_2$ -graphite mixtures. This increase results from the sintering of MgO particles after the reaction, as shown in the inset photographs, caused by the high temperatures and extended reaction time. Sintering is a major challenge in conventional CTR because it reduces reduction efficiency by decreasing contact between the metal oxide and the solid reductant [346]. Unlike the conventional heating reactor, the intensity of the MgO phase in the residues from the microwave heating reactor decreased after MW-CTR, indicating an efficient conversion of MgO and $\text{Mg}(\text{OH})_2$ to Mg metal. As shown in the insert photograph, no significant sintering of particles was observed in the microwave heating reactor after the MW-CTR. This is because rapid volumetric heating of graphite by electromagnetic waves minimizes sintering effects on MgO reactivity, thereby making the MW-CTR more efficient.

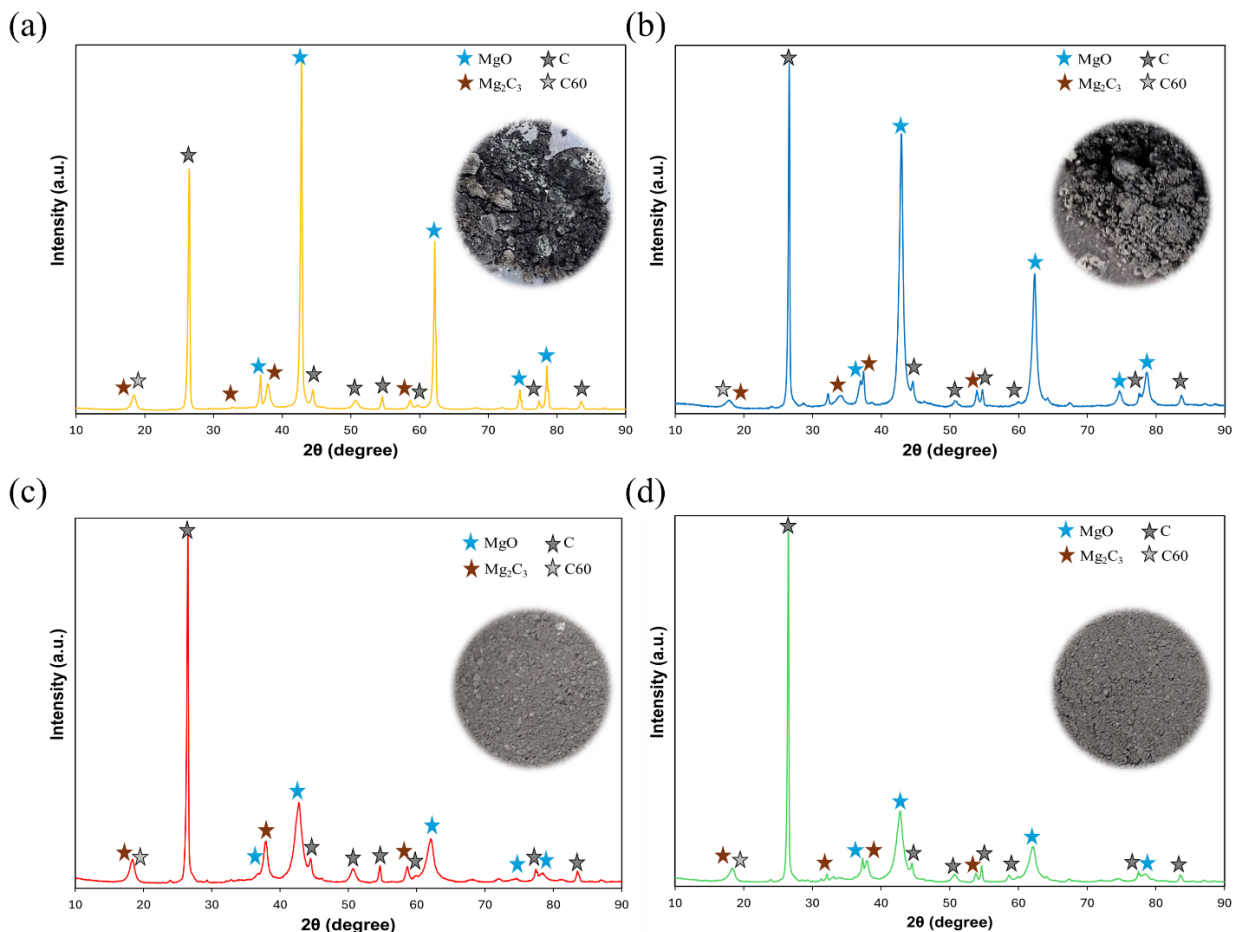


Figure 7.7 XRD patterns of residue obtained from (a) conventional CTR of MgO, (b) conventional CTR of $\text{Mg}(\text{OH})_2$, (c) MW-CTR of MgO, and (d) MW-CTR of $\text{Mg}(\text{OH})_2$.

Regarding the XRD of condensed particles shown in Figure 7.8, the diffraction peaks at 2θ of 32.3° , 34.4° , 36.6° , 47.8° , 57.5° , 62.3° , 67.8° , 69.5° , 72.6° , and 77.5° with Miller index of (100), (002), (101), (102), (110), (103), (200), (201), (004), and (202) is attributed to the hexagonal crystal structure of Mg metal with $P6_3/mmc$ space group (JCPD card No. 01-073-3812). The XRD pattern of the condensed particles in the conventional heating reactor also revealed the presence of MgO and carbon phases. As described in Section 7.4.2, the CO_2 generated by the Boudouard reaction through the gradual condensation of Mg vapor and CO gas reoxidizes Mg metal, resulting in these compounds. However, the condensed particles from microwave-heating reactors contained only Mg metal, indicating that the large temperature difference between the bulk and the reactor walls and rapid condensation on the reactor walls in the microwave-heating system suppressed reoxidation.

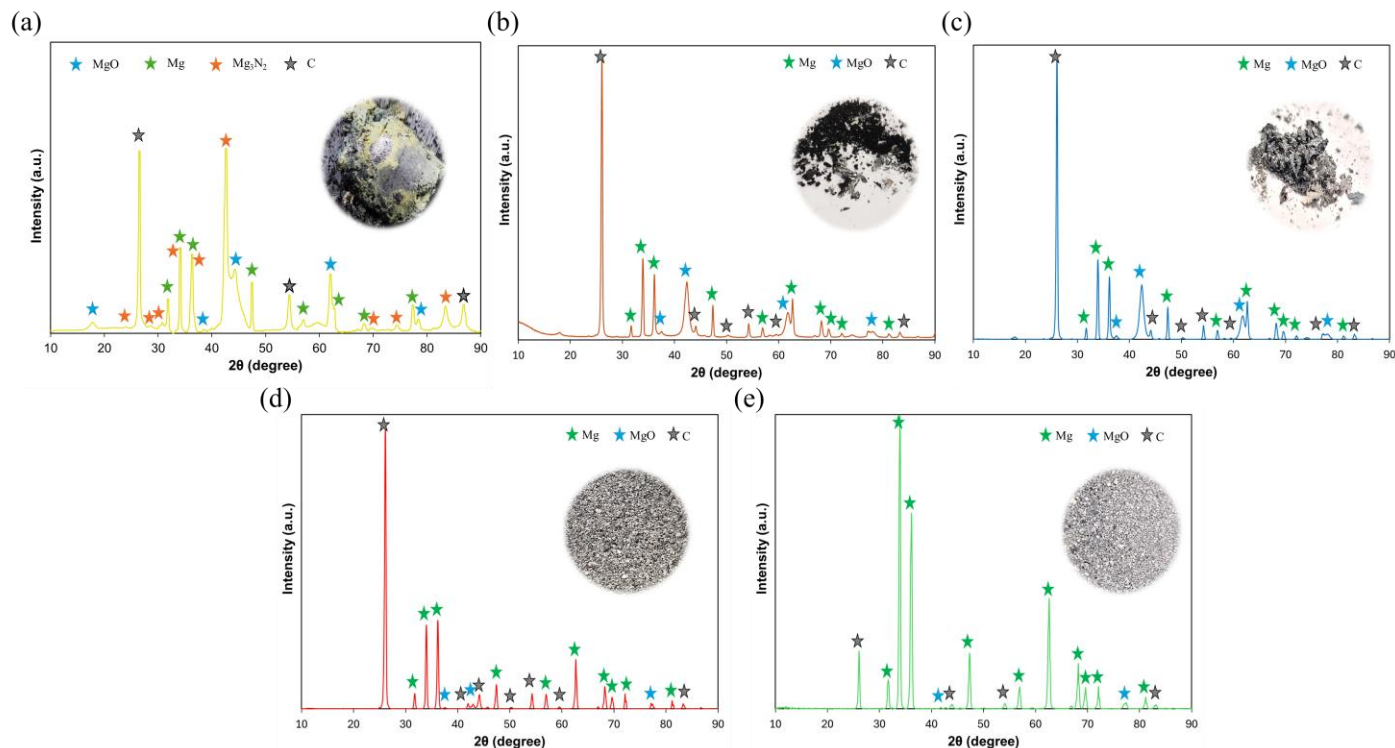


Figure 7.8 XRD patterns of condensates (a) conventional CTR of $\text{Mg}(\text{OH})_2$ under N_2 , (b) conventional CTR of MgO under argon, (c) conventional CTR of $\text{Mg}(\text{OH})_2$ under argon, (d) MW-CTR of MgO under argon, and (e) MW-CTR of $\text{Mg}(\text{OH})_2$ under argon.

It is worth noting that we selected argon as the inert gas for performing the CTR in both conventional and microwave-heating reactors. If nitrogen is selected as the inert gas, the nitridation reaction is expected to occur on the condensed metal product. As shown in Reaction (7.11), the condensed Mg metal at high temperatures reacts with N_2 gas to form Mg_3N_2 . According to Figure 7.8, the diffraction peak at 31.2° , 33.6° , 36° , 42.6° , 46.5° , 51.9° , 57.1° , 60.4° , 63.2° , 64.6° , 68.9° , and 76.8° with Miller index of (222), (321), (400), (332), (431), (440), (611), (541), (631), (444), (721) and (800) are related to the cubic crystal structure of Mg_3N_2 with $\text{Ia}\bar{3}$ space group (JCPD card No. 04-009-5970). The yellow powder shown in the insert photograph is Mg_3N_2 , which was formed after CTR of $\text{Mg}(\text{OH})_2$ within a conventional heating reactor under a N_2 gas atmosphere. Therefore, it is compulsory to conduct atmospheric CTR processes under argon gas flow.



7.4.3.2 XPS analysis

Figure 7.9 illustrates the elemental composition and electronic state of the residue and condensed particle obtained by CTR in the microwave heating reactor. The wide survey scan spectra in Figures 7.9(a-1) and 7.9(b-1) display the photoelectron lines of carbon (C 1s), oxygen (O 1s), and magnesium (Mg 2p, 2s) along with the Auger transition line (Mg KLL). Regarding the XPS data of the residue, the high-resolution C 1s spectrum (Figure 7.9(a-2)) reveals six peaks at binding energies of 284 eV, 287 eV, 288.8 eV, 290 eV, and 290.7 eV, attributed to C-C, C-O, O-C=O, CO₃, and pi-pi* transition bonds. The high-resolution O 1s spectrum (Figure 7.9(a-3)) also shows four peaks at binding energies of 529.5 eV, 531 eV, 532.2 eV, and 533 eV, which are assigned to lattice oxygen (Mg-O), oxygen vacancies, and adsorbed oxygen (C=O and C-O). The oxygen vacancy in MgO of the residue resulted from the non-thermal effect of Microwave heating, which was also confirmed by EPR analysis. The high-resolution Mg 1s spectrum (Figure 7.9(a-4)) consisted of four peaks at binding energies of 1302.4 eV for Mg-O crystal structure, 1304.6 eV for Mg-O amorphous structure, and 1305.2 eV and 1306.6 eV for MgCOO- bonds. Therefore, the residue of MW-CTR is composed of graphite reductant and unreacted MgO, which was also confirmed by XRD analysis.

Regarding the XPS of condensed particles, the high-resolution C 1s spectrum (Figure 7.9(b-2)) showed four peaks in the binding energy range of 280-290 eV, including 284.8 eV for the C-C bond, 286.7 eV for the C-O bond, 288.8 eV for the O-C=C bond, and 290 eV for the CO₃ bond. According to the high-resolution O 1s spectrum (Figure 7.9(b-3)), oxygen in the condensed particle mainly bonds with carbon, showing two peaks at 532.3 eV for the C=O bond and 533.1 eV for the C-O bond. The high-resolution Mg 1s spectrum (Figure 7.9(b-4)) also displayed a dominant peak at a binding energy of 1303.6, which is characteristic of Mg metal. A weak peak at binding energy of 1306.7 eV is also attributed to the MgCOO- bond. Furthermore, no peak of argon gas adsorption was observed in the condensed particles, meaning that argon gas is an appropriate carrier for conducting CTR at atmospheric pressure. According to XPS analysis, we can conclude that the rapid condensation in a microwave heating reactor, combined with the presence of syngas, was effective in producing Mg metal through MW-CTR of Mg(OH)₂.

Figure 7.9 XPS spectra of (a) residue and (b) condensed particle obtained from MW-CTR of $\text{Mg}(\text{OH})_2$.

7.4.3.3 Raman spectroscopy

The Raman spectra of $\text{Mg}(\text{OH})_2$ -graphite and MgO -graphite mixtures before and after CTR under microwave and conventional heating are presented in Figure 7.10. The spectra primarily exhibit the characteristic bands of graphitic carbon. It should be noted that the MgO and $\text{Mg}(\text{OH})_2$ phases are difficult to detect directly in the present mixtures using the 532 nm excitation laser and the low power employed in this study. MgO exhibits weak Raman activity and often generates fluorescence background under visible excitation, while the strong Raman scattering of graphite dominates the spectra and masks potential weak signals from Mg-containing phases. Therefore, Raman analysis in this work mainly probes the structural evolution of the graphite reductant, while the phase evolution of Mg-containing species was confirmed using XRD and XPS analyses (Sections 7.4.3.1 and 7.4.3.2).

For all mixtures, five peaks were observed at approximately 1350, 1580, 2450, 2720, and 3240 cm^{-1} . The weak peak around 1350 cm^{-1} corresponds to the D band of graphite and is associated with defects in the graphene layers of hexagonal graphite. This band originates from the breathing modes of A_{1g} hexagonal rings and is activated by structural defects such as dangling bonds, sp^3 hybridization, or lattice distortions in the sp^2 carbon network [359]. The dominant sharp peak at approximately 1580 cm^{-1} represents the G band of crystalline graphite and is attributed to the first-order phonon scattering of sp^2 carbon arising from the E_{2g} vibrational mode [360]. The peak at around 2720 cm^{-1} corresponds to the 2D band (also known as the G' band), which results from a second-order double-resonance process involving two zone-boundary phonons near the K-point and serves as the overtone of the D band [361]. Additional weak features near 2450 cm^{-1} and 3240 cm^{-1} correspond to the G^* and $2D'$ bands of graphite, respectively, which are generally associated with structural imperfections such as edges, dislocations, cracks, or vacancy defects [362].

After CTR under both microwave and conventional heating, a slight redshift of the characteristic graphite peaks was observed. This shift is more pronounced for the $\text{Mg}(\text{OH})_2$ -graphite mixtures than for the MgO -graphite mixtures. Redshifts in Raman spectra are typically associated with tensile strain, lattice distortion, or increased structural disorder within graphitic domains [363, 364].

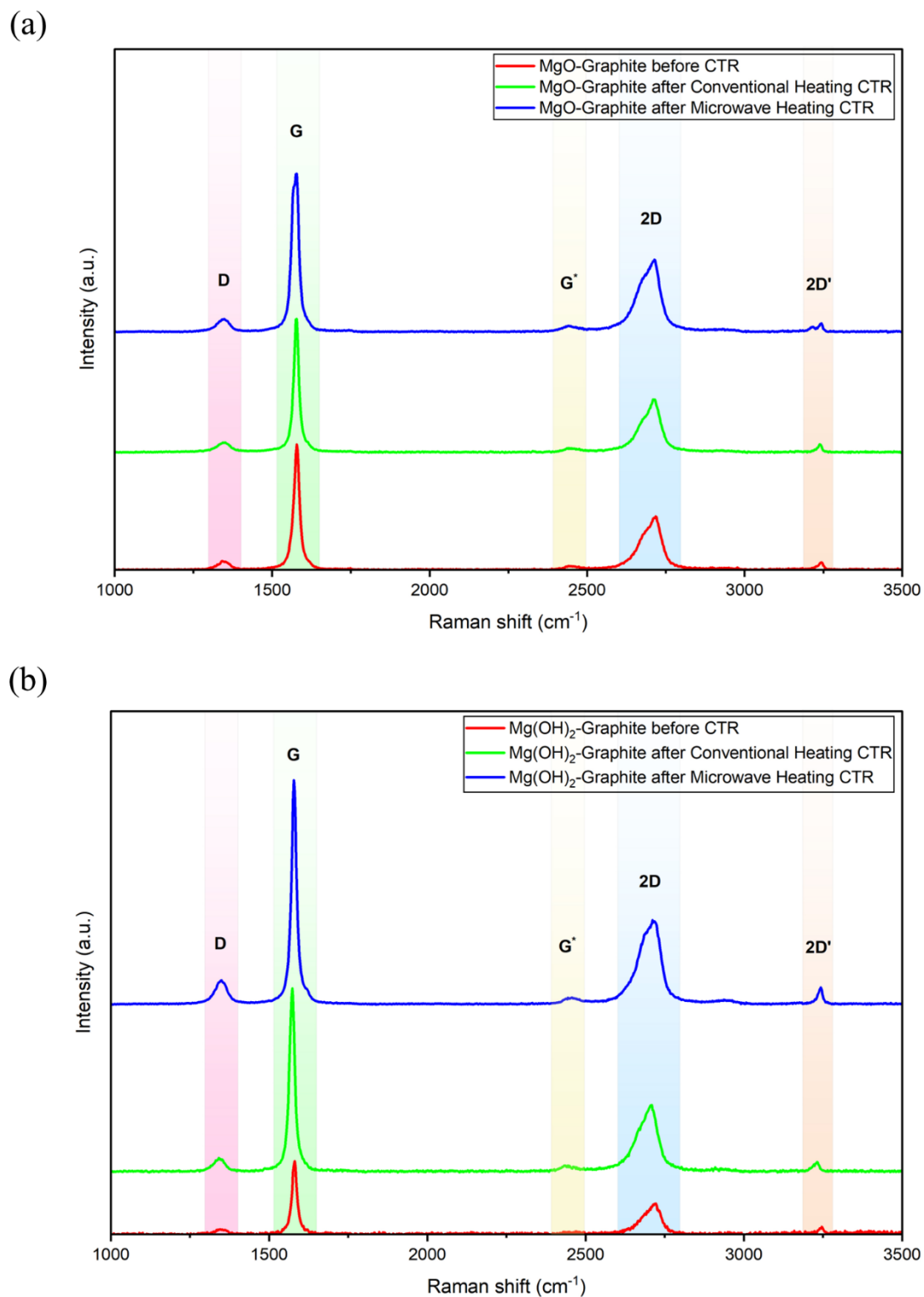


Figure 7.10 Raman spectra of (a) MgO-graphite mixtures and (b) $\text{Mg}(\text{OH})_2$ -graphite mixtures before and after CTR under conventional heating and microwave heating.

The structural disorder and graphite layer stacking were further evaluated using the intensity ratios of the D and G bands (I_D/I_G) and the 2D and G bands (I_{2D}/I_G), respectively. A higher I_D/I_G ratio indicates an increased density of structural defects in graphite, whereas a lower I_{2D}/I_G ratio generally corresponds to thicker multilayer graphene structures [365]. The in-plane crystallite size (L_a) can also be used to assess the structural order of sp^2 carbon materials, where smaller L_a values correspond to greater defect density [366]. The crystallite size L_a (nm) was calculated using the equation proposed by Mallet-Ladeira et al. [367]:

$$L_a = \frac{4.4}{\frac{I_D}{I_G}} \left(\frac{2.41}{E_L} \right)^4 \quad (7.12)$$

where E_L is the excitation energy of the laser (eV). For the 532 nm Raman laser used in this study, the E_L is 2.33 eV. The calculated Raman parameters are summarized in Table 7.1.

Table 7.1 Raman characteristics of $Mg(OH)_2$ -graphite and MgO -graphite mixtures before and after CTR

Samples	I_D/I_G	I_{2D}/I_G	L_a (nm)
MgO -graphite before reaction	0.066	0.42	76
MgO -graphite after conventional CTR	0.069	0.41	73
MgO -graphite after MW-CTR	0.077	0.43	65
$Mg(OH)_2$ -graphite before reaction	0.065	0.41	77
$Mg(OH)_2$ -graphite after conventional CTR	0.074	0.36	68
$Mg(OH)_2$ -graphite after MW-CTR	0.11	0.37	46

Raman analysis indicates that the graphite reductant undergoes reaction-induced structural disorder during the CTR process, as evidenced by the increase in I_D/I_G and the corresponding decrease in L_a after reduction. For the $Mg(OH)_2$ -graphite mixture, I_D/I_G increased from 0.065 to 0.074 after conventional CTR and further to 0.11 after MW-CTR, while L_a decreased from 77 to 68 and 46 nm, respectively. These changes indicate progressive defect formation and fragmentation of ordered sp^2 domains, with microwave heating causing substantially stronger structural modification of graphite than conventional heating.

In contrast, the MgO-graphite mixture exhibited smaller changes in I_D/I_G and L_a , suggesting milder graphite degradation. A plausible explanation for the stronger structural modification observed in the $Mg(OH)_2$ system is the decomposition of $Mg(OH)_2$ during heating, which releases H_2O and hydroxyl-derived species prior to or during the reduction process. The presence of these species can promote additional gas-solid reactions, including carbon-steam interactions, generating CO and H_2 and creating a more dynamic reaction environment. These processes can enhance carbon gasification and defect formation in graphite, resulting in increased disorder within the carbon structure.

The I_{2D}/I_G ratios remained below one for all samples, indicating that the carbon residue retains a multilayer graphitic structure (more than four layers) rather than undergoing extensive exfoliation [368]. Overall, the Raman results demonstrate that MW-CTR, particularly in the $Mg(OH)_2$ -based system, promotes stronger structural modification of graphite, consistent with intensified local heating and enhanced carbon participation in the reduction reaction.

7.4.3.4 SEM-EDS analysis

The morphologies of beds before and after the CTR, as well as condensed particles, are presented in Figures 7.11 to 7.13. According to Figure 7.11, the microsphere particles of $Mg(OH)_2$ and MgO are well mixed with flake-like graphite that guarantees a good contact during the thermal reduction reaction. As shown in Figures 7.11(f) and 7.11(g), the D_{50} of this mixture after grinding was measured at 18.5 μm and 13 μm , respectively. The microwave penetration depth in graphite particles with a size less than 80 μm is around 1.34-2.09 cm, indicating their excellent microwave heating capability [165].

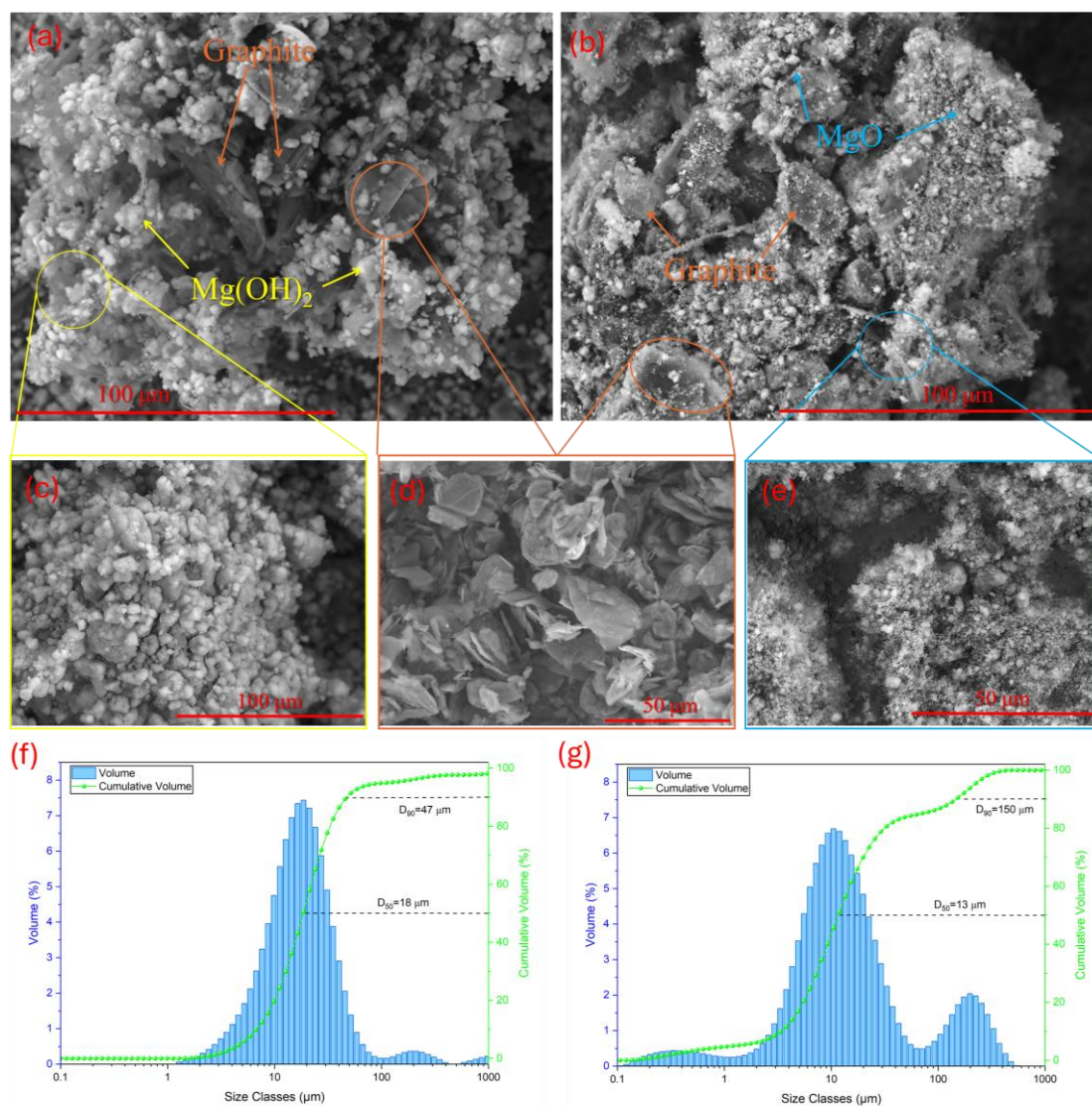


Figure 7.11 SEM of (a) Mg(OH)_2 -Graphite mixture, (b) MgO -graphite mixture, (c) Mg(OH)_2 , (d) graphite, (e) MgO , (f) PSD of Mg(OH)_2 -Graphite mixture, and (g) PSD MgO -graphite mixture.

According to Figures 7.12(a) to 7.12(d), sintering of particles was observed in the residues of both Mg(OH)_2 -graphite and MgO -graphite mixtures after conventional heating, where the D_{50} increased significantly from 18.5 μm to 105 μm and from 13 μm to 225 μm , respectively. High temperatures and prolonged process times are the main causes of this densification. Sintering reduces effective contact between metal oxide/hydroxide particles and graphite reductants. Additionally, in the case of volatile metals like Mg, sintering is problematic because pore closure by sintering blocks the diffusion of the produced metal gas, hindering the reaction's completion and potentially leading to incomplete reduction. Furthermore, it obstructs the indirect gas-solid reaction pathway for CO and H_2 , making CTR less efficient. As opposed to conventional heating, no significant volumetric

expansion due to sintering was observed in the residues obtained after CTR in microwave heating reactors (Figures 7.12(e) to 7.12(h)). The residue from MW-CTR showed a slight increase in particle size, with a D_{50} ranging from 23 μm to 26 μm . The selective, volumetric, and rapid thermal reduction were the primary reasons that microwave heating prevented the sintering of metal oxide particles. This advantage is one of the reasons why CTR in a microwave heating reactor was more efficient than in a conventional heating reactor, as shown in Section 7.4.2.

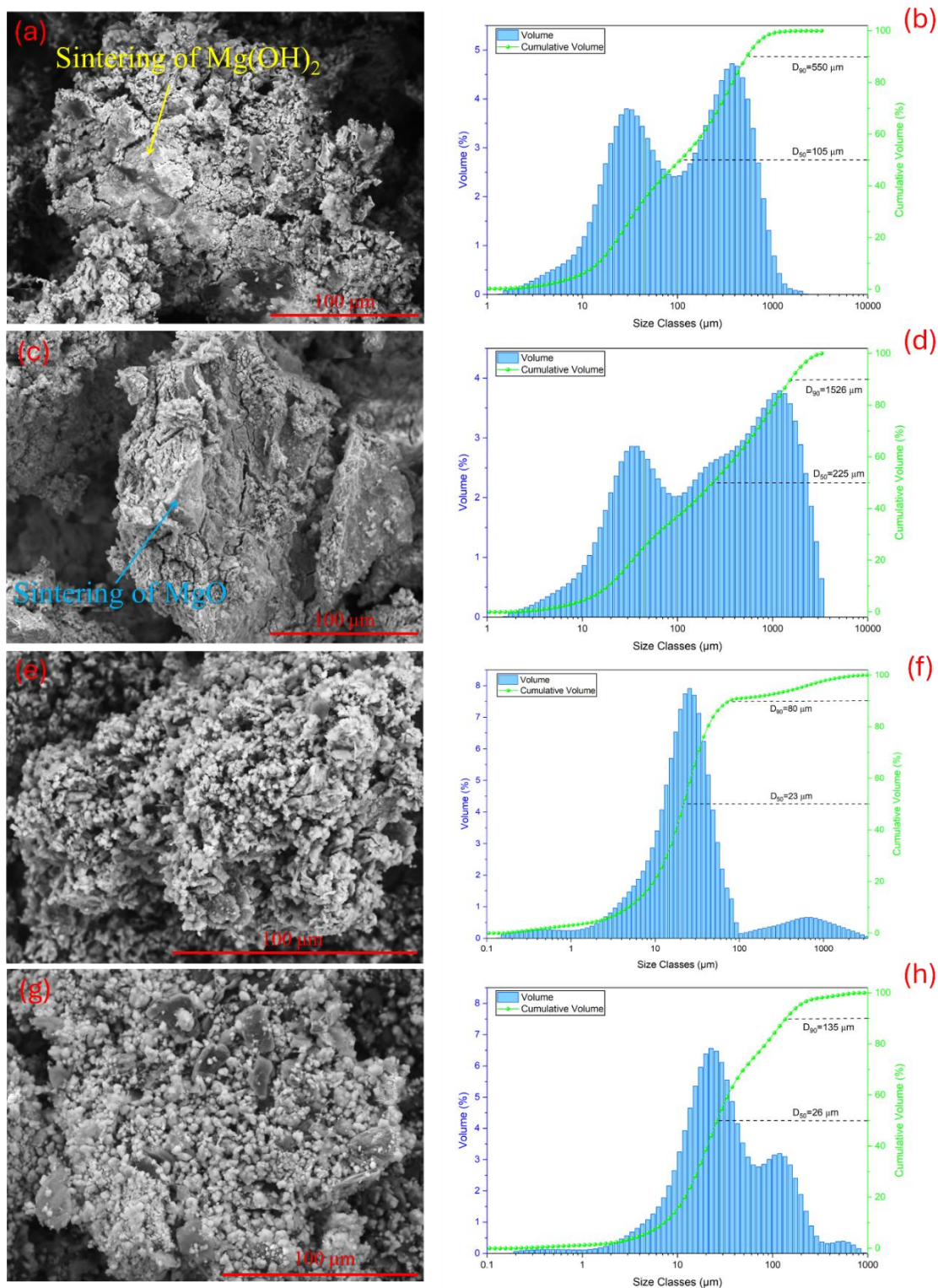


Figure 7.12 SEM and PSD of residues after the CTR of (a, b) $\text{Mg}(\text{OH})_2$ -Graphite mixture in conventional heating, (c, d) MgO -graphite mixture in conventional heating, (e, f) $\text{Mg}(\text{OH})_2$ -Graphite mixture in microwave heating, (g, h) MgO -graphite mixture in microwave heating.

Figure 7.13 illustrates the morphology of condensed particles inside both conventional and microwave heating reactors. The CTR in the conventional heating reactor, conducted under argon gas flow, resulted in the formation of a hexagonal Mg prism with a D₅₀ size range of 11 μm to 12 μm (Figures 7.13(a)-7.13(d)). This faceted morphology arises from the condensation of supersaturated Mg vapor onto the colder tube walls, where heterogeneous vapor-solid nucleation is followed by thermodynamically governed two-dimensional growth along the low-energy basal planes of the hexagonal close-packed Mg lattice, ultimately yielding the characteristic hexagonal geometry [31]. More inspection of these figures also revealed submicron whisker-like MgO agglomerates and microsphere carbon particles, originating from the Boudouard reaction and reverse Mg metal oxidation. Regarding Figures 7.13(e) to 7.13(h), the hexagonal Mg prisms condensed in the microwave heating reactor exhibited smaller particle sizes with D₅₀ in the range of 4 μm to 5 μm . Unlike the conventional furnace, which shows a gradual axial temperature decrease, the microwave reactor features a significant temperature gradient between the bed and the reactor wall, as discussed in Section 7.4.1. This temperature gradient leads to vapor condensation at lower temperatures, often below the melting point of Mg, causing numerous nuclei to form simultaneously and limiting atom migration and coalescence, thereby yielding smaller Mg particles [369].

Comparison of the two feedstocks further shows that the Mg(OH)₂-graphite mixture produced more densely packed hexagonal Mg prisms than the MgO-graphite bed in both conventional and microwave heating reactors. This effect is attributed to the presence of H₂ in the outlet gas during Mg(OH)₂ reduction, which suppresses reverse oxidation reactions and thus favors more nucleation and growth of Mg.

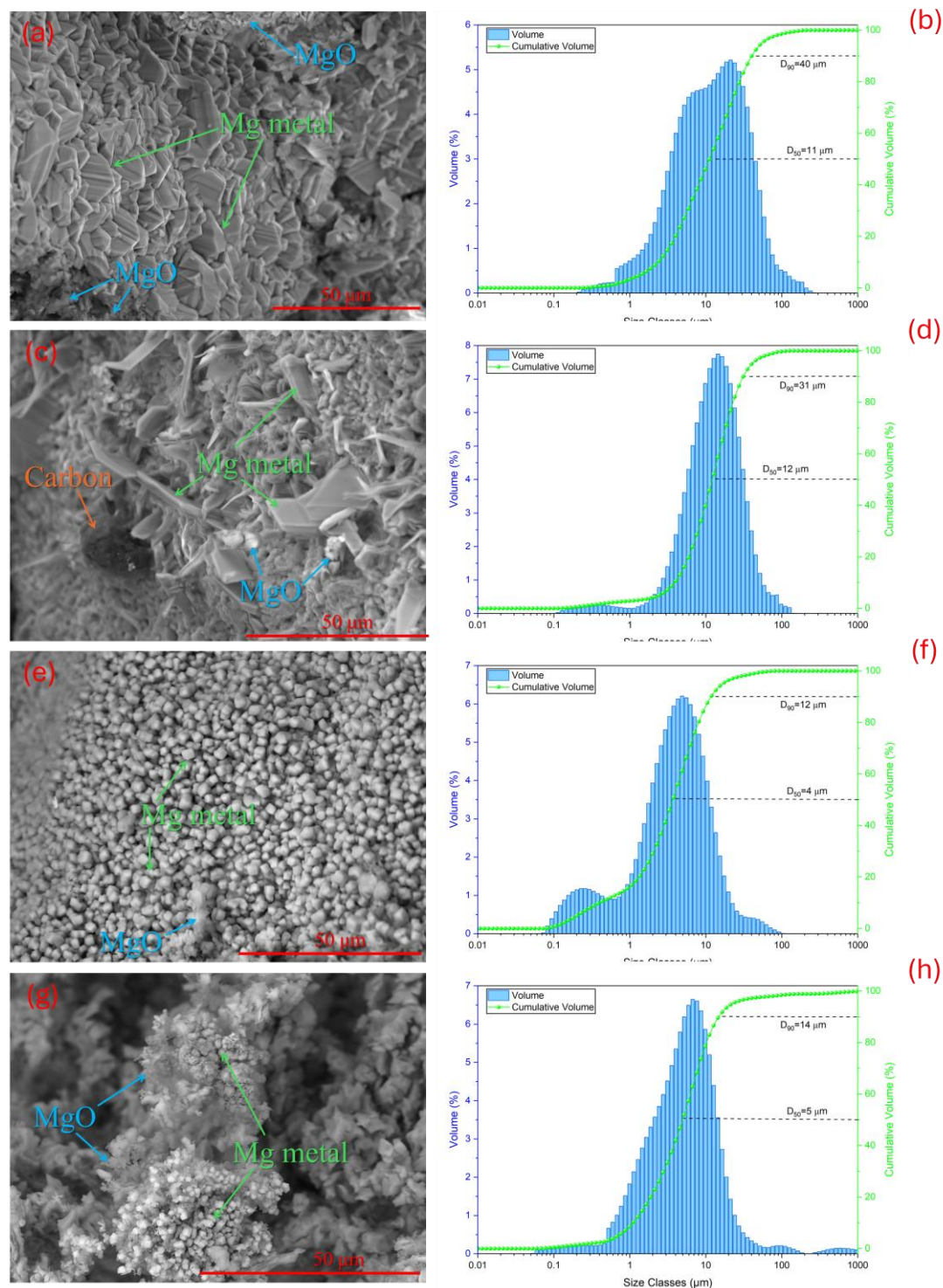


Figure 7.13 SEM and PSD of condensed particles obtained from the CTR of (a, b) $\text{Mg}(\text{OH})_2$ -Graphite mixture in conventional heating, (c, d) MgO-graphite mixture in conventional heating, (e, f) $\text{Mg}(\text{OH})_2$ -Graphite mixture in microwave heating, (g, h) MgO-graphite mixture in microwave heating.

7.4.3.5 HRTEM analysis

An HRTEM analysis was performed to gain deeper insight into the microstructure and lattice characteristics of the $\text{Mg}(\text{OH})_2$ -graphite mixtures before and after CTR under microwave and conventional heating. The results reveal the spatial distribution of C, Mg, and O, confirming that Mg-containing particles are dispersed on the surface of graphite flakes prior to reaction and remain associated with the carbon matrix after CTR. Figures 7.14(a-1) to 7.14(h-1) present the STEM image, elemental mappings, HRTEM images, and SAED pattern of the $\text{Mg}(\text{OH})_2$ -graphite mixture before reaction. As shown in Figures 7.14(a-1) to 7.14(d-1), $\text{Mg}(\text{OH})_2$ particles are homogeneously dispersed on the surface of graphite flakes. Although elemental mapping cannot detect hydrogen atoms, lattice fringes with an interplanar spacing of 0.23 nm observed in Figure 7.14(f-1) correspond to the $\text{Mg}(\text{OH})_2$ (101) plane. The lattice spacing of 0.34 nm in Figure 7.14(g-1) corresponds to the graphite (002) plane. The SAED pattern in Figure 7.14(h-1) displays diffraction rings and spots corresponding to $\text{Mg}(\text{OH})_2$ (101), (110) and graphite (100), (110) planes.

After CTR, the Mg-containing phases transform into MgO. As shown in Figures 7.14(a-2) and 7.14(a-3), MgO particles produced after conventional heating tend to agglomerate on the graphite surface, whereas those formed during microwave-assisted CTR retain a morphology similar to the initial structure. The lattice fringes with spacings of 0.20-0.21 nm observed in Figure 7.14(f-2) and 14(f-3) correspond to the MgO (200) plane, confirming the complete dehydration of $\text{Mg}(\text{OH})_2$ into MgO during the thermal reduction process. Lattice fringes corresponding to graphite (002) are observed in Figures 7.14(g-2) and 7.14(g-3) with spacings of 0.36 and 0.37 nm, respectively. The slightly expanded spacing and diffuse lattice fringes suggest the presence of structural disorder in graphite after CTR [370], which is consistent with the Raman analysis discussed in Section 7.4.3.3.

Furthermore, localized lattice distortion observed in Figure 7.14(f-3) may be associated with oxygen vacancy formation in MgO during microwave-assisted CTR [371], consistent with the defect signals detected by EPR analysis. Such lattice distortion may originate from localized microwave heating and defect formation, which can facilitate oxygen vacancy generation and enhance the reduction reaction. The SAED pattern of the residue after conventional CTR (Figure 7.14(h-2)) exhibits diffraction rings corresponding to MgO (111), (200), (220), and (311) together with graphite (110) and (201) reflections. Likewise, the SAED pattern of the microwave-treated

residue (Figure 7.14(h-3)) shows diffraction rings corresponding to MgO (200) and (220) along with graphite (110) and (002) reflections.

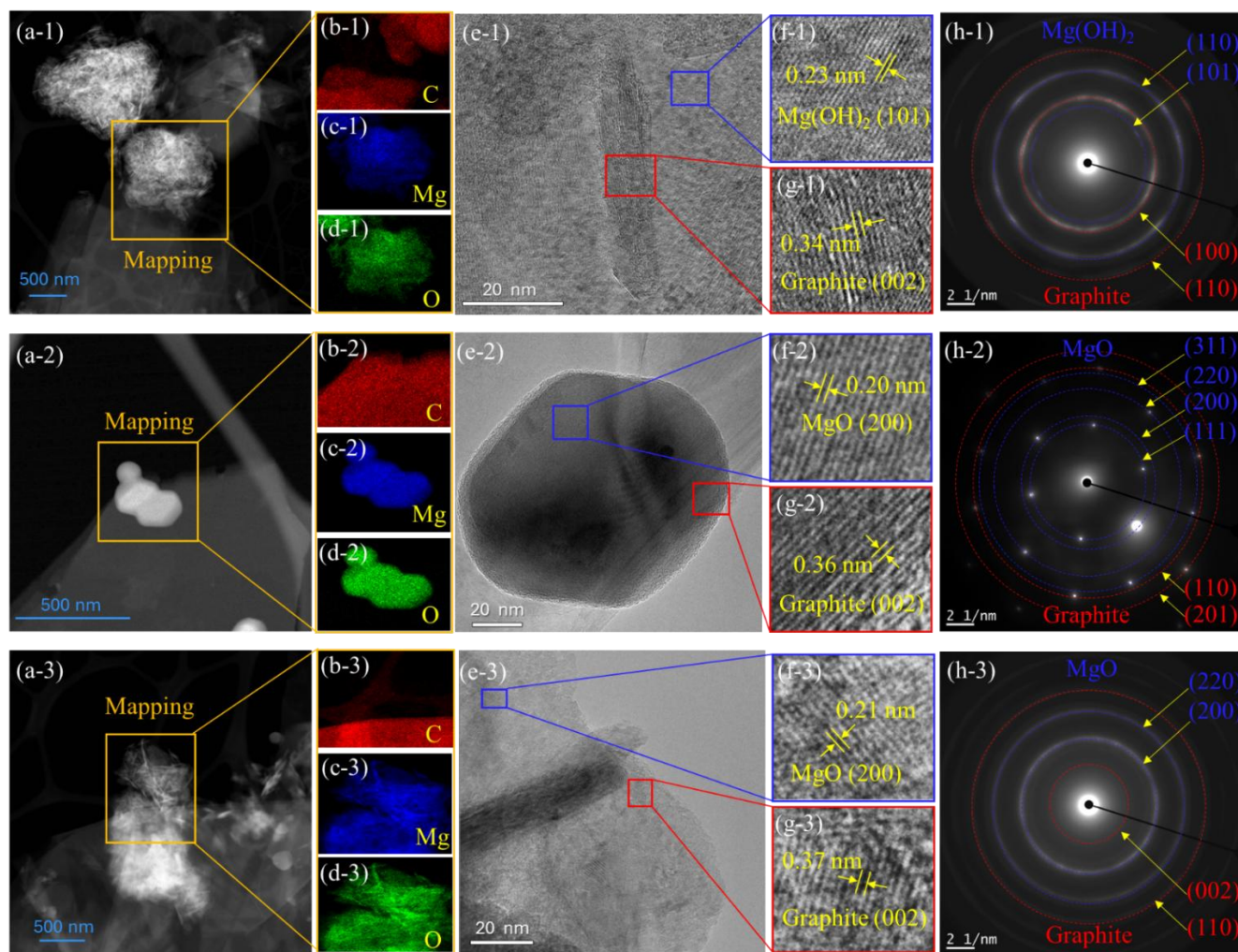


Figure 7.14 (a) STEM images, (b)-(d) elemental mappings, (e)-(g) HRTEM images, and (h) SAED patterns of Mg(OH)₂-graphite mixture before reaction (row 1) and after CTR under conventional heating (row 2) and microwave heating (row 3).

7.4.4 Contributing parameters in microwave-assisted carbothermic reduction

The molar ratio of Graphite to Mg(OH)₂ and microwave input power are two main factors that influence the efficiency of CTR. Figure 7.15 shows the effect of the Graphite:Mg(OH)₂ molar ratio, ranging from 1 to 3, under microwave irradiation at 880 W for 20 min. To assess this factor at roughly constant temperature, the initial weight of graphite was kept the same, while the weight of

$\text{Mg}(\text{OH})_2$ was varied according to the molar ratio. This approach maintained temperatures between 1210-1290 °C. As shown in Figure 7.15(a), the reduction efficiency of $\text{Mg}(\text{OH})_2$ at a molar ratio of 1 was low, about 10%, suggesting insufficient carbon for effective CTR. Increasing the molar ratio to the stoichiometric value of 2 resulted in nearly a nine-fold increase in reduction efficiency. According to Figure 7.15(b), raising the molar ratio from 1 to 2 increased CO gas production from 43 vol% to 62 vol% and lowered H_2 evolution from 52 vol% to 33 vol%. The change in the CO/H_2 ratio from 0.83 to 1.86 reflects the occurrence of CTR and water splitting. When the C molar ratio is too low, CTR is inefficient and produces little CO gas. However, under the same conditions, dehydration of $\text{Mg}(\text{OH})_2$ at temperatures above 1200 °C, followed by water splitting via steam-carbon gasification and the non-thermal effects of microwave radiation, occurs and generates more H_2 gas than CO gas. When the C molar ratio is sufficient, $\text{Mg}(\text{OH})_2$ reduction proceeds efficiently, resulting in more CO production than H_2 , leading to a CO/H_2 gas ratio greater than 1.8.

Regarding Figure 7.15(c), the reoxidation of condensed magnesium was negligible across all molar ratios due to the rapid quenching of Mg vapor in the microwave heating reactor, which resulted in Mg with a purity ranging from 91% to 94%. Increasing the Graphite: $\text{Mg}(\text{OH})_2$ molar ratio to 3 slightly improved the reduction efficiency to 89% and produced Mg metal with a purity of 95%, along with syngas having a CO/H_2 ratio of 2.1.

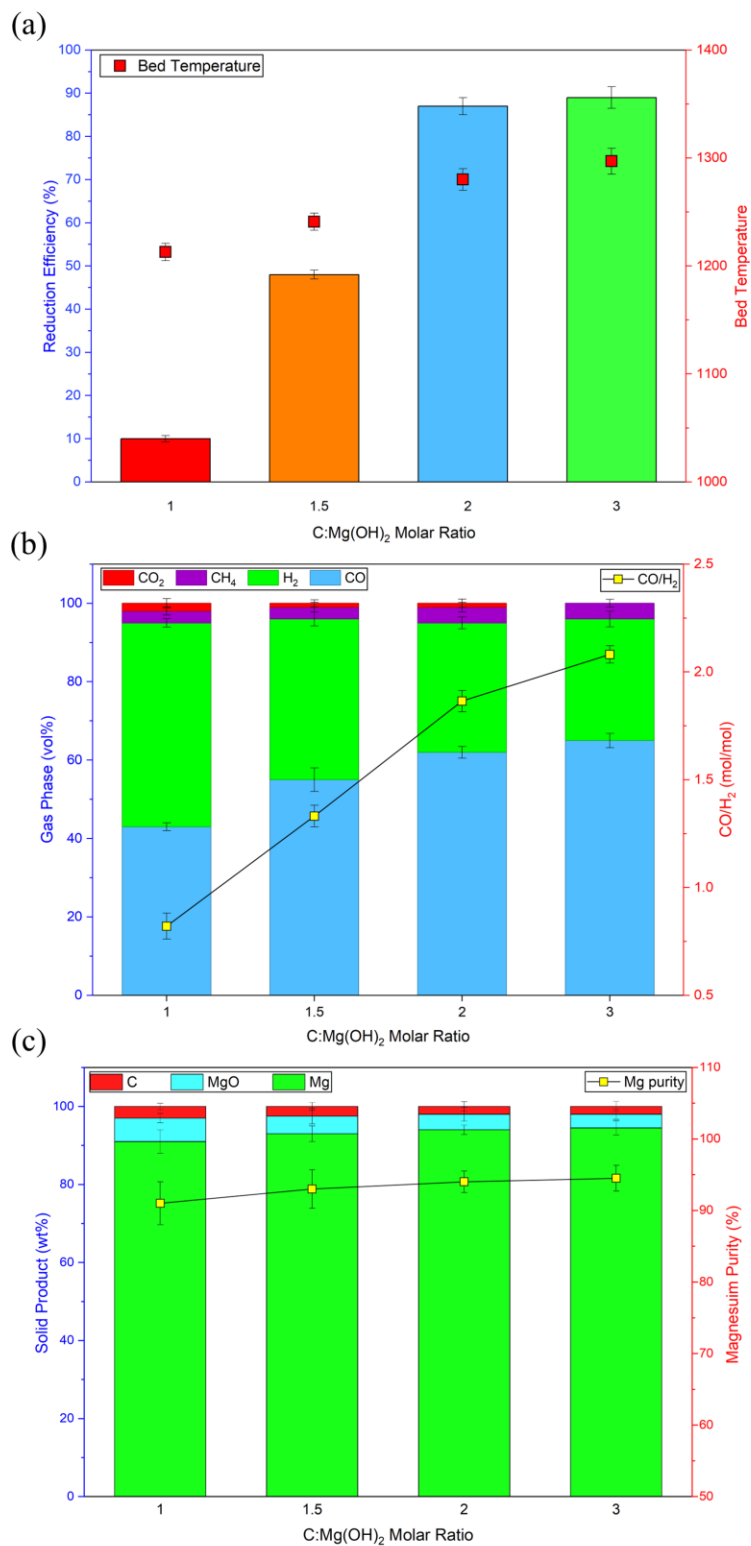


Figure 7.15 The effect of the graphite to Mg(OH)₂ ratio on MW-CTR over 20 min at 880 W (a) reduction efficiency, (b) evolved gases, and (c) condensed solid products.

According to Figure 7.16(a), changing the microwave input power also significantly affects the reduction efficiency. At a fixed molar ratio of Graphite to $\text{Mg}(\text{OH})_2$ of 2:1, decreasing the power from 880 W to 550 W over 20 min decreased the reduction efficiency from 87% to 22%. Based on Figures 7.16(b) and 7.16(c), when the input power was decreased by 330 W, the CO/H_2 ratio and Mg purity dropped from 1.86 to 0.91 and from 94% to 90%, respectively. This decline is related to the bed temperature, which is directly proportional to the microwave input power. Lowering the microwave power reduces the energy available to the graphite, slowing electron movement and resulting in fewer collisions with the graphite lattice. Consequently, less heat is generated, leading to a bed exposed to lower input powers. Lower bed temperatures can decrease reduction efficiency through both thermodynamic and kinetic effects. As the temperature drops, the Gibbs free energy change for Reaction (7.10) becomes less negative, shifting the equilibrium toward reactants and reducing the maximum metal yield. Simultaneously, the reaction kinetics slow down considerably because diffusion rates and reaction constants, as described by the Arrhenius equation, decrease with temperature. [324]. Therefore, a drop in the reduction efficiency occurs at lower temperatures.

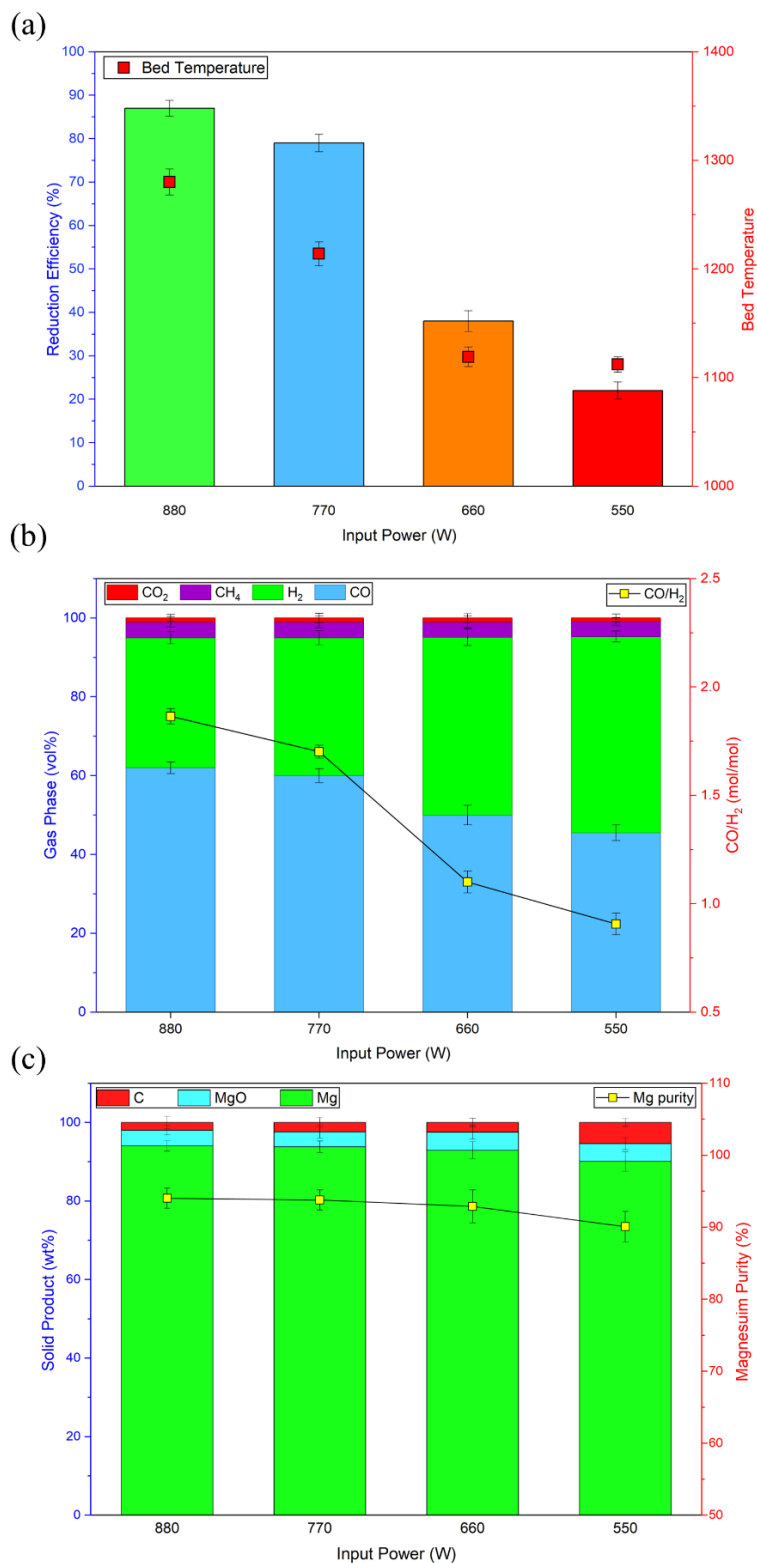


Figure 7.16 The effect of input power on MW-CTR over 20 min with Graphite to Mg(OH)₂ of 2:1 (a) reduction efficiency, (b) evolved gases, and (c) condensed solid products.

7.4.5 Proposed Mechanism of microwave-assisted carbothermic reduction

Based on thermodynamic simulations and experimental results, a mechanistic pathway for MW-CTR of $\text{Mg}(\text{OH})_2$ was proposed, as illustrated in Figure 7.17. In the first step, graphite acts as a microwave susceptor, rapidly reaching high temperatures, while the surrounding environment remains relatively cold. This temperature gradient results from the microwave thermal effect. Then, heat is transferred from the hot graphite to the nearby $\text{Mg}(\text{OH})_2$ by conduction, causing its dehydration into MgO and H_2O vapor. During this process, H_2O vapor partially reacts with graphite, producing syngas via steam-carbon gasification. In the second step, two non-thermal microwave effects occur in addition to the thermal effect. First, the oscillating electromagnetic field polarizes the H_2O vapor and the $\text{Mg}(\text{OH})_2$ lattice, weakening the O-H bonds and facilitating dissociation into syngas in the presence of carbon. Second, the interaction between the microwave field and the MgO lattice excites electrons and creates oxygen vacancies, which lowers the energy barrier for MgO reduction. These two steps are the red zone in the actual photograph. In the final step, carbon and in-situ generated syngas participate in direct and indirect CTR, producing and vaporizing Mg metal (the green zone shown in the actual photograph). At this stage, as Mg encounters the cold environment and reactor walls, it quickly condenses into Mg droplets and solid particles, separating from the gas stream. Notably, CO_2 and H_2O produced from the indirect CTR are converted back into CO and H_2 by reacting with the existing graphite in the bed, thereby sustaining the indirect reaction pathway.

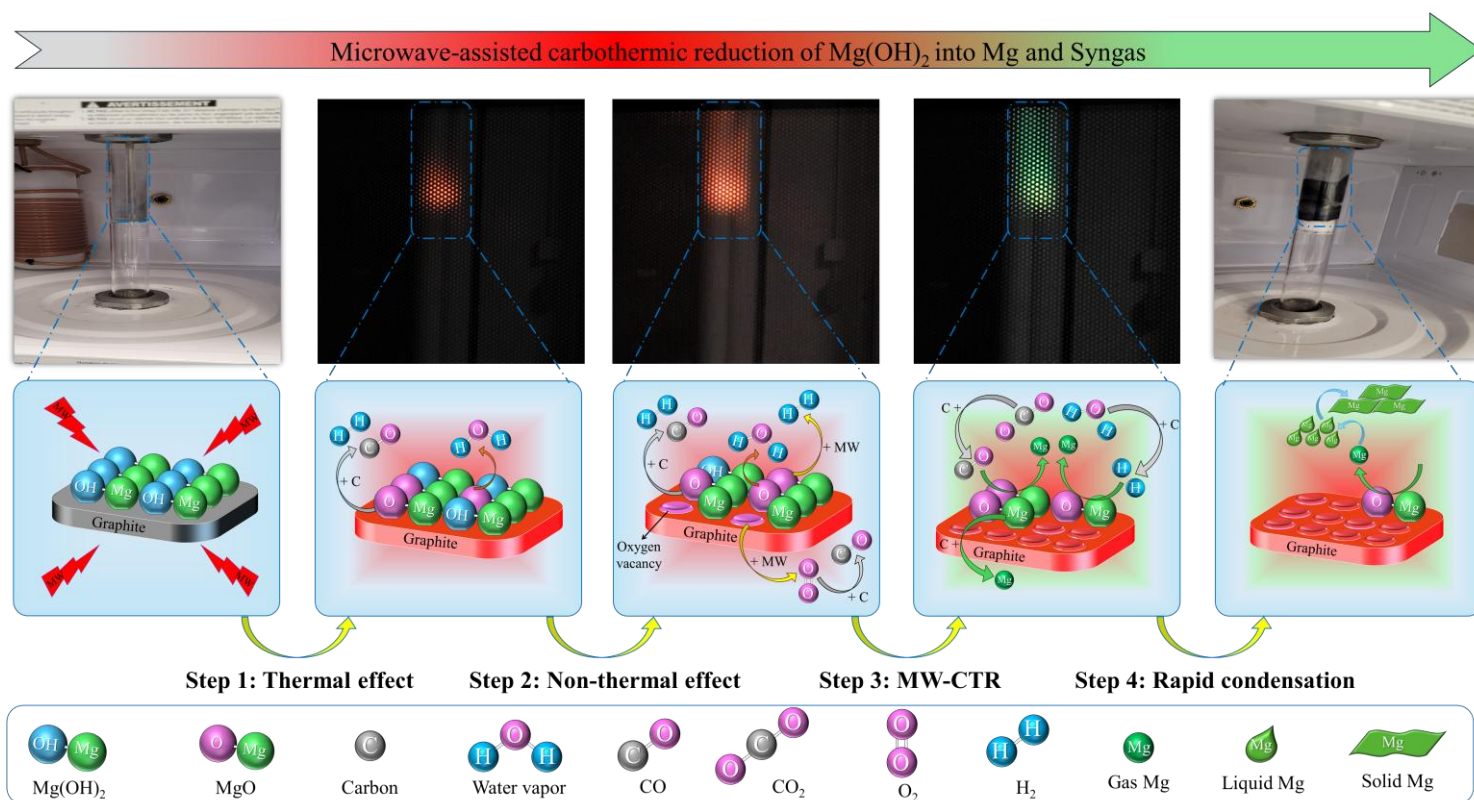


Figure 7.17 The schematic illustration of the proposed mechanism for MW-CTR of $\text{Mg}(\text{OH})_2$ and actual photographs.

7.4.6 Comparison of thermal approaches to produce magnesium metal

A detailed comparison between the developed process and previously reported thermal reduction routes for magnesium production, particularly the CTR process, is presented in Table 7.2. In most reported studies, pure MgO or calcined dolomite has been used as the feedstock for thermal reduction under either vacuum or atmospheric conditions. Operating CTR under reduced pressures (10 Pa-10 kPa) lowers the reaction temperature to approximately 1200-1500 °C, compared with the thermodynamic requirement at atmospheric pressure. However, the moderate reduction efficiency typically observed in conventional heating systems has often required the addition of fluxing agents to improve conversion, achieving reduction degrees of approximately 72-95% [138, 140, 328, 372, 373]. Common fluxing additives include CaF_2 , KF , $\text{Ni}(\text{NO}_3)_2$, and $\text{Fe}(\text{NO}_3)_3$. Nevertheless, the use of these additives can generate hazardous gaseous byproducts, such as F_2 and

NO_x , which represent an important environmental drawback that has not been sufficiently addressed in previous studies.

Operating under vacuum conditions also increases energy consumption and complicates reactor design, thereby limiting the feasibility of continuous industrial operation. These limitations increase greenhouse gas emissions and labor requirements, ultimately raising large-scale operating expenditures (Opex). In recent years, several studies have demonstrated the possibility of producing magnesium thermally at atmospheric pressure under argon using Pidgeon, aluminothermic, and CTR processes [38, 108, 204, 205, 330, 332, 374]. Atmospheric operation eliminates the need for vacuum systems and facilitates continuous processing and scale-up. However, both the Pidgeon and aluminothermic routes rely on energy-intensive reductants, namely ferrosilicon and metallic aluminum, respectively. In addition, these processes generate substantial quantities of solid oxide byproducts such as SiO_2 , Ca_2SiO_4 , Al_2O_3 , and $\text{CaO} \cdot n\text{Al}_2\text{O}_3$, which require further handling or disposal and reduce the overall environmental attractiveness of these methods.

In contrast, atmospheric CTR offers several advantages. Carbon is abundant, inexpensive, and widely available from diverse resources, including petroleum coke, biochar, plastic-waste pyrolysis, and methane pyrolysis. The primary gaseous product is CO, which can be captured and utilized as a chemical feedstock or energy carrier, improving the overall sustainability of the process. Despite these advantages, conventional atmospheric CTR typically requires temperatures exceeding $1500\text{ }^\circ\text{C}$ to achieve significant magnesium yields. Yoshikawa and Morita [204] demonstrated the possibility of rapid CTR at atmospheric pressure using microwave heating. However, limitations in reactor design and thermodynamic constraints resulted in a relatively low reduction efficiency of 46% at $1600\text{ }^\circ\text{C}$.

The process developed in this work addresses these limitations through three key innovations. First, replacing MgO with $\text{Mg}(\text{OH})_2$ exploits the in-situ release of H_2O during dehydroxylation. The generated steam reacts with carbon or undergoes microwave-assisted dissociation to form H_2 and CO, creating a stronger reducing atmosphere, lowering the effective reduction temperature to approximately $1280\text{ }^\circ\text{C}$, and suppressing magnesium reoxidation. Second, microwave irradiation provides rapid, selective, and volumetric heating, which accelerates the CTR kinetics. In addition to this thermal effect, microwave-induced non-thermal interactions may further promote MgO dissociation and solid-state reduction. Finally, the steep thermal gradient between the reaction bed

and the reactor wall enables rapid in-situ quenching of Mg vapor, preventing back-oxidation and facilitating the recovery of high-purity magnesium.

Using this approach in a fixed-bed reactor with cross-flow argon purging, a reduction efficiency of 87% and magnesium purity of 94% were achieved at atmospheric pressure, significantly outperforming previously reported atmospheric CTR systems. Furthermore, the simultaneous generation of syngas provides additional value by enabling integrated magnesium and fuel production, a feature not reported in earlier CTR studies.

The specific energy consumption (SEC) for MW-CTR of $\text{Mg}(\text{OH})_2$ was calculated from the ratio of consumed microwave heating energy (E_{MW} (kWh)) to the mass of produced magnesium (m_{mg} (kg)) [375].

$$SEC = \frac{E_{MW}}{m_{Mg}} \quad (7.13)$$

where the microwave energy consumption is defined as:

$$E_{MW} = P_{MW} \times t_{\text{React}} \quad (7.14)$$

where P_{MW} is the effective absorbed microwave power (kW), and t_{react} is the reaction time (h). The effective microwave power was determined using the water calorimetric method as follows [376]:

$$P_{MW} = \frac{m_w C_{pw} \Delta T_w + m_q C_{pq} \Delta T_q}{\Delta t} \quad (7.15)$$

where m_w and m_q are the masses of water and the quartz container (kg), C_{pw} and C_{pq} are the specific heat capacities of water and the quartz container (kJ/kg.K), and ΔT_w and ΔT_q are their corresponding temperature increases (K), and Δt is the heating duration (s).

At the optimized reaction time (20 min), the effective microwave heating energy consumption was 0.07 kWh. Considering that 0.0009 kg of Mg was produced at lab scale, the SEC of the MW-CTR process was calculated to be 77.8 kWh/kg Mg. For comparison, the reported energy consumption of conventional magnesium production processes is approximately 8.68 tce per ton Mg for the Pidgeon process and 4 tce per ton Mg for vacuum CTR at an industrial scale [128]. By converting 1 tce equal to 8141 kWh, the corresponding SEC values are approximately 70.7 kWh/kg Mg for

the Pidgeon process and 32.5 kWh/kg Mg for vacuum CTR. The relatively higher SEC observed in this study mainly reflects the laboratory-scale batch microwave reactor configuration, microwave coupling inefficiencies, and the absence of heat recovery systems. Significant reductions in SEC are expected during scale-up, driven by improved microwave interaction efficiency, enhanced reactor insulation, and the integration of thermal energy recovery. In addition to magnesium production, the MW-CTR of $\text{Mg}(\text{OH})_2$ generates syngas as a valuable co-product, which may further improve the overall process energy balance at larger scales. Despite a comparable SEC to the Pidgeon process at laboratory scale, MW-CTR offers advantages, including electrified operation, atmospheric-pressure processing, shorter reaction times, and simultaneous syngas generation.

From an engineering perspective, scaling the MW-CTR process requires careful consideration of microwave-material interactions and reactor configuration. Key challenges include the limited power capacity of commercial magnetrons, non-uniform electromagnetic field distribution within large cavities, and variations in dielectric properties of the reacting bed with temperature and composition [377, 378]. These factors can lead to uneven energy deposition and localized temperature gradients that affect reduction uniformity and Mg vapor formation. Therefore, scale-up will require optimized microwave reactor designs such as multimode cavities, distributed waveguide injection, or hybrid heating systems that combine microwave and auxiliary thermal inputs [170, 195, 379]. Reactor configurations, including moving-bed, rotary, or fluidized-bed systems, may further improve heat and mass transfer during large-scale operation [170, 380].

In addition to reactor design, successful scale-up will require integration of process modeling, product-separation strategies, and energy-management approaches. Multiphysics simulations (e.g., Computational Fluid Dynamics (CFD) and Ansys Fluent) that couple electromagnetic fields, heat transfer, and reaction kinetics can support reactor optimization and iterative scale-up [381]. Efficient condensation of Mg vapor, utilization of syngas co-products, and heat-recovery strategies will also be important for improving energy efficiency. Finally, techno-economic analysis and life-cycle assessment (LCA) will be necessary to evaluate the economic feasibility and environmental impact of implementing MW-CTR for sustainable magnesium production.

Table 7.2 Comparison of thermal approaches to produce magnesium metal

Process	Heating Method	Feed	Reductant	Fluxing agent	Pressure (atm)	Temperature (°C)	Time of reaction (min)	Reduction efficiency (%)	Main gas product	Ref
Carbothermic	Conventional electric heating	MgO	Coking coal	KF	0.00079	1277	120	91.48	CO	[140]
Carbothermic	Conventional electric heating	Calcined dolomite	Coke	CaF ₂	0.000099	1300	60	83.7	CO	[372]
Carbothermic	Conventional electric heating	MgO	Coking coal	CaF ₂	0.0003	1450	120	72	CO	[373]
Carbothermic	Joule heating	Calcined dolomite	Semi-coke	CaF ₂	0.000099	1492	2	95.83	CO	[328]
Carbothermic	Conventional electric heating	MgO	Petroleum coke	Ni(NO ₃) ₂ or Fe(NO ₃) ₃	0.099	1550	30	90	CO	[138]
Aluminothermic-carbothermic	Microwave heating	Calcined dolomite	Aluminum and graphite	-	1	1050	17	44.37	CO	[205]
Pidgeon	Conventional electric heating	Calcined dolomite	Ferrosilicon	CaF ₂	1	1200	120	82.36	-	[332]
Aluminothermic	Conventional electric heating	Calcined dolomite	Aluminum	CaF ₂	1	1200	120	89	-	[374]

Table 7.2 Comparison of thermal approaches to produce magnesium metal (cont'd)

Process	Heating Method	Feed	Reductant	Fluxing agent	Pressure (atm)	Temperature (°C)	Time of reaction (min)	Reduction efficiency (%)	Main gas product	Ref
Aluminothermic	Conventional									
	electric heating	MgO	Aluminum	-	1	1250	120	70	-	[330]
Pidgeon	Conventional									
	electric heating	Calcined dolomite	Ferrosilicon	CaF ₂	1	1300	300	92	-	[108]
Pidgeon	Conventional									
	electric heating	Calcined dolomite	Ferrosilicon	CaF ₂	1	1400	150	94.88	-	[38]
Carbothermic	Microwave heating									
		MgO	Graphite	-	1	1600	10	46	CO	[204]
Carbothermic	Microwave heating									
		Mg(OH) ₂	Graphite	-	1	1280	20	87	CO and H ₂	This study

7.5 Conclusion

This study established a new paradigm for circular and carbon-neutral magnesium metallurgy by coupling electrified pyrometallurgy with the valorization of solid waste. Unlike conventional heating for CTR of MgO, which requires temperatures above 1300 °C and a vacuum pressure (10-100 Pa), our process employed microwave heating coupled with CTR to reduce Mg(OH)₂ recycled from dolomitic limestone waste rock into Mg and syngas at atmospheric pressure and lower temperatures. Thermodynamic and experimental results revealed that the onset reduction temperature of Mg(OH)₂ at 1 atm decreased by over 700 °C compared to that of MgO reduction, leading to the generation of Mg vapor at 1280 °C. This approach yielded an 87% Mg(OH)₂ reduction efficiency and 94% Mg purity, surpassing the efficiency of all previous atmospheric CTR

or Pidgeon for MgO feed. Importantly, the in-situ decomposition of $\text{Mg}(\text{OH})_2$ generated a syngas atmosphere with a $\text{CO}:\text{H}_2$ molar ratio of 1.86, serving both as a valuable co-product and as a dynamic reducing atmosphere that suppresses magnesium reoxidation. The implementation of microwave heating contributed through two cooperative mechanisms not typically observed in conventional heating. First, the thermal effect of microwaves, arising from their electromagnetic penetration and absorption mechanisms, caused rapid volumetric and selective heating of the $\text{Mg}(\text{OH})_2$ -graphite mixture with heating rates exceeding $990\text{ }^\circ\text{C}/\text{min}$, and created an approximately $800\text{ }^\circ\text{C}$ difference between the bed and wall of the reactor. As a consequence of this thermal effect, sintering was suppressed, and an instantaneous quenching of the magnesium vapor was established. Second, in addition to the thermal effect, the non-thermal effect of microwaves, arising from interactions between the electromagnetic field and material molecules, could enhance $\text{Mg}(\text{OH})_2$ decomposition, water splitting, and oxygen-vacancy formation in MgO. Together, these effects enhance the MW-CTR process, resulting in a 42% higher reduction efficiency at atmospheric pressure than with conventional heating. Beyond Mg production, our developed MW-CTR process paves the way for low-carbon recovery of critical metals from industrial waste streams. Future work will focus on scaling the MW-CTR process through optimized microwave reactor design, improved electromagnetic field distribution, and integration of heat-recovery and product separation systems. These developments, together with techno-economic and life-cycle assessment, will be necessary to evaluate the feasibility of deploying MW-CTR as an electrified route for sustainable Mg production.

7.6 Acknowledgments

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CHAPTER 8 GENERAL DISCUSSION

At the beginning of this dissertation, a concept for the low-carbon recycling of metallic Mg from dolomitic limestone waste rock was proposed. The central hypothesis was that magnesium contained in carbonate mining waste could be selectively recovered through a hybrid processing route combining carbon-neutral hydrometallurgy with electrified thermal reduction, thereby overcoming the environmental and operational limitations of conventional Mg metal production technologies. The results presented in Chapters 4-7 demonstrate that this concept is technically feasible and scientifically well supported.

The hydrometallurgical component of the process was designed to selectively extract Mg from DLWR while minimizing energy consumption and secondary emissions. Conventionally, carbonate ores are subjected to pre-calcination prior to leaching in order to convert carbonates into more reactive oxide phases. However, the results presented in Chapter 4 demonstrate that this assumption is not universally valid. Thermodynamic analysis of the Mg-Ca-C-O system, supported by TGA characterization, showed that thermal decomposition of dolomite under different atmospheres leads to distinct phase transformations. Under a CO₂ atmosphere at approximately 700 °C, MgCO₃ decomposes preferentially to MgO while Ca remains stabilized as CaCO₃. Complete conversion to MgO.CaO requires higher temperatures near 900 °C under air.

Experimental comparison between calcined and uncalcined DLWR revealed that the presence of carbonate phases significantly influences leaching selectivity. Direct acid leaching of DLWR using dilute H₂SO₄ resulted in preferential dissolution of Mg while suppressing the co-leaching of impurities, even though thermodynamics alone would predict improved dissolution after calcination. Detailed physicochemical characterization indicated that carbonate buffering played a critical role in controlling the reaction environment. Carbonate phases introduced local pH stabilization and hydrophobic surface behavior that hindered acid penetration toward impurity phases. As a result, direct carbonate leaching achieved high Mg extraction efficiency while maintaining low impurity dissolution under optimized conditions.

Kinetic analysis further showed that Mg extraction follows a shrinking-core model with shrinking particle size, where the rate-limiting step is diffusion through the product layer. This finding highlights the importance of mass-transfer phenomena in carbonate dissolution systems and

explains the strong dependence of leaching rate on particle size, temperature, and solid-to-liquid ratio.

Following dissolution, selective recovery of Mg and Ca required careful control of precipitation chemistry. Although thermodynamic predictions suggested limited Ca solubility in sulfuric acid, experimental results showed that 10-50% of Ca can dissolve, depending on operating conditions. Integrating thermodynamic simulations with experimental studies allowed the establishment of a robust separation strategy based on pH-controlled precipitation. Through a multi-step alkaline precipitation process, Mg and Ca were successfully recovered as $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ at pH values of approximately 9 and 11, respectively. The strongly alkaline effluent produced during Ca precipitation provided an opportunity for CO_2 capture and utilization, enabling the formation of NaHCO_3 and establishing a closed-loop hydrometallurgical process. This integration of metal recovery with carbon capture represents a key advancement over conventional hydrometallurgical approaches, which typically treat CO_2 emissions as unavoidable by-products of the process.

Further process optimization, described in Chapter 6, simplified the hydrometallurgical flowsheet. Since Ti, Al, Mn, and Fe are present only in trace concentrations relative to Mg and Ca, their individual separation was considered unnecessary for practical implementation. Instead, a single precipitation step near neutral pH enabled simultaneous removal of these minor impurities while preserving Mg selectivity. Additionally, calcium recovery was improved by merging the water-leaching liquor with the alkaline precipitation effluent and performing direct CO_2 carbonation to produce CaCO_3 . These modifications eliminated the need for strongly alkaline effluent streams and produced a simplified carbon-neutral separation route yielding high-purity $\text{Mg}(\text{OH})_2$ and CaCO_3 .

Although hydrometallurgy provides an effective route for Mg recovery from DLWR, it produces magnesium in compound forms rather than metallic Mg. Converting these compounds into metal requires high-temperature metallization processes. Conventional Mg metal production relies on MgO-based thermal reduction routes, such as the Pidgeon process, which are energy-intensive and typically require vacuum conditions to drive reaction equilibrium. The present dissertation explored an alternative strategy based on direct carbothermic reduction of waste-recycled $\text{Mg}(\text{OH})_2$ under microwave heating.

A key innovation of this work is the use of $\text{Mg}(\text{OH})_2$ as the precursor for carbothermic reduction. Unlike MgO, $\text{Mg}(\text{OH})_2$ undergoes dehydroxylation during heating, releasing H_2O that reacts with

carbon to produce H_2 and CO through gasification reactions. This generates an in-situ syngas atmosphere within the reaction zone. As a consequence, the reduction mechanism shifts from a purely solid-solid reaction to a gas-assisted gas-solid reduction pathway. Thermodynamic analysis and experimental observations indicate that this change significantly lowers the effective reduction temperature and facilitates Mg vapor generation under atmospheric pressure. The onset reduction temperature was reduced by approximately 700 °C compared with conventional MgO-based carbothermic reduction, demonstrating the advantages of this alternative reaction pathway.

The second major innovation concerns the electrification of the carbothermic reduction process through microwave heating. Carbonaceous reductants exhibit strong microwave absorption due to electronic conduction losses, enabling rapid volumetric heating within the reaction mixture. In the microwave-assisted carbothermic reduction reactor developed in this work, electromagnetic energy was selectively deposited in carbon particles, generating localized hot spots at carbon-oxide interfaces. These localized heating effects accelerated interfacial reactions and promoted the rapid formation of Mg vapor.

Microwave heating also introduced several additional phenomena that were not observed under conventional furnace heating. Rapid volumetric heating generated steep thermal gradients that facilitated immediate condensation of Mg vapor and reduced the potential for reoxidation. At the same time, localized electromagnetic interactions promoted the formation of oxygen vacancies within the MgO lattice, potentially lowering activation barriers for reduction reactions. The combination of thermal and non-thermal microwave effects therefore produced a fundamentally different reaction pathway compared with conventional carbothermic reduction.

These effects collectively enabled rapid Mg metal production under atmospheric pressure within minutes, eliminating the need for vacuum conditions and significantly shortening reaction times. Furthermore, the simultaneous generation of CO and H_2 during reduction created a valuable syngas co-product, providing an additional pathway for energy and carbon valorization.

Taken together, the results of this dissertation demonstrate that DLWR can be transformed from an environmental threat into a valuable resource for Mg and syngas production. By integrating selective hydrometallurgical extraction with electrified carbothermic reduction, the proposed process establishes a circular pathway for recovering Mg from mining waste while reducing energy consumption and greenhouse gas emissions relative to conventional technologies.

Beyond Mg metal production itself, this work contributes broader methodological insights to sustainable metallurgy. It demonstrates how process integration, thermodynamic analysis, reaction engineering, and electrified heating technologies can be combined to design new metallurgical pathways that simultaneously address resource recovery and decarbonization objectives. The concepts developed in this dissertation may therefore be extended to other metal recovery systems where conventional high-temperature processes remain energy-intensive or environmentally challenging.

CHAPTER 9 CONCLUSION AND RECOMMENDATIONS

9.1 Conclusion of dissertation

This dissertation developed a new approach for the low-carbon and circular production of magnesium metal from secondary resources, specifically dolomitic limestone waste rock. By integrating selective hydrometallurgical processing with electrified carbothermic reduction, this work demonstrated that magnesium recovery can be achieved without reliance on high-temperature calcination, vacuum operation, or fossil-fuel-based heating. Beyond process development, this research provided new mechanistic insights into carbonate-assisted leaching, selective alkaline precipitation, CO₂ carbonation, and microwave-matter interactions during high-temperature reduction. Collectively, the results contribute to both the scientific understanding and technological advancement of sustainable magnesium metallurgy.

Concerning the first specific objective of achieving carbon-neutral recycling of Mg(OH)₂ from DLWR, outlined in chapters 4-6, the key conclusion is as follows:

1. Direct carbonate leaching of DLWR using dilute H₂SO₄ was demonstrated to be more selective than conventional pre-calcination routes, revealing that carbonate phases play a beneficial role in suppressing impurity co-leaching rather than hindering magnesium extraction.
2. Carbonate buffering and surface effects were identified as key mechanisms controlling selectivity, decreasing impurity dissolution from 87% to 36%, thereby enabling high-purity Mg recovery without thermal pretreatment.
3. Magnesium leaching followed a diffusion-controlled shrinking-core mechanism with relatively low activation energy (16 kJ/mol), and was governed primarily by acid concentration and initial DLWR particle size.
4. A thermodynamically guided precipitation strategy enabled selective recovery of metals using a single reagent (i.e., NaOH), eliminating the need for additional oxidants, reductants, or complexing agents.
5. High-purity products, including Mg(OH)₂, Ca(OH)₂, and CaCO₃ (>99.5%), were successfully obtained through controlled pH adjustment and stepwise precipitation.

6. Integration of CO₂ capture and utilization within the hydrometallurgical process enabled conversion of system emissions into NaHCO₃ and CaCO₃, establishing a closed-loop, carbon-neutral hydrometallurgical process.
7. Process intensification led to a simplified flowsheet that reduced chemical consumption and eliminated strong alkaline effluents, improving both environmental and operational performance.
8. Preliminary economic analysis confirmed the technical and economic feasibility of DLWR valorization, supporting its potential for industrial implementation.

Regarding the second specific objective, the microwave-assisted carbothermic reduction of MgO and Mg(OH)₂ covered in chapter 7, the following major conclusion is drawn:

1. A fundamentally new pathway for magnesium production was demonstrated by using Mg(OH)₂ instead of MgO as the reduction feedstock, which altered the reaction mechanism from solid-solid to gas-assisted gas-solid reduction.
2. In-situ generation of syngas during Mg(OH)₂ decomposition created a highly reducing environment, lowering the onset atmospheric reduction temperature from 1900 °C to around 1200 °C and enabling magnesium production at 1 atm.
3. Microwave-assisted carbothermic reduction enabled rapid, volumetric, and selective heating, achieving heating rates exceeding 990 °C/min and significantly improving thermal reduction efficiency.
4. The MW-CTR process achieved 87% reduction efficiency and 94% Mg purity, surpassing conventional carbothermic and atmospheric-pressure reduction routes.
5. Microwave thermal effects generated significant temperature gradients between the bed inventory and reactor wall (around 800 °C), facilitating rapid condensation and suppression of Mg reoxidation, which is a major limitation in conventional systems.
6. Non-thermal microwave effects, including oxygen vacancy formation and enhanced radical pathways, were experimentally validated (e.g., via EPR and HRTEM), demonstrating their role in lowering kinetic barriers and accelerating reduction reactions.

7. The process enabled simultaneous production of value-added syngas ($\text{CO}:\text{H}_2$ molar ratio of 1.86), providing an additional pathway for energy and carbon valorization.

Overall, this dissertation addressed many scientific and technological problems in sustainable Mg metal production. The major contributions that have resulted from this dissertation can be summarized as follows:

1. Demonstration of a fully integrated hydrometallurgical-pyrometallurgical route for low-carbon footprint magnesium production from mining waste.
2. Elimination of pre-calcination, vacuum operation, and fossil-fuel-based heating, addressing key limitations of conventional magnesium production technologies.
3. Establishment of a circular and carbon-neutral process framework combining waste valorization, CO_2 utilization, and electrified thermal processing.
4. Development of microwave-assisted carbothermic reduction as a viable atmospheric-pressure metallization route.
5. Introduction of a novel pathway for the co-production of syngas, enhancing overall process efficiency and valorization potential.
6. Advancement in the fundamental understanding of carbonate-assisted leaching mechanisms, selective precipitation thermodynamics, and microwave-induced thermal and non-thermal effects in metallurgical systems.
7. Provision of a scalable and sustainable pathway aligned with decarbonization and critical material supply security objectives.

These contributions, together, position the proposed hybrid metallurgical process as a promising pathway toward the next generation of sustainable magnesium production technology.

9.2 Future work and recommendations

This dissertation has established a comprehensive framework for the low-carbon production of magnesium from dolomitic limestone waste rock by integrating carbon-neutral hydrometallurgy with electrified carbothermic reduction. The work has successfully addressed key scientific and technological challenges at the laboratory scale, including reaction mechanisms, process selectivity, and proof-of-concept validation. Building on these achievements, the next stage of development involves advancing the process toward larger-scale implementation and system integration. Future work should focus on extending the current findings to more complex operating conditions, including feedstock variability, continuous processing, and large-scale CO₂ utilization strategies.

On the hydrometallurgical side, further development can enhance process robustness under industrial conditions and expand opportunities for effluent valorization and circular resource integration. On the pyrometallurgical side, the MW-CTR process offers a promising pathway for atmospheric-pressure magnesium production, and future research should focus on reactor design, kinetic modeling, and large-scale magnesium vapor condensation. In addition, comprehensive techno-economic and life-cycle assessments will be essential to quantify the full industrial and environmental potential of the proposed process.

The following subsections outline key directions for future research and development to advance this technology from laboratory validation to industrial application.

9.2.1 Process scale-up and technology transfer

The experimental investigations presented in this dissertation were conducted at laboratory scale, using 1-10 g of DLWR in hydrometallurgical experiments and approximately 5 g of Mg(OH)₂-graphite mixtures in MW-CTR experiments. These conditions were intentionally selected to enable detailed investigation of reaction mechanisms, kinetics, and process feasibility. Building on these results, the next stage of development involves scaling the process toward bench-scale and pilot-scale systems. In terms of technology readiness level (TRL), the current work corresponds to TRL 4 (component and/or validation in a laboratory environment), and future efforts should progressively advance the process toward TRL 7-9 through prototype demonstrations and actual technology deployment in an operational setting.

A stepwise scale-up strategy is recommended. Initial studies should focus on bench-scale reactors (100-500 g) to evaluate process reproducibility, mixing behavior, and phase separation under more representative conditions. Subsequently, kilogram-scale pilot units should be developed to assess throughput, operational stability, and integration of hydrometallurgical and pyrometallurgical steps. For the hydrometallurgical process, scale-up will benefit from the development of continuous reactor configurations, such as continuous stirred-tank reactors (CSTRs), along with efficient solid-liquid separation techniques (e.g., filtration, thickening, and washing). Optimization of these operations will enhance process productivity and enable continuous processing.

For the MW-CTR process, scaling requires careful consideration of microwave energy distribution and reactor configuration. Future work should explore advanced designs, such as multimode microwave cavities, hybrid heating systems, and fluidized-bed reactors, to improve temperature uniformity and enhance heat and mass transfer. Multiphysics modeling tools (e.g., CFD coupled with electromagnetic field simulations) can play a key role in guiding reactor design and optimizing operating conditions by capturing the interactions between microwave fields, thermal gradients, and reaction kinetics. In parallel, further development of magnesium vapor condensation systems is recommended, including rapid condensation strategies, continuous metal collection, and integration of syngas utilization. These aspects are essential for improving overall process efficiency and enabling continuous operation.

Finally, the development of an integrated process flowsheet, supported by pilot-scale data and validated through techno-economic and environmental assessments, will facilitate technology transfer and industrial implementation. Collaboration with industrial partners, such as the OCP group, will further accelerate this transition by enabling validation under real operating conditions.

9.2.2 Process variants

The hydrometallurgical investigations presented in this dissertation were conducted using dolomitic limestone waste rock collected from phosphate interlayers in the Gantour Basin (Benguerir mine, Morocco). While this feedstock is representative of a major industrial source, the composition and mineralogy of DLWR can vary significantly depending on geological origin and mining conditions. Such variations may influence both leaching behavior and downstream separation efficiency. To ensure process robustness and broader applicability, future work should extend the developed methodology to DLWR samples with varying compositions. In particular,

changes in the Mg/Ca ratio, impurity content (e.g., silicates, iron oxides, and phosphates), and particle morphology may require adjustments to key operating parameters, including the solid-to-liquid ratio, particle size distribution, acid concentration, precipitation pH, and reaction time. Systematic studies across different feedstocks will enable the development of adaptive operating windows and improve the process's generalizability.

In this work, dilute H_2SO_4 (0.5 M) was used as a model leaching agent, representing wasted acid streams generated during the wet-process production of phosphoric acid. In industrial practice, such wasted acid streams may contain additional components, including rare earth elements and trace heavy metals (e.g., Cd, As, Zn, Cu, Cr, and Pb). Although thermodynamic analysis suggests that these elements can be selectively precipitated prior to $\text{Mg}(\text{OH})_2$ formation, future experimental studies at bench- and pilot-scales are recommended to validate their behavior under realistic process conditions. This will ensure that product purity and process selectivity are maintained in complex industrial matrices, while also opening opportunities for co-recovery of valuable trace elements.

For the carbothermic reduction step, graphite flakes were selected due to their excellent microwave absorption and well-defined physicochemical properties. For large-scale implementation, however, alternative carbonaceous materials, such as biochar, charcoal, petroleum coke, and waste-derived carbon sources (e.g., tire pyrolysis char), may offer more economically attractive options. Future work should therefore evaluate the performance of these alternative reductants, taking into account their dielectric properties, impurity content, reactivity, and structural characteristics. Variations in carbon sources may influence microwave absorption efficiency, local temperature distribution, reduction kinetics, and ultimately magnesium purity. Establishing correlations between carbon material properties and MW-CTR performance will be essential for selecting optimal reductants at scale.

Overall, extending the process to a wider range of feedstocks and reductant materials will enhance its flexibility, economic viability, and industrial relevance, supporting its application across diverse resource streams and operating conditions. Such flexibility is essential for integration with geographically diverse phosphate mining operations and for ensuring long-term process resilience.

9.2.3 CO₂ storage and utilization for carbonation

In this dissertation, the term carbon-neutral is defined at the process-concept level, referring to a closed-loop hydrometallurgical system in which the CO₂ released during the acidolysis of carbonate minerals is internally recycled for carbonation reactions rather than emitted to the atmosphere. This approach enables direct coupling between leaching and precipitation steps, forming an integrated carbon circulation pathway within the process. Thermodynamic analysis confirms that the molar quantity of CO₂ generated during DLWR leaching is sufficient to carbonate dissolved calcium species to form CaCO₃ or to react with alkaline effluents to produce NaHCO₃. In the laboratory experiments, a pure CO₂ stream was used to intentionally decouple carbonation reactions from gas-liquid mass-transfer limitations. This strategy allowed a clear demonstration of the intrinsic feasibility, selectivity, and kinetics of carbonation reactions under controlled conditions.

For future development, extending this concept to industrial-scale operations requires consideration of realistic CO₂ capturing and utilization strategies. In practice, carbonation efficiency depends on factors such as CO₂ partial pressure, temperature, gas flow rate, and gas composition. Therefore, a closed-loop system can be designed in which CO₂ released during leaching is captured, temporarily stored in a buffer tank, and subsequently recirculated through the carbonation unit. Under such a configuration, the overall extent of carbonation is governed by the total CO₂ inventory in the system rather than its instantaneous concentration, enabling stable, controlled operation even under fluctuating process conditions.

Future work may also explore advanced reactor configurations for gas-liquid-solid interactions, such as bubble column reactors, packed columns, or membrane contactors, to enhance CO₂ absorption and carbonation kinetics. In addition, integration with external CO₂ sources (e.g., flue gas from industrial operations) could further expand the process scope toward net-negative carbon utilization. Overall, the development of efficient CO₂ storage, recirculation, and utilization strategies represents a key step toward realizing a fully integrated and industrially viable carbon-managed hydrometallurgical process.

9.2.4 Separation of Si and P from the effluent of the hydrometallurgy process

Following the hydrometallurgical treatment and selective recovery of Mg and Ca from DLWR, residual silicon and phosphorus remain in the final effluent at low concentrations. Depending on the solution pH, silicon predominantly exists as dissolved silicic acid ($\text{H}_2\text{SiO}_{3(\text{aq})}$), while phosphorus is present in various protonation states (H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-}), governed by acid-base equilibria. Under the operating conditions of the developed process (pH 8-11), thermodynamic analysis indicates that precipitation of Si and P is not favored in the absence of additional reagents. This behavior was experimentally confirmed through ICP-OES and ICP-MS analyses, which showed that less than 0.7% of total Si and P co-precipitated during alkaline treatment. As a result, these elements remain predominantly in the effluent, while the recovered $\text{Mg}(\text{OH})_2$ and Ca-based products maintain high purity, with no detectable Si or P phases by XRD or EDS.

For future process integration, targeted recovery of Si and P from the effluent can be considered to further enhance resource efficiency and environmental performance. Based on established approaches in the literature, silicon can be recovered through acid-induced polymerization of silicic acid under conditions of high acidity and ionic strength. Specifically, adjustment of the effluent to strongly acidic conditions (e.g., 2-8 M mineral acid) promotes rapid conversion of monomeric silicic acid into polymeric species via siloxane bond formation. These species subsequently nucleate to form primary nanoparticles (around 20-50 nm), which aggregate into colloidal particles and eventually form silica gels that can be separated by filtration. Following silica separation, phosphorus recovery can be achieved through either precipitation or solvent extraction pathways. In precipitation-based approaches, the use of complexing agents such as Na_2EDTA in combination with calcium sources (e.g., CaO) enables controlled recovery of phosphorus as dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). Alternatively, liquid-liquid extraction systems, such as benzyl dimethylamine dissolved in kerosene, can be employed for selective phosphorus extraction from acidic solutions. Integrating these recovery steps into the overall process creates opportunities to further valorize minor components, improve effluent management, and advance toward a fully closed-loop metallurgical system. Future research may focus on optimizing these separation routes to reduce reagent consumption, improve selectivity, and ensure compatibility with both upstream and downstream operations. Such downstream recovery strategies may be particularly attractive in

phosphate-processing regions, where phosphorus valorization aligns with existing industrial value chains.

9.2.5 Magnesium vapor condensation and refinery

One of the key engineering considerations in industrializing carbothermic magnesium production is the efficient condensation and stabilization of Mg vapor. During conventional vacuum carbothermic reduction, magnesium vapor is prone to reoxidation during condensation because CO₂ is produced via the Boudouard reaction. As the gas stream cools toward the reactor outlet, the partial pressure of CO₂ increases, and the thermodynamic driving force for the reverse reaction ($\text{Mg}_{(s)} + \text{CO}_{2(g)} \rightleftharpoons \text{MgO}_{(s)} + \text{CO}_{(g)}$) becomes significant, leading to loss of metallic magnesium yield. Advanced industrial concepts have addressed this challenge through rapid quenching and controlled condensation strategies. For example, CSIRO's MagSonic™ process employs a supersonic Laval nozzle to achieve shock quenching, with cooling rates exceeding 10⁶ °C/s, effectively suppressing reoxidation by limiting reaction time. Similarly, Big Blue Technologies utilizes a moving-bed condenser, in which magnesium vapor is rapidly deposited onto a high-surface-area solid medium, enabling efficient heat removal and Mg separation from the CO-rich gas stream.

In the MW-CTR system developed in this dissertation, a distinct condensation behavior is observed due to the strong temperature gradient between the bed inventory and the reactor walls. This gradient promotes rapid in-situ condensation of Mg vapor on cooler reactor surfaces, effectively acting as an internal quenching mechanism. Under atmospheric-pressure conditions, magnesium condensation proceeds through a two-step pathway: vapor → liquid → solid. During this process, a portion of the transient liquid magnesium may migrate or drip back toward the reacting bed, resulting in partial mixing with carbonaceous residues. For future development, dedicated condensation and refining strategies should be explored to enhance magnesium recovery and product purity. These may include: (I) design of controlled condensation zones with optimized temperature profiles, (II) implementation of external condensers or staged cooling systems to in-situ separate Mg from reactive gas streams, (III) development of continuous Mg collection systems, including scraping, draining, or filtration-based separation. In addition, post-condensation refining steps, such as density-based separation, vacuum distillation, or flux-assisted purification, may be

required to remove residual carbon and impurities and to produce magnesium with industrial-grade purity on a large scale.

A detailed investigation of magnesium vapor transport, nucleation, condensation kinetics, and phase transformation behavior under microwave-assisted conditions will further support the design of efficient condensation systems. Such developments are essential for translating the MW-CTR process from laboratory-scale demonstration to continuous, large-scale magnesium production.

9.2.6 Magnesium alloying during thermal reduction

Magnesium metal is highly reactive and pyrophoric, particularly when produced as fine particles, posing challenges for handling, storage, and transportation on a large scale. One promising strategy to address these challenges is the in-situ formation of magnesium-based alloys during the reduction and condensation stages. Such an approach can simultaneously enhance process safety and produce value-added alloy products. In this context, the introduction of alloying elements, such as aluminum, into the MW-CTR system offers a particularly attractive pathway. Aluminum can serve multiple roles within the process: (I) it may participate in synergistic reduction pathways that combine carbothermic and aluminothermic reactions, and (II) it can promote the direct formation of Mg-Al alloys during magnesium vapor condensation. Mg-Al alloys are widely used in automotive and aerospace applications due to their favorable strength-to-weight ratio and corrosion resistance. Future work should investigate the feasibility and optimization of this concept by examining key parameters, including the type and concentration of alloying metal, reaction temperature, residence time, and reactor configuration. In particular, understanding the interaction between alloying elements and magnesium vapor during condensation will be essential to control alloy composition and microstructure. In addition, this approach may reduce the need for downstream alloying processes and improve the overall safety and economic performance of magnesium production. The integration of alloy formation into the reduction step, therefore, represents a promising direction for advancing the MW-CTR process toward multi-functional, value-added metallurgical systems. This concept may also be extended to other alloy systems (e.g., Mg-Si or Mg-Zn), enabling the tailored production of alloys directly from secondary resources.

9.2.7 Kinetics, techno-economics, and life cycle assessment for the MW-CTR

Advancing the MW-CTR process from laboratory validation to pilot-scale operation requires a transition from demonstrating scientific feasibility to establishing process reliability, efficiency, and industrial viability. At the laboratory scale, microwave heating enables rapid and effective reduction under controlled conditions. Building on these results, future work should focus on developing a comprehensive understanding of reaction kinetics and heat transfer behavior under scaled operating conditions. At larger reactor scales, the distribution of electromagnetic fields becomes more complex, and the interaction between microwave energy and the reacting bed evolves with temperature and composition. As a result, spatial variations in energy absorption may lead to localized differences in temperature and reaction rate. Developing robust kinetic models that couple electromagnetic field distribution, heat transfer, and reaction kinetics will be essential to ensure uniform reduction and consistent magnesium yield throughout the reactor volume. Such models will also support the design of optimized reactor configurations and operating strategies.

In parallel with kinetic modeling, evaluation of the process through techno-economic analysis is necessary to assess its industrial potential. Key parameters to be considered include electricity consumption, microwave generation efficiency, reactor design and materials, and system durability under high-temperature and high-field conditions. Factors such as magnetron performance, energy coupling efficiency, and reactor configuration will influence overall process economics and should be systematically analyzed. Complementary to techno-economic analysis, life-cycle assessment is essential for quantifying the environmental performance of the MW-CTR process. By accounting for the full system boundary, including feedstock transportation, electricity source, process emissions, and co-product utilization, LCA can provide a comprehensive evaluation of the carbon footprint and environmental benefits of the proposed technology. This analysis is particularly important for verifying the contribution of MW-CTR to decarbonized magnesium production and for identifying opportunities to further reduce environmental impact.

Together, the integration of kinetic modeling, techno-economic analysis, and life cycle assessment will provide a robust framework for optimizing the MW-CTR process and guiding its transition toward industrial-scale implementation. This strategy will be essential to positioning MW-CTR as a competitive and scalable alternative to conventional magnesium production technologies.

9.2.8 Development of Methanothermic Reduction under Microwave Heating

The co-production of syngas during microwave-assisted carbothermic reduction of $\text{Mg}(\text{OH})_2$ provides additional value by generating a mixture of CO and H_2 that can serve as both an energy carrier and a chemical feedstock. In the current process, the CO: H_2 molar ratio was approximately 2, which is suitable for certain applications but may limit its direct use in downstream processes that require hydrogen-enriched syngas. To further enhance the value of the process, methanothermic reduction under microwave heating represents a promising extension. In this approach, methane is introduced as a hydrogen carrier, undergoing in-situ decomposition and reforming reactions (e.g., $\text{Mg}(\text{OH})_{2(\text{s})} + \text{C}_{(\text{s})} + 4\text{CH}_{4(\text{g})} \rightleftharpoons \text{Mg}_{(\text{g})} + 2\text{CO}_{(\text{g})} + 9\text{H}_{2(\text{g})} + 3\text{C}_{(\text{s})}$), thereby generating additional hydrogen and modifying the gas composition. As a result, a strongly reducing gas-solid environment is established without the need for external hydrogen supply, while the syngas composition can be shifted toward H_2 -rich syngas ($\text{H}_2:\text{CO} \approx 4$). This H_2 -enriched syngas is particularly attractive for downstream applications such as methanol synthesis, Fischer-Tropsch processes, and hydrogen-based energy systems, thereby expanding the process beyond metal production into an integrated materials-energy platform.

Preliminary results presented in Appendix B demonstrate the feasibility of simultaneously producing magnesium and H_2 -enriched syngas under microwave-assisted methanothermic reduction (MW-MTR). Building on these findings, future work should focus on optimizing key parameters, including methane flow rate, temperature, carbon-to-methane ratio, and reactor configuration, to enhance reduction efficiency and product yield. In addition, further investigation of reaction pathways, carbon deposition behavior, and syngas composition control will be essential to fully realize the potential of this approach. The integration of methanothermic reduction with MW-CTR, therefore, represents a promising direction for developing high-value, multifunctional magnesium production systems aligned with emerging hydrogen and carbon-utilization technologies. This approach opens a pathway toward coupling magnesium metallurgy with hydrogen-rich fuel and chemical production, enabling integrated resource and energy valorization.

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APPENDIX A SUPPORTING INFORMATION FOR CHAPTER 5

Table A.1 Summary of studies on the precipitation of magnesium from secondary resources.

Target Metal	Feed	Leachate	Precipitant	Additive	Temperature (°C)	Precipitation Time (min)	pH	Recovery (%)	Purity (%)	Co-Precipitate	Ref
Mg, Ca	Dolomite-talc ore	HCl	NH ₄ OH (For Mg)	NaClO	NA	NA (Mg)	>12	94	99 (Mg)	NA	[232]
			CO ₂ (for Ca)			120 (Ca)			98 (Ca)		
Mg	Calcined dolomite	(NH ₄) ₂ SO ₄	NH ₄ OH and (NH ₄) ₂ CO ₃	H ₂ O ₂	50	120	>7	NA	NA	NA	[23]
Mg	Tailings of saprolite laterite ore	H ₂ SO ₄	(NH ₂) ₂ CO ₃	H ₂ O ₂	NA	105	9.7	99.2	NA	Ca, Al, F, Si, S, and trace elements	[268]
Al, REEs*, Co, Mn	Acid mine drainage	NA	Na ₂ CO ₃ and NH ₄ OH	None	25	48	5 (Al)	93 (Al)	NA	Mg, Ca, REEs (pH 5)	[269]
							7 (REEs)	87 (REEs)		Mg, Ca, Al, Mn (pH 7)	
							10 (Mn, Co)	100 (Co, Mn)		Mg, Ca, REEs (pH 9)	
Mg	Dolomitic phosphate ore	Waste acid from TiO ₂ production	Ca(OH) ₂	None	45	30	10	99.9	NA	Fe, Mn, Ti	[270]

Table A.1 Summary of studies on the precipitation of magnesium from secondary resources (cont'd).

Target Metal	Feed	Leachate	Precipitant	Additive	Temperature (°C)	Precipitation Time (min)	pH	Recovery (%)	Purity (%)	Co-Precipitate	Ref
Mg	Synthetic seawater	HCl	NaOH and Na ₂ CO ₃	None	90	10	11.5-12.5	95	NA	Ca and Mn	[271]
Ni, Co, Al, Cr,	saprolite-limonite laterite	HCl	Aqueous NH ₃ and NaOH	None	25	30	11-12	93 (Ni) 92(CO) 92(Al) 90(Cr)	NA	Fe, Mg, Mn	
Ti	Steelmaking slag leachate	H ₂ SO ₄	NaOH	None	80	20	3 (Ti)	72.1 (Ti)	72.1 (Ti), 93.4 (Al), 95.4 (Mg)	Mg, Al, Mn, Ca (pH 3) Mg, Ti, Ca, Fe (pH 4.9) Ca, Mn (pH 9.6)	[272]
Al							4.9 (Al)	90 (Al)			
Mg							9.6 (Mg)	90 (Mg)			
Mg	Dolomitic limestone waste rock	H ₂ SO ₄	NaOH	None	80	20-40	11 (Ca)	90 (Ca)	99 (Ca)	Al (pH 3)	This study
Ca							9 (Mg)	98 (Mg)	99 (Mg)	Al, Mn (pH 6)	
Mn							7 (Mn)	91 (Mn)	90 (Mn)	Fe (pH 7)	
Fe							6 (Fe)	96 (Fe)	95 (Fe)	Ca (pH 9)	
Al							4 (Al)	99 (Al)	99 (Al)		
Ti							3 (Ti)	97 (Ti)	90 (Ti)		

* Rare earth elements

Table A.2 The elemental composition of dolomitic limestone leach liquor was measured by ICP-OES analysis.

Sample	Concentration (ppm)									
	Mg	Ca	Si	Al	Na	Fe	P	K	Mn	Ti
Dolomitic limestone leach liquor	1187	551	22	6.5	1.6	3	7	4	3	2

Table A.3 The calculation of Avrami kinetic parameters and activation energy

Element	Temperature (°C)	Avrami kinetic parameters		Activation energy
		n	k (min ⁻¹)	
Mg	80	1.44	0.12	19
	60	1.20	0.06	
	40	1.15	0.04	
	20	1.13	0.03	
Ca	80	1.18	0.04	9
	60	1.29	0.03	
	40	1.32	0.02	
	20	1.42	0.02	
Mn	80	1.43	0.09	10
	60	1.70	0.06	
	40	1.71	0.05	
	20	1.82	0.04	
Fe	80	1.59	0.03	16
	60	1.74	0.03	
	40	1.56	0.02	
	20	1.44	0.01	
Al	80	1.56	0.11	15
	60	1.44	0.07	
	40	1.28	0.05	
	20	1.36	0.04	
Ti	80	1.48	0.86	10
	60	1.58	0.64	
	40	1.62	0.53	
	20	1.68	0.44	

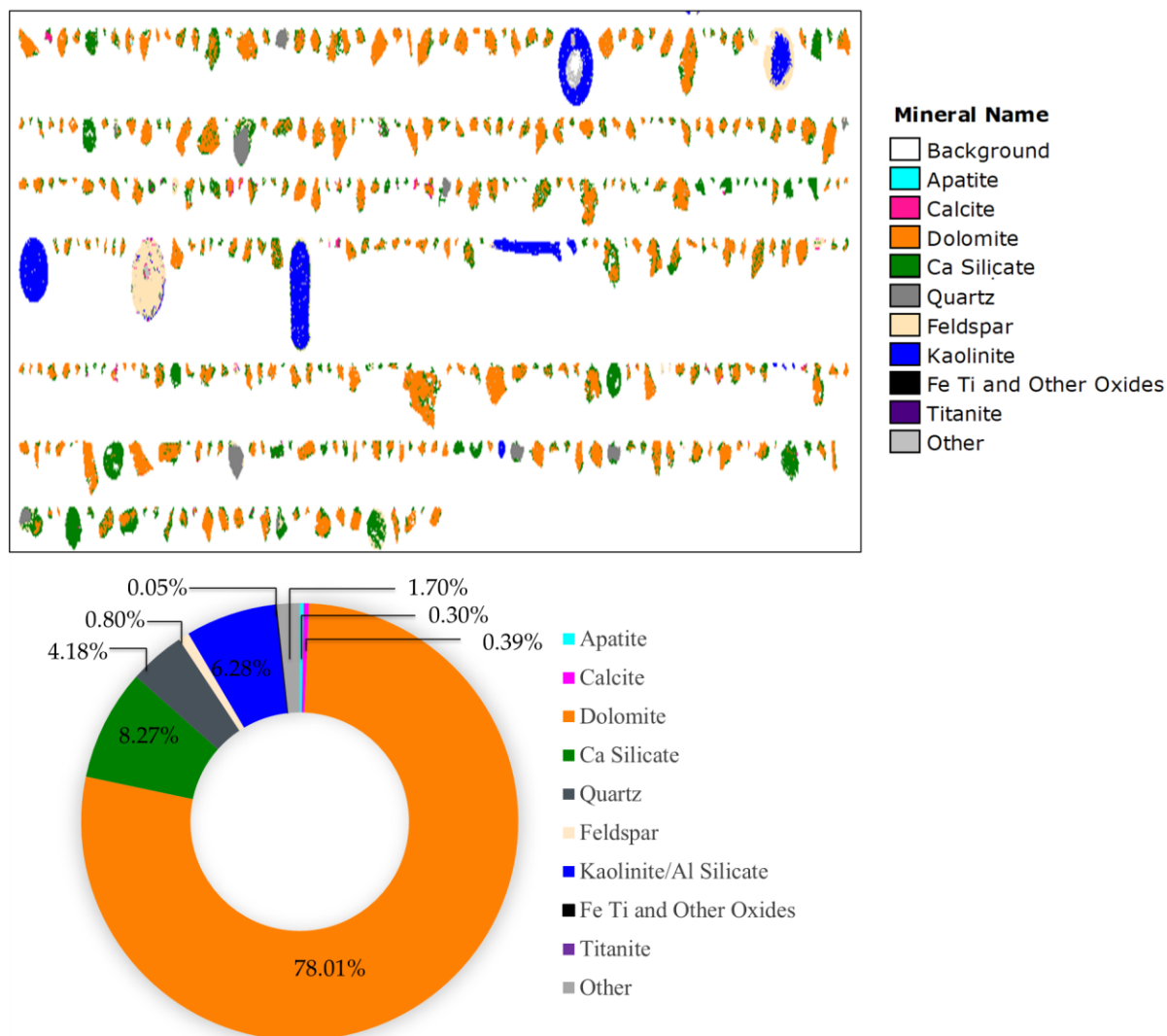


Figure A.1 Mineralogy of Moroccan dolomitic limestone waste rocks.

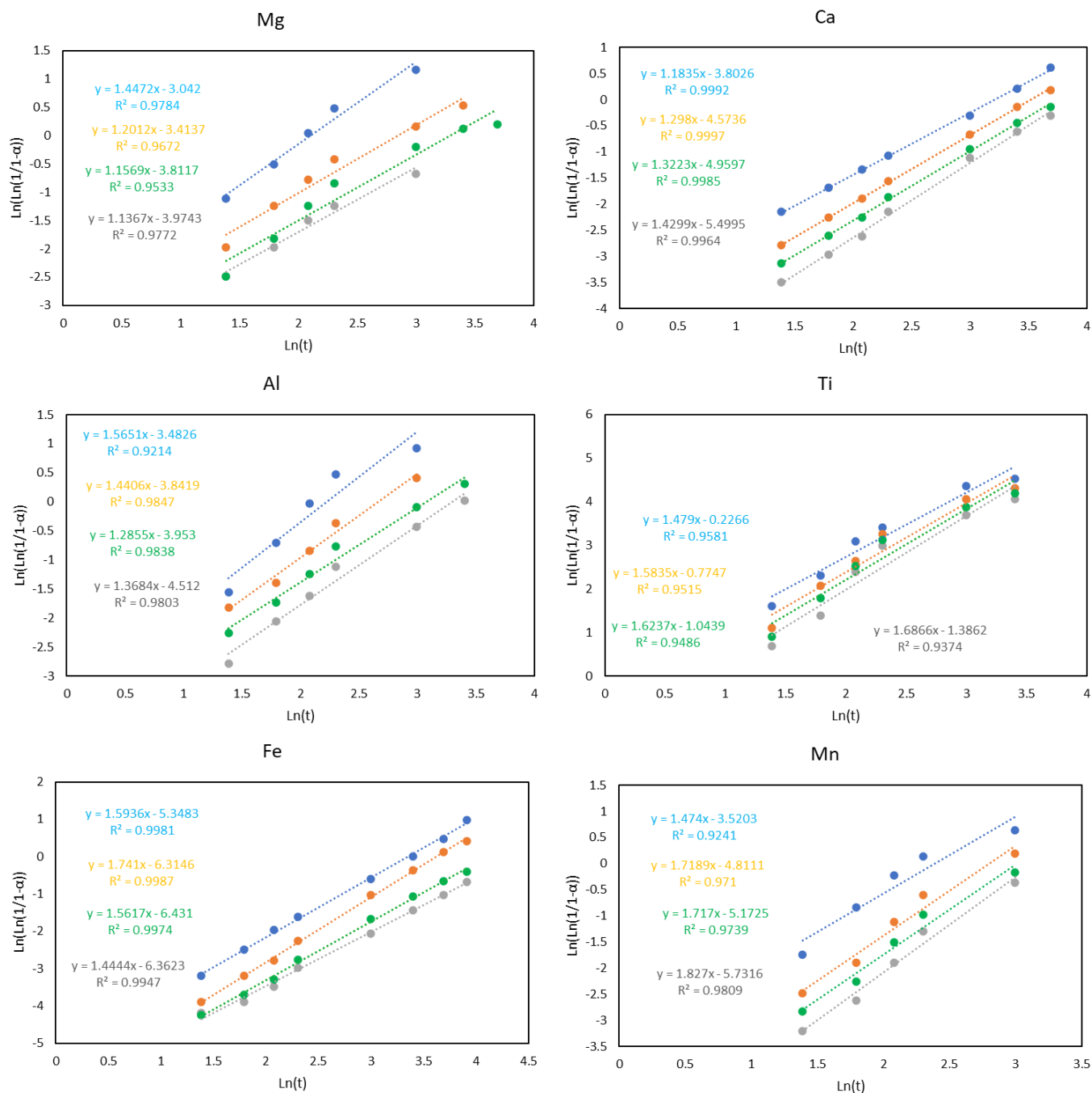


Figure A.2 Kinetics fitting based on the linearized Avrami kinetic model

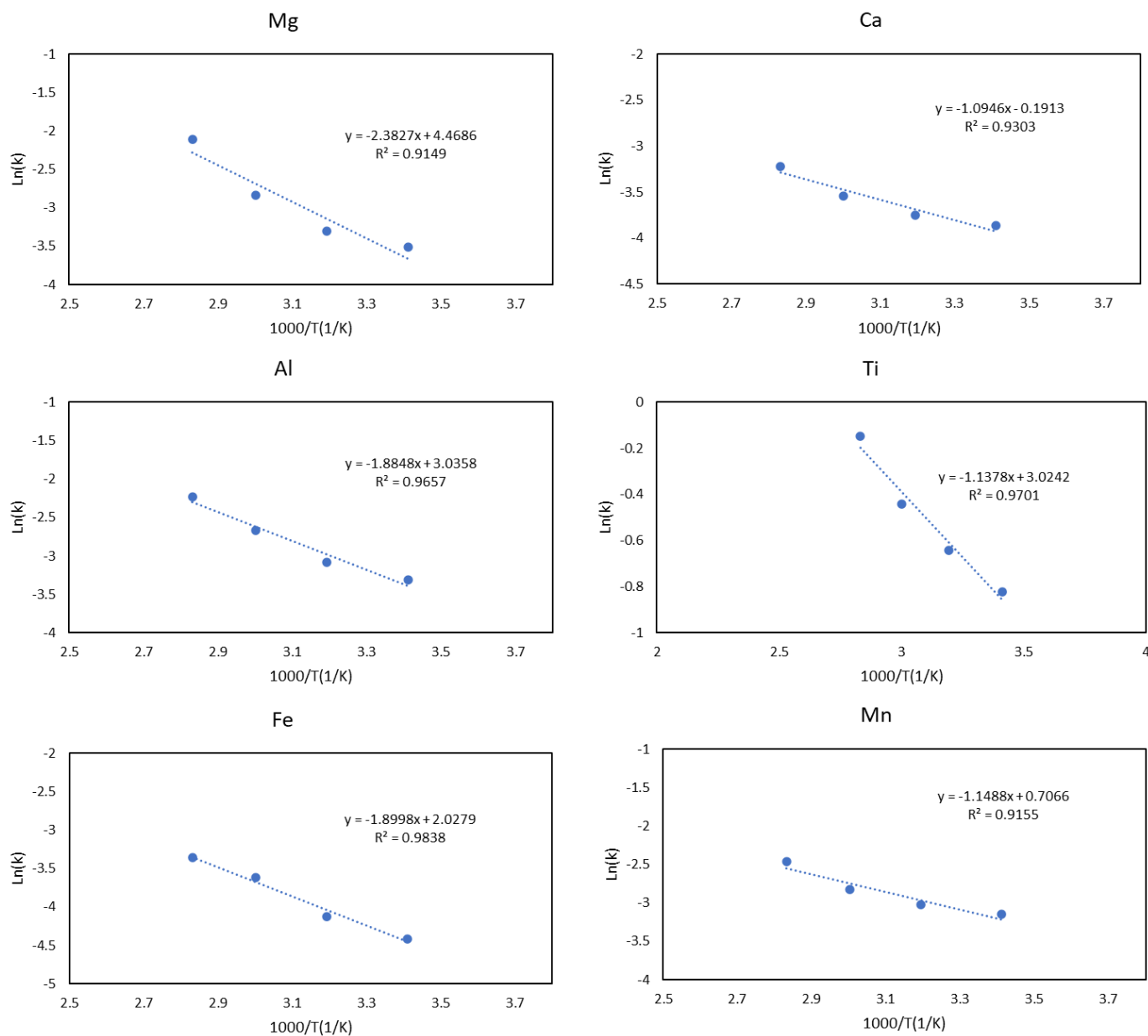


Figure A.3 Logarithmic plot of Arrhenius for alkaline precipitation

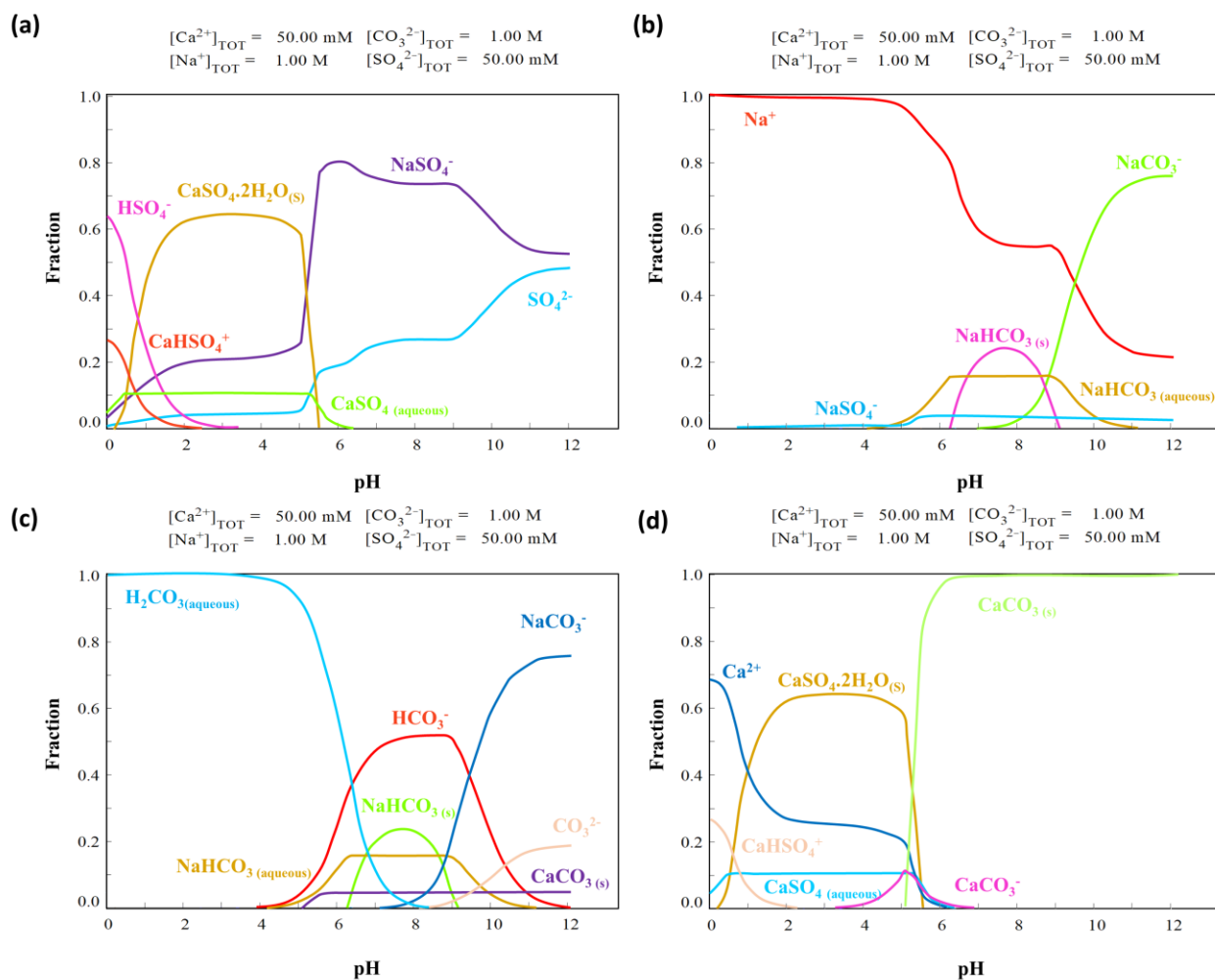


Figure A.4 Distribution fraction at different pH in the Ca-S-O-H-C-Na system for (a) sulfate anions, (b) Na cations, (c) carbonate anions, and (d) Ca cations.

A.1 Appendix - Description of the preliminary economic analysis

A.2 Economic analysis objectives and assumptions

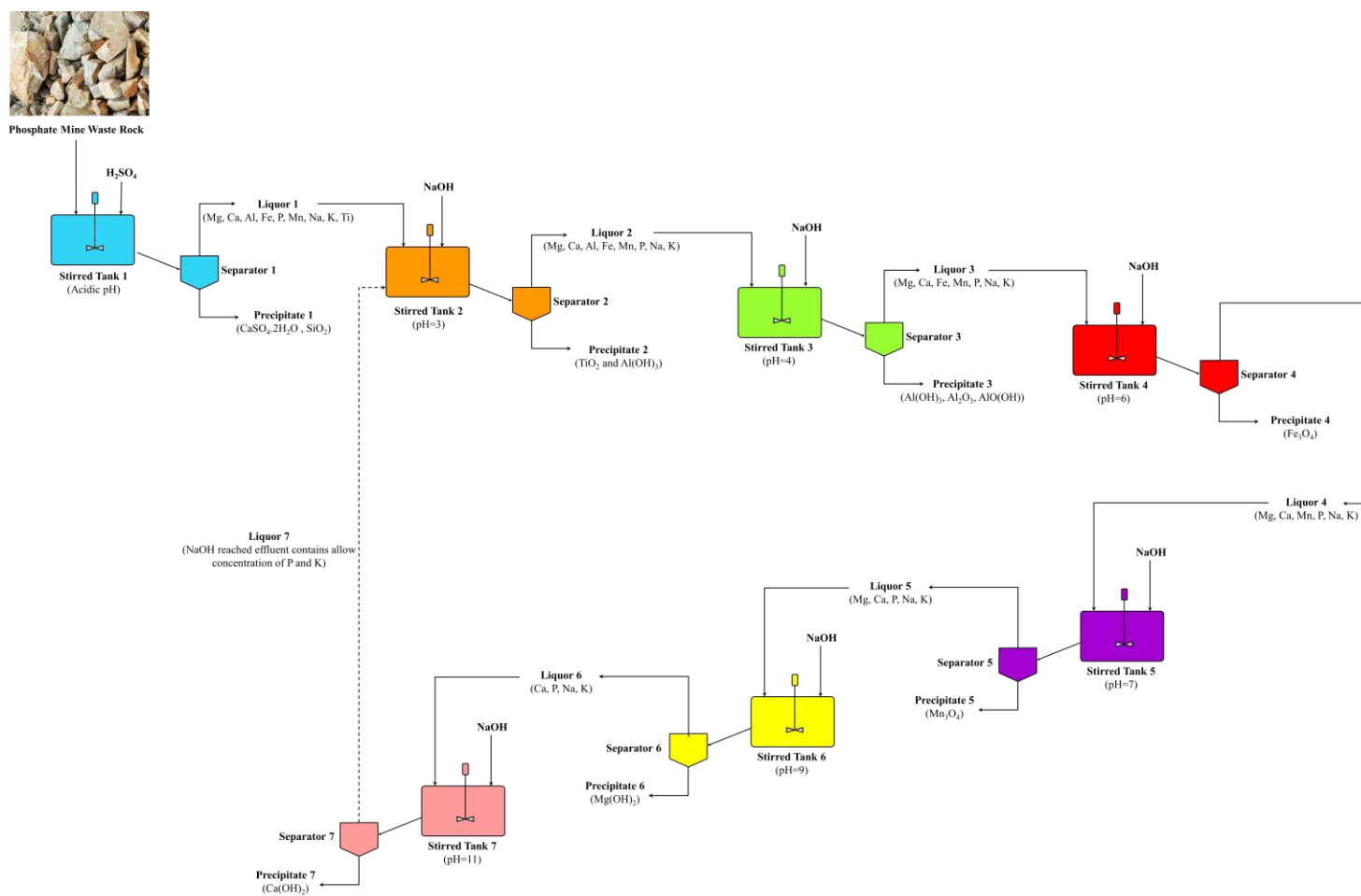


Figure A.5 Block flow diagram of the industrial-scale acid leaching and selective precipitation.

The main object of this section is to study the economic analysis of a two-step hydrometallurgical process for the selective recovery of Mg, Ca, Al, Si, Fe, Mn, and Ti. The step-by-step economic calculations involving raw material cost, utility cost, product cost, fixed capital cost, and operating capital cost were performed based on the procedure outlined by Turton et al. [299]. This economic analysis can assist in getting an insight into the process's feasibility and profitability.

For this process, seven stirred vertical tanks were considered for dilute H_2SO_4 acid leaching (1 tank) and selective alkaline precipitation by NaOH (6 tanks). In addition, seven gravity filters were considered between each stirred tank to separate solids from liquids. To calculate the economics of the process, several assumptions were made as follows, based on optimum conditions obtained during acid leaching and alkaline precipitation:

Laboratory experiments can be directly applied to the industry.

The filtration process is efficient enough to separate solids and liquids.

$\text{Al}(\text{OH})_3$ is the dominant phase of precipitated Al.

0.5 M H_2SO_4 and 1 M NaOH are applied for the industrial process.

0.01 mol H_2SO_4 is consumed for the digestion of 1 g ore.

0.42 mol NaOH is consumed to precipitate 1 L of leachate from dolomitic limestone.

H_2SO_4 leaches 20% of Ca in dolomitic limestone, and the rest is recovered as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

A.3 Process operating parameters

The optimal process parameters were selected based on the optimum results obtained from previous work on acid leaching and this work on alkaline precipitation. Table A.4 indicates the process setting parameters.

Table A.4 Process setting parameters.

Parameters	Value
H ₂ SO ₄ Concentration (M)	0.5
Solid-to-Liquid (g/l)	10
NaOH Concentration (M)	1
Leaching Temp (°C)	80
Precipitation Temp (°C)	80
Leaching process Time (h)	1
Precipitation process Time (h)	1
Dolomitic limestone Feed (kg/h)	400

The calculation was established based on the initial 400 kg/h dolomitic limestone feed rate.

A.4 Products

The valuable metals in dolomitic limestone that can be recovered include Mg, Ca, Si, Al, Fe, Mn, and Ti. The final product of the two-step hydrometallurgical process consists of Mg(OH)₂, CaSO₄·2H₂O, Ca(OH)₂, SiO₂, Al(OH)₃, Fe₃O₄, Mn₃O₄, TiO₂. Each component's feed and product quantifications were performed using the results obtained from ICP-OES analysis and mass balance calculations. The recent prices of products (January 2024) were taken from the Made-in-China website, which offers the lowest price. As illustrated in Tables A.5 and A.6, US\$ 4.6 million is estimated as the annual value of products obtained from 400 kg/h dolomitic limestone treatment.

Table A.5 Value estimation of products obtained from a two-step hydrometallurgical process.

Elements	Feed rate (kg/h)	Feed Concentration (kg/l)	Product Phase	Product Value (US\$/kg) *	Recovery value (US\$/h)
Mg	40	0.004	Mg(OH) ₂	1.5	141.09
Ca	96	0.0096	Ca(OH) ₂	1	34.79
Ca	96	0.0096	CaSO ₄ ·2H ₂ O	1	323.38
Al	0.8	0.00008	Al(OH) ₃	1	2.27
Fe	0.12	0.000012	Fe ₃ O ₄	0.8	0.39
Mn	0.28	0.000028	Mn ₃ O ₄	2.5	2.86
Ti	0.04	0.000004	TiO ₂	1.6	0.10
Si	2.4	0.00024	SiO ₂	4	20.13

* The price was taken from "Made-in-China.com"

A.5 Raw materials cost

Sulfuric acid, sodium hydroxide, and water are the raw materials for acid leaching and alkaline precipitation. 10000 L/h H₂SO₄ 0.5 M is utilized to leach Mg, Ca, Si, Al, Fe, Mn, and Ti from 400 kg/h dolomitic limestone. Regarding the estimated H₂SO₄ price (0.16 US\$/kg), the sulfuric acid cost for the proposed process is calculated based on Equation (A.1):

$$\begin{aligned} \frac{\$}{\text{h}} \text{H}_2\text{SO}_4 &= \frac{10000 \text{ L Solution}}{1 \text{ h}} \times \frac{0.5 \text{ mol H}_2\text{SO}_4}{1 \text{ L Solution}} \times \frac{98.079 \text{ g H}_2\text{SO}_4}{1 \text{ mole}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{0.16 \$}{1 \text{ kg H}_2\text{SO}_4} \quad (\text{A.1}) \\ &\approx 78 \frac{\$}{\text{h}} \end{aligned}$$

In addition, 4200 L/h NaOH solution (1M) is used to recover Mg(OH)₂, Ca(OH)₂, SiO₂, Al(OH)₃, Fe₃O₄, Mn₃O₄, and TiO₂ from the leachate solution. Considering 0.2 US\$/kg for NaOH, the cost of sodium hydroxide is estimated according to Equation (A.2):

$$\begin{aligned} ? \frac{\$}{h} \text{ NaOH} &= \frac{4200 \text{ L Solution}}{1 h} \times \frac{1 \text{ mol NaOH}}{1 \text{ L Solution}} \times \frac{39.997 \text{ g NaOH}}{1 \text{ mol NaOH}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{0.2 \$}{1 \text{ kg NaOH}} \\ &\approx 80 \frac{\$}{h} \end{aligned} \quad (\text{A.2})$$

To provide 0.5M H₂SO₄ and 1M NaOH solution, about 14200 L/h water is consumed. The price of water can be considered as US\$ 1/1000 kg by conversion of 2001 prices to 2023 prices with the CEPCI price index (2001: 397 and 2023:793.5).

$$? \frac{\$}{h} \text{ H}_2\text{O} = \left[10000 \frac{\text{L}_{\text{H}_2\text{SO}_4}}{h} + 4200 \frac{\text{L}_{\text{NaOH}}}{h} \right] \times \frac{1 \text{ kg H}_2\text{O}}{1 \text{ l H}_2\text{O}} \times \frac{1 \$}{1000 \text{ kg H}_2\text{O}} \approx 14 \frac{\$}{h} \quad (\text{A.3})$$

Based on the above calculations, the total cost of raw materials is around US\$ 1.7 million/year.

A.6 Utilities' cost

The heat required to perform leaching and precipitation reactions at 80 °C for Québec province can be provided by hydropower. Equation (A.4) can estimate the extent of heat for four stirred tanks. In this equation, the heat capacity of leachate (0.5 M H₂SO₄) and precipitation agent (1M NaOH) was supposed to be the same as pure water, equal to C_p= 4.184 kJ/(kg.K).

$$Q = [m_{\text{Leachate}} C_{p,\text{Leachate}} (\text{Reaction Temp}-25)] + [m_{\text{NaOH}} C_{p,\text{NaOH}} (\text{Reaction Temp}-25)] \quad (\text{A.4})$$

$$Q = 3267704 \frac{\text{kJ}}{h}$$

According to the Hydro-Québec, the energy cost for industrial sectors in 2023 is 3.3 ¢/kWh, equal to US\$ 9.17/GJ. Therefore, the total cost of utilities for a two-step hydrometallurgical process can be estimated as follows:

$$? \$ \text{ Utility cost} = 3267704 \frac{\text{kJ}}{h} \times \frac{1 \text{ GJ}}{10^6 \text{ kJ}} \times \frac{9.17 \$}{1 \text{ GJ}} \approx 30 \frac{\$}{h} \quad (\text{A.5})$$

A.7 Overall cost comparison (Products, Raw Materials, Utilities)

Table A.6 demonstrates the cost of raw materials, utilities, and products. This table estimates the operating time in a year to be 95%. Having around US\$ 1.7 million/year cost of raw material and

utilities and boating US\$ 4.6 million/year value from products results in a positive materials profit of US\$ 2.6 million/year.

Table A.6 Overall materials cost comparison.

Costs	Daily (US\$/h)	Annual (US\$/year)
Raw material cost	192.66	1,687,677.07
Utilities cost	29.83	261,347.04
Products value	525.00	4,599,004.49
Profit (Materials)	302.51	2,649,980.38

A.8 Capital costs

The 2001 purchased equipment cost for the two-step hydrometallurgical process was estimated by the following heuristic formula suggested by Turton et al. [299]:

$$C_{p,2001}^0 = 10^{K_1 + K_2 \log_{10} A + K_3 (\log_{10} A)^2} \quad (\text{A.6})$$

where A is the capacity or size parameter for the equipment. K_1 , K_2 , and K_3 are heuristic formula constants. Table A.7 presents the equipment cost data to be adopted by the heuristic formula.

Table A.7 Equipment cost data is required for the heuristic formula.

Equipment	Type	A	K_1	K_2	K_3
Stirred tank	Process vessel, horizontal	Volume, m ³	3.5565	0.3776	0.0905
Mixer	Turbine	Power, kW	3.4092	0.4896	0.003
Separator	Gravity filter	Area, m ²	4.2756	0.352	0.0714

The purchase cost of 2001 can be converted to 2023 prices by applying the CEPCI price index as follows:

$$c_{p,2023}^0 = c_{p,2001}^0 \times \frac{793.5}{397} \quad (\text{A.7})$$

A.9 Purchased cost of stirred tank and mixer

The leaching and precipitation tank volumes are estimated by multiplying the liquid volumetric flow rate (H_2SO_4 and NaOH) with the time of the leaching and precipitation processes, respectively. To have an adequate headspace, the estimated volume is divided by the filled fraction, which is assumed to be 50%. The required power for the stirrer was set as 10 kW/m^3 . The capital cost of the stirred tank and mixer are presented in Table A.8.

Table A.8 Estimation of the purchase cost of the stirred tank and mixer.

Item	Value	Unit	Calculation formula
Liquid volumetric flow rate	14.20	m^3/h	
Stirred tank power input	10.00	kW/m^3	
Stirred tank filled fraction	0.50		
Process time	1.00	h	
Stirred tank volume	28.40	m^3	$(\text{Liquid volumetric flow rate} \times \text{Process time}) / \text{Filled fraction}$
Stirred tank power	284.00	kW	$\text{Stirred tank volume} \times \text{Power input}$
$c_{p,2023}^0$ Tank	39,552.83	US\$	
$c_{\text{BM},2023}$ Tank	312,150.94	US\$	$(2.25 + 1.82 \times F_{\text{M}}F_{\text{P}}) \times c_{p,2023}^0$
$c_{\text{TM},2023}$ Tank	368,338.11	US\$	$F_{\text{TM}} \times c_{\text{BM},2023}$
$c_{p,2023}^0$ Mixer	15,942.50	US\$	
$c_{\text{BM},2023}$ Mixer	22,000.65	US\$	$F_{\text{BM}} \times c_{p,2019}^0$
$c_{\text{TM},2023}$ Mixer	25,960.77	US\$	$F_{\text{TM}} \times c_{\text{BM},2019}$

In Table A.8, the bare module for vertical tanks (F_{BM}) is calculated as follows:

$$F_{BM} = 2.25 + 1.82 \times F_M F_P \quad (A.8)$$

Where F_M for stainless steel is 3.1, and F_P for atmospheric pressure is equal to 1. Meanwhile, the F_{BM} for the mixer is 1.38. To implement extra installation expenses, the bare module cost is multiplied by a total module factor, denoted as F_{TM} , with a value of 1.18.

A.10 Purchased cost of the separator

A gravity filter with a height/diameter ratio of 0.5 was selected to separate the leaching residual and precipitated solids. With a retention time of 1 h and utilizing the previously established liquid volumetric flow rate, the cost of the gravity filter separator is calculated and presented in Table A.9. In this table, the F_{BM} and F_{TM} of gravity filter separators are set as 1.65 and 1.18, respectively.

Table A.9 Estimation of the purchase cost of the separator.

Item	Value	Unit	Calculation formula
Liquid volumetric flow rate	14.2	m ³ /h	
Separator retention time	1	h	
Separator volume	14.2	m ³	
Separator height/diameter ratio	0.5		
Separator height	1.653405929	m	
Separator area	17.17666515	m ²	
$c_{p,2023}^0$	131,809.03	US\$	
$c_{BM,2023}$	217,484.91	US\$	$F_{BM} \times c_{p,2023}^0$
$c_{TM,2023}$	256,632.19	US\$	$F_{TM} \times c_{BM,2023}$

A.11 Total fixed capital investment

The total fixed capital investment (FCI) is tabulated in Table A.10. This table shows that the two-step hydrometallurgical process requires a US\$ 4.5 million fixed capital investment.

Table A.10 Total fixed capital investment for selective precipitation.

Equipment	Unit number	C _{TM,2019}
Stirred tank	7	US\$ 2,578,366.79
Mixer	7	US\$ 181,725.37
Separator	7	US\$ 1,796,425.34
Total (FCI)		US\$ 4,556,517.49

A.12 Auxiliary Operating Costs

A.12.1 Operating Labor Cost

If we consider that running and monitoring this process necessitates three extra operators, with two shifts per operator per week and an annual salary of \$60,000 per operator, the estimated cost for operating labor can be calculated as $C_{OL} = \$360,000$ per year.

A.12.2 Waste Treatment

In the current stage of process development, we lack adequate information to project the costs associated with waste treatment. However, these costs are anticipated to primarily involve recovering sulfuric acid after leaching and treating the sodium hydroxide after separating precipitated solids.

A.12.3 Other auxiliary facilities' costs

All other auxiliary facilities costs associated with the two-step hydrometallurgical process can be estimated from the materials, utilities, labor costs, and the FCI. The total cost of manufacture is written by Equation (A.9).

$$C_{\text{total}} = (C_{\text{UT}} + C_{\text{RM}} + C_{\text{WT}} + 2.215 C_{\text{OL}} + 0.146 \text{ FCI}) \frac{1}{(1 - 0.19)} \quad (\text{A.9})$$

The separate individual auxiliary costs can be itemized as follows:

Table A.11 Individual auxiliary costs

Individual auxiliary costs	Cost (US\$/year)	Formula
Raw Materials	1,687,677.07	
Utilities	261,347.04	
Operating Labour	360,000.00	
Direct Supervisory and Clerical Labour	64,800.00	$0.18 \times C_{\text{OL}}$
Maintenance and Repairs	273,391.05	$0.06 \times \text{FCI}$
Operating Supplies	41,008.66	$0.009 \times \text{FCI}$
Laboratory Charges	54,000.00	$0.15 \times C_{\text{OL}}$
Patents and Royalties	126,358.36	$0.03 \times C_{\text{total}}$
Local Taxes and Insurance	145,808.56	$0.032 \times \text{FCI}$
Plant Overhead Costs	418,914.63	$0.708 \times C_{\text{OL}} + 0.036 \times \text{FCI}$
Administration Costs	104,728.66	$0.177 \times C_{\text{OL}} + 0.009 \times \text{FCI}$
Distribution and Selling Costs	463,313.98	$0.11 \times C_{\text{total}}$
Research and Development	210,597.26	$0.05 \times C_{\text{total}}$
Cost of manufacture	4,211,945.27	

A.13 Final project cost summary

Table A.12 indicates the cost summary for two-step hydrometallurgical recovery of Mg, Ca, Al, and Si from dolomitic limestone.

Table A.12 Final project cost summary

Final cost/profit	Annual final cost/profit (US\$/year)	Hourly final cost/profit (US\$/h)
Raw materials cost	1,687,677.07	192.66
Utilities cost	261,347.04	29.83
Waste treatment cost	NA	NA
Operating labor	360,000.00	41.10
FCI	4,556,517.49	520.15
Cost of manufacture	4,211,945.27	480.82
Products value	4,599,004.49	525.00
Profit	387,059.22	44.18

The probability of the proposed two-step hydrometallurgical process strongly relies on the feeding rate of dolomitic limestone. According to the preliminary economic analysis presented in Figure A.6, 322 kg/h is the minimum breakeven feeding rate of dolomitic limestone. Above this point, the revenue surpasses the total operating cost, resulting in a positive cash flow. Below the dolomitic limestone feeding rate of 322 kg/h, the capital and operating costs defeat the profits from product value, leading to negative revenue. As demonstrated in Figure A.6, increasing the flow rate of dolomitic limestone above 322 kg/h increases the probability of the proposed two-step hydrometallurgical process. It should be noted that the initial cost breakdown provided herein is a tentative approximation and should be regarded as predominantly qualitative rather than strictly quantitative. Additional investigation into system dynamics, equipment sizing, and vendor materials selection is imperative to refine the ultimate cost estimation.

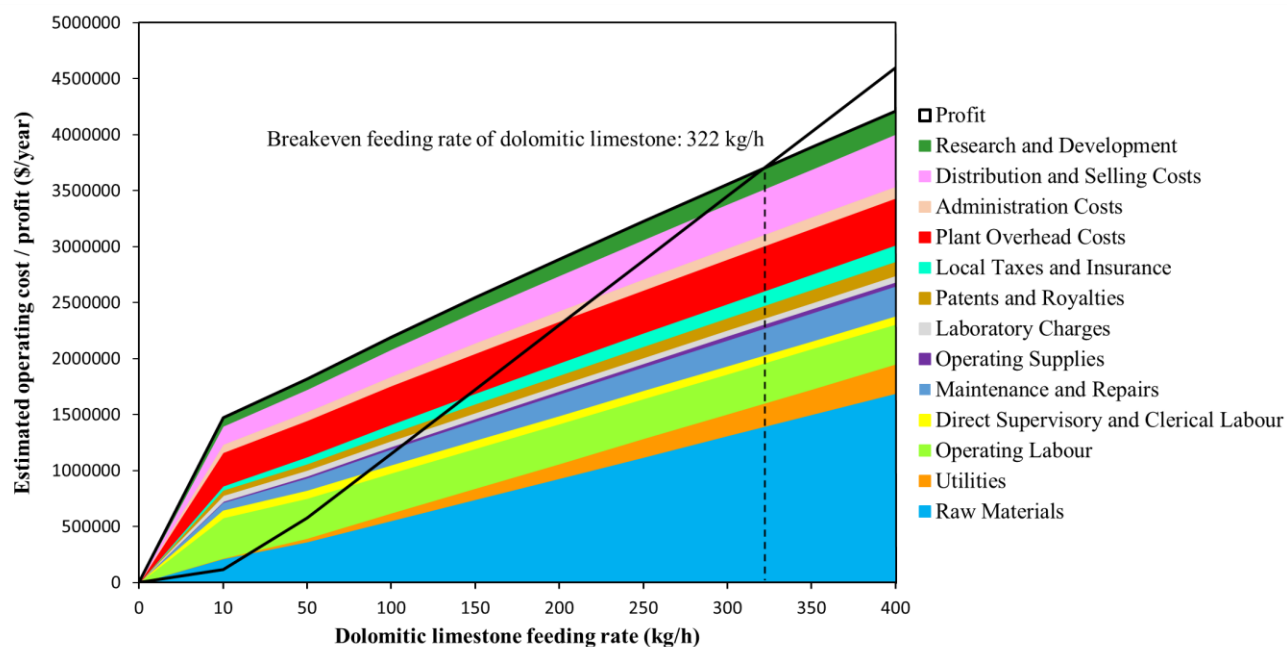


Figure A.6 Breakdown of costs and revenues as a function of dolomitic limestone feeding rate.

APPENDIX B DECARBONIZING MAGNESIUM PYROMETALLURGY THROUGH METHANOTHERMIC REDUCTION UNDER MICROWAVE HEATING

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B.1 Abstract

The decarbonization of pyrometallurgical processes requires practical hydrogen-based reduction strategies to facilitate the reduction reaction and an electrified thermal reactor to avoid the high carbon footprint of externally produced H_2 . In this study, waste-derived $Mg(OH)_2$ recovered from dolomitic limestone waste rock was converted to metallic magnesium through microwave-assisted methanothermic reduction (MTR) in the presence of carbon under atmospheric pressure. Methane was employed as a hydrogen carrier, generating in situ H_2 and CO through high-temperature CH_4 decomposition and reforming reactions with carbon, thereby creating a strongly reducing gas-solid environment without an external hydrogen supply. Under 880 W microwave irradiation at around 1200 °C, magnesium metal was produced within 30 min. Increasing CH_4 concentration from 10 to 50 vol% improved reduction efficiency from 31% to 56%, while enriching syngas composition ($H_2:CO$) from 1.8 to 4.5 mole/mole. Microwave heating provided rapid, volumetric, and selective heating. This efficient heating facilitated thermal reduction and Mg vapor formation at atmospheric pressure, eliminating the need for high-vacuum operation, which is typical of conventional carbothermic or silicothermic reduction processes. By integrating methane-derived hydrogen generation, microwave process intensification, and secondary-resource valorization, this work demonstrates a hydrogen-enabled, low-carbon pathway for magnesium metallurgy that simultaneously produces hydrogen-rich syngas.

Keywords: Light critical metals; Electrified pyrometallurgy; Non-conventional heating; Magnesium; Carbon emission; Waste valorization; Syngas; Methane gas

B.2 Introduction

Magnesium (Mg) is recognized as a critical lightweight metal due to its strategic importance in transportation, energy storage, aerospace, and advanced structural applications [32]. With a density of 1.74 g/cm^3 , Mg is the lightest structural metal currently used at scale, offering significant potential for vehicle lightweighting and greenhouse gas mitigation [33, 34]. Its high specific strength, excellent castability, and compatibility with emerging electrochemical systems have further reinforced its relevance in the global transition toward electrification and low-carbon technologies [4, 36-39]. Despite its geological abundance, Mg supply chains remain geographically concentrated and vulnerable to disruption, prompting increasing attention toward sustainable and diversified production routes. In response to environmental and supply security concerns, secondary magnesium resources from industrial wastes are increasingly seen as promising alternatives to traditional mining. [47-49]. In our previous works, we demonstrated a carbon-neutral hydrometallurgical process for recovering high-purity Mg(OH)_2 from dolomitic limestone waste rock generated during phosphate ore extraction [275, 324, 339]. This approach enables valorization of mining wastes while significantly reducing carbon footprint compared to primary extraction. Nonetheless, the recovered magnesium exists as a hydroxide, and conversion to metallic Mg requires a subsequent high-temperature reduction step. Therefore, integrating hydrometallurgical recycling with pyrometallurgical upgrading requires developing an efficient, electrified, and low-carbon thermal reduction process that can fully realize the circular valorization of secondary magnesium resources.

Commercial metallic magnesium production is currently dominated by silicothermic reduction (Pidgeon process), in which calcined dolomite reacts with ferrosilicon at temperatures above 1200°C under severe vacuum conditions [107]. Although technologically mature, this process is energy-consuming, carbon-intensive, batch-operated, and produces large volumes of slag [128]. These limitations have motivated interest in carbothermic reduction (CTR), where carbon replaces ferrosilicon as the reductant [382]. Carbon is inexpensive and widely available. Nonetheless, the CTR of MgO typically requires temperatures exceeding 1200°C and a vacuum to shift the equilibrium toward Mg vapor formation. Furthermore, the predominance of solid-solid reaction pathways limits mass transfer and reactor scalability.

To overcome these limitations, gas-assisted reduction strategies have gained attention. Methane, in particular, offers unique advantages because it can act as both a reductant and a hydrogen carrier, decomposing at elevated temperatures to generate H_2 and CO [29, 383]. The presence of gas-phase reducing agents enhances gas-solid interaction and lowers effective oxygen potential, potentially enabling Mg production at atmospheric pressure [135]. Nevertheless, conventional furnace heating limits process intensification due to slow heat transfer and temperature gradients.

Microwave heating presents an alternative electrified thermal platform characterized by selective, rapid, and volumetric energy deposition [133, 204, 205, 214]. By directly interacting electromagnetic fields with microwave-absorbing phases such as carbon, high local temperatures can be achieved while maintaining a cooler reactor environment [20]. Although microwave-assisted carbothermal reduction of Mg compounds has been investigated, microwave-assisted methanothermic reduction (MTR) of $Mg(OH)_2$ has not been systematically explored. In this research, we introduce and experimentally investigate a microwave-assisted MTR process for converting waste-derived $Mg(OH)_2$ into metallic magnesium at atmospheric pressure. This method combines methane-derived hydrogen production, microwave process enhancement, and secondary resource valorization to create a low-carbon magnesium metallurgy platform. The conceptual process flow diagram is presented in Figure B.1.

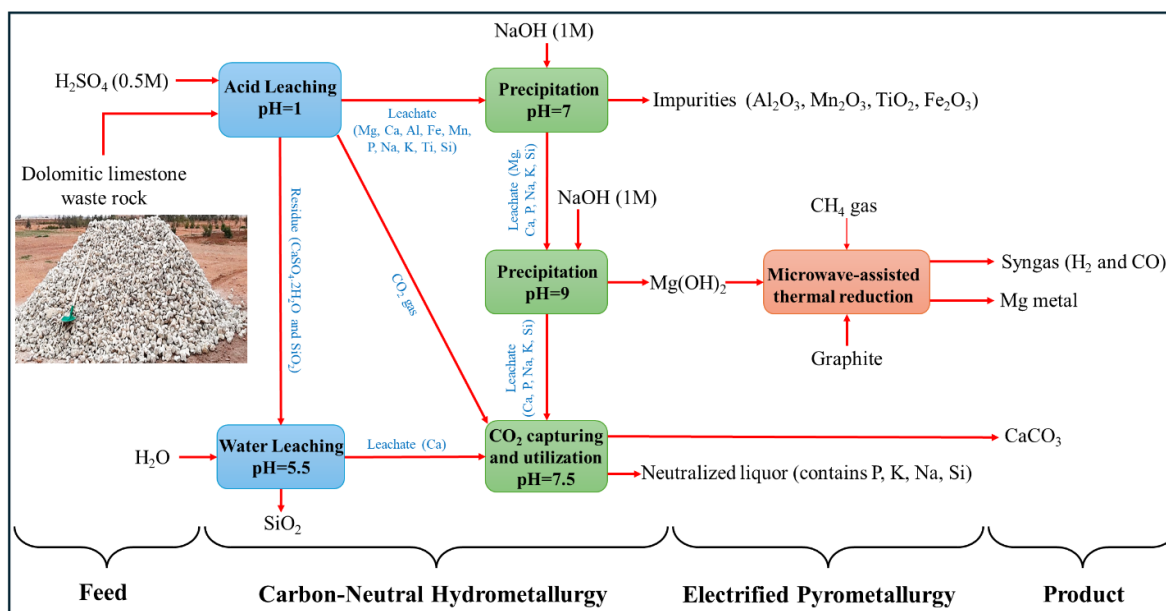


Figure B.1 The conceptual process flow diagram for recycling magnesium and syngas from dolomitic limestone waste rocks.

B.3 Experimental approach for microwave-assisted MTR of $\text{Mg}(\text{OH})_2$

The High-purity $\text{Mg}(\text{OH})_2$ (>99%) was synthesized from dolomitic limestone waste rock via a previously reported carbon-neutral hydrometallurgical route [275, 324]. Natural graphite flakes (99%, -325 mesh) were used as the microwave susceptor and auxiliary reductant. For methanothermic reduction experiments, $\text{Mg}(\text{OH})_2$ and graphite were mixed at a molar ratio of 1:1 using mechanical blending. Approximately 5 g of the mixture was loaded onto a quartz fritted disc positioned at the center of a fused quartz reactor tube (OD: 3.2 cm, length: 40 cm). Prior to reaction, the bed was purged with argon for 30 min to remove residual oxygen. Methane diluted in argon (10-50 vol% CH_4) was introduced at controlled flow rates using a mass flow controller, and all experiments were conducted at atmospheric pressure. Figure B.2 shows a schematic illustration of the microwave-assisted MTR process.

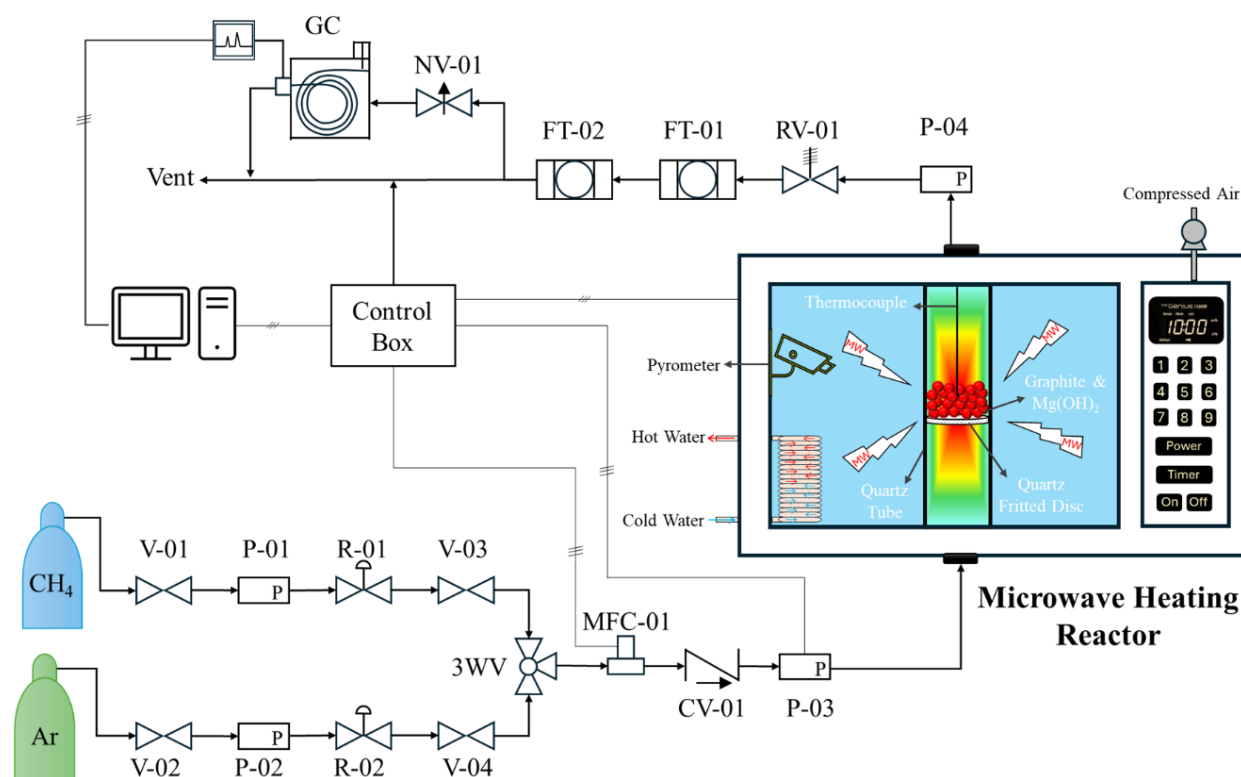


Figure B.2 The process flow diagram for the atmospheric MTR of $\text{Mg}(\text{OH})_2$ (V: valve, P: pressure gauge, R: pressure regulator, 3WV: three-way valve, CV: check valve; RV: relief valve, FT: particles filter, NV: needle valve, and GC: gas chromatography).

Microwave-assisted MTR was performed in a modified multimode microwave cavity (2.45 GHz) equipped with a 1100 W magnetron. An input power of 880 W was applied for 30 min. Bed temperature was monitored using a non-contact infrared pyrometer (200-1500 °C range), while reactor wall temperature was measured with a thermocouple. The gas effluent was filtered and analyzed by gas chromatography to determine the concentrations of H₂ and CO (GC; Agilent 8890 Series, USA). After cooling under an inert atmosphere, condensed Mg particles deposited along the reactor wall were mechanically separated from the residual solid bed. Reduction efficiency was calculated as the mass of recovered metallic Mg divided by the theoretical Mg content in the feed. The reduction efficiency (R) was calculated according to:

$$R (\%) = \left[1 - \left(\frac{m_{MgO,f}}{m_{MgO,i}} \right) \right] * 100 \quad (B.1)$$

where $m_{MgO,i}$ is the theoretical MgO-equivalent mass derived from the initial Mg(OH)₂ (based on stoichiometric dehydration), and $m_{MgO,f}$ is the remaining MgO mass in the residue after reduction. Semi-quantitative phase analysis was also performed using the Reference Intensity Ratio (RIR) method from XRD data. As an independent validation, HCl leaching (1 M) was employed, where metallic Mg reacted to form MgCl₂ and H₂ gas. The dissolved Mg concentration (measured by ICP-OES) and the evolved H₂ volume (measured by the water displacement method) were correlated through mass balance to determine the Mg metal content. Agreement among these three methods ensured reliable determination of reduction efficiency and product purity.

Thermodynamic simulations were conducted using FactSage 8.3 to evaluate reaction feasibility and phase evolution. The Gibbs free energy variations as a function of temperature and pressure were calculated using the Reaction module. Thermodynamic data were obtained from the FToxid and FactPS databases. These simulations provided theoretical validation for the experimentally observed reduction thresholds and syngas compositions.

B.4 Results and discussions

B.4.1 Thermodynamic evaluation

The carbothermal reduction of MgO proceeds according to:



Thermodynamically, the reaction feasibility is governed by the relative stability of MgO with respect to CO/CO₂ equilibria and the partial pressure of Mg vapor. Since Mg is produced in the gaseous phase, the equilibrium strongly depends on total system pressure through:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_{Mg} P_{CO}}{\alpha_{MgO} \alpha_C} \right) \quad (B.3)$$

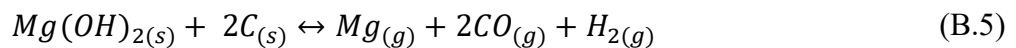
where P_{Mg} and P_{CO} are the partial pressures of Mg and CO (Pa), and α_{MgO} and α_C represent the activities of MgO and C, respectively.

As shown in Figure B.3(a), at 1 atm, the Gibbs free energy change remains positive up to 1800 °C, indicating that the CTR of MgO is not thermodynamically favorable under atmospheric conditions. Reducing total pressure significantly shifts the equilibrium toward Mg vapor formation. At 100 Pa, reduction becomes feasible above 1300 °C, while at 10 Pa the threshold temperature decreases to 1100 °C. This explains the necessity of vacuum operation in conventional carbothermal Mg production from MgO.

It should be mentioned that conventional CTR of MgO occurs in two stages: (I) direct reduction with carbon (a solid-solid reaction) and (II) indirect reduction with CO gas (a gas-solid reaction) [29, 347]. The indirect reduction pathway over CTR is sustained by the reverse Boudouard reaction:



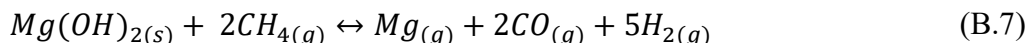
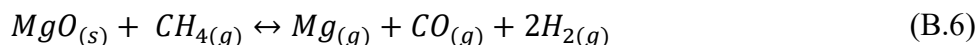
The assessment of equilibrium compositions for solid-solid reactions of Mg(OH)₂-C revealed that the CTR of Mg(OH)₂ follows a distinctly different pathway compared to MgO. Initially, Mg(OH)₂ dehydrates below 500 °C, producing water vapor and MgO. Subsequently, the water vapor reacts with solid carbon to generate syngas through steam-carbon gasification at temperatures above 500 °C. The formation of syngas, rather than CO, enhances the CTR process, allowing Mg(OH)₂ to reduce to Mg vapor and syngas at lower temperatures (Reaction (B.5)).



As shown in Figure B.3(b), the ΔG for $\text{Mg}(\text{OH})_2$ carbothermic reduction at 1 atm shifts from positive to negative at around 1200 °C, indicating that the process is spontaneous at atmospheric pressure and temperatures above this point. Further lowering the total pressure from 1 atm to 10 Pa reduces the CTR temperature of $\text{Mg}(\text{OH})_2$ from 1200 °C to 700 °C.

The enhanced feasibility of CTR for $\text{Mg}(\text{OH})_2$ relative to MgO arises from both chemistry and gas-phase effects. $\text{Mg}(\text{OH})_2$ is less stable than MgO at elevated temperatures due to dehydration and the associated formation of additional gaseous species, which increases entropy and decreases the effective oxygen potential [134, 384]. Simultaneously, in situ generation of H_2 and CO improves gas-solid transport and lowers the oxygen partial pressure of the system [348]. Consequently, H_2 in syngas can synergize with CO in the indirect CTR of $\text{Mg}(\text{OH})_2$, enabling reduction at lower temperatures than in the MgO -C system.

Using methane as a reductant instead of solid carbon further enhances the thermodynamic feasibility of MgO and $\text{Mg}(\text{OH})_2$ reduction at atmospheric pressure. The decrease in the reduction temperature threshold under methanothermic conditions arises primarily from the increased participation of gaseous species and the in-situ generation of H_2 and CO . Methane thermally decomposes above 600 °C to produce H_2 and carbon, and in the presence of metal oxides or hydroxides, it can additionally reform to generate syngas. The coexistence of CH_4 , H_2 , and CO shifts the reduction pathway from a solid-solid mechanism toward predominantly gas-solid reactions, thereby lowering the effective oxygen potential and enabling Mg production at atmospheric pressure, as described in Reactions (B.6) and (B.7).



As illustrated in Figures B.3(c) and B.3(d), atmospheric methanothermic reduction becomes thermodynamically feasible at approximately 1500 °C for MgO and 1100 °C for $\text{Mg}(\text{OH})_2$. Compared with the CTR of $\text{Mg}(\text{OH})_2$, which produces CO -enriched syngas (H_2 : CO molar ratio of 1:2), methanothermic reduction yields H_2 -enriched syngas (H_2 : CO molar ratio of 5:2). The generation of H_2 -enriched syngas is advantageous not only for suppressing reverse oxidation during Mg vapor condensation but also for potential downstream utilization, such as methanol synthesis, which typically requires an H_2 : CO molar ratio close to 3.

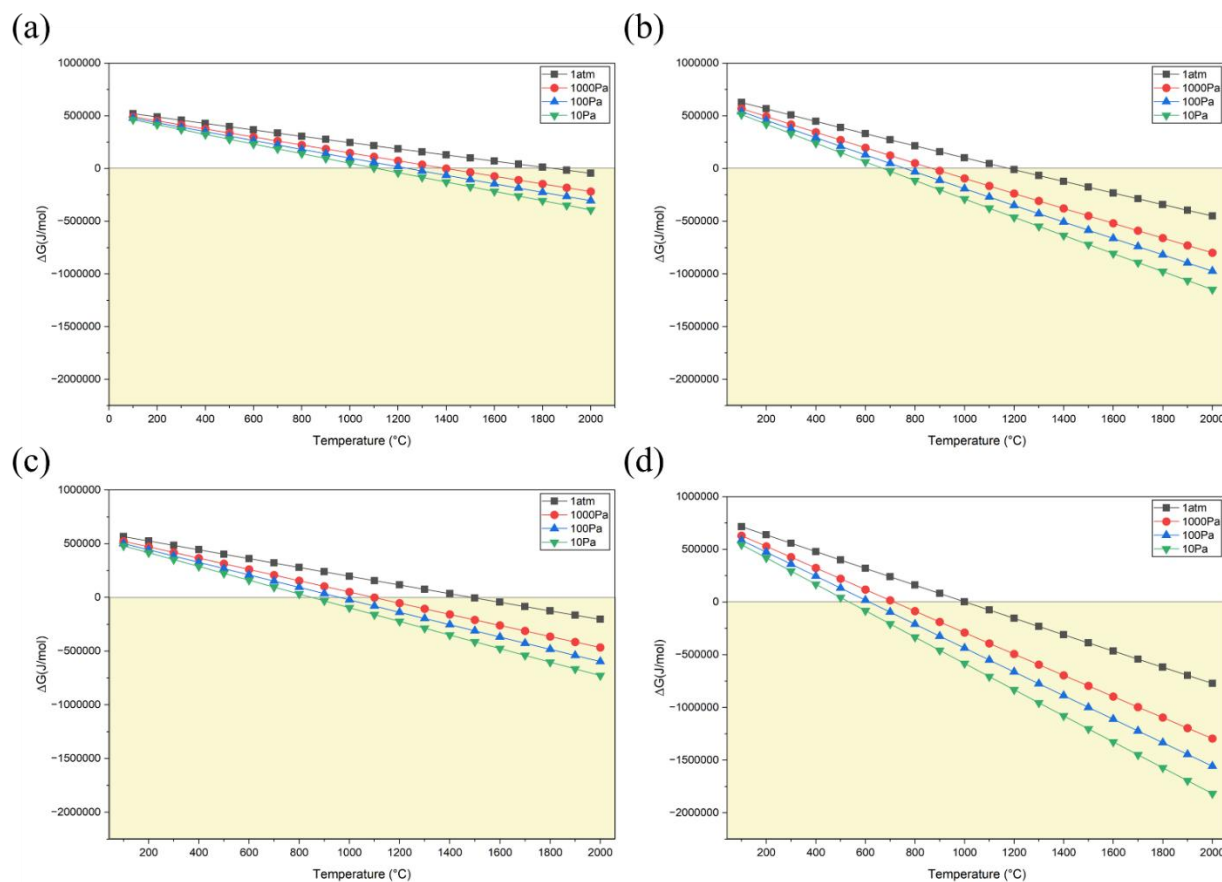
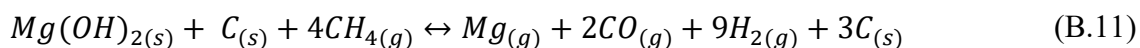
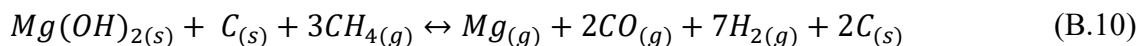
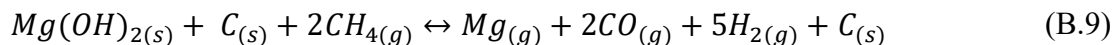
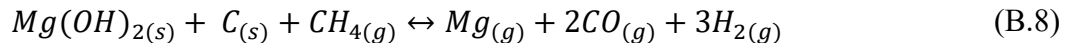


Figure B.3 Thermodynamic stability domain at various temperatures and pressures for (a) MgO-C system, (b) Mg(OH)₂-C system, (c) MgO-CH₄ system, and (d) Mg(OH)₂-CH₄ system.

It is important to note that microwave heating can be effectively applied to the CTR of Mg(OH)₂ because solid carbon exhibits high dielectric loss and acts as an efficient microwave susceptor, enabling rapid and volumetric heating under electromagnetic irradiation [204]. In contrast, methane gas is microwave transparent, while Mg(OH)₂ is a poor microwave absorber under typical conditions and cannot couple efficiently with microwave radiation. Therefore, conducting MTR under microwave irradiation requires the presence of a material with high dielectric loss and moderate dielectric constant, such as carbonaceous materials (e.g., graphite, charcoal, activated carbon, or carbon nanotubes) or certain metal carbides (e.g., SiC, Al₄C₃, Mo₂C, and TiC). Carbonaceous materials are preferred due to their lower cost and minimal slag formation during reduction.

To thermodynamically evaluate the role of carbon in microwave-assisted MTR, reactions were modeled in which 1 mol of Mg(OH)₂ reacts with varying molar ratios of methane in the presence

of 1 mol of carbon, as expressed in Reactions (B.8)-(B.11). The selected carbon amount here serves primarily as a microwave susceptor and heat-transfer medium and is insufficient to independently drive full carbothermal reduction.



The Gibbs free energy variations for these Reactions (B.8) to (B.11) at atmospheric pressure are shown in Figure B.4. For equimolar C and CH₄ (Reaction (B.8)), Mg vapor and syngas formation become feasible above 1100 °C, comparable to the pure MTR process. However, the resulting syngas composition shifts to an H₂:CO molar ratio of 3:2, lower than that obtained from Reaction (B.7) (H₂:CO molar ratio 5:2). Increasing the methane molar ratio from 1 to 4 reduces the thermodynamic reduction threshold from 1100 °C to around 950 °C and increases the H₂:CO molar ratio from 3:2 to 9:2.

These results indicate that the combined presence of carbon and methane can synergistically enhance Mg production by lowering the effective oxygen potential while simultaneously enriching hydrogen in the product gas. Nevertheless, there is a trade-off between initial carbon content and methane supply. Although higher CH₄ ratios favor H₂-enriched syngas and lower reduction temperatures, excessive carbon deposition from methane decomposition may promote localized overheating, hot-spot formation, and non-uniform temperature distribution under microwave irradiation.

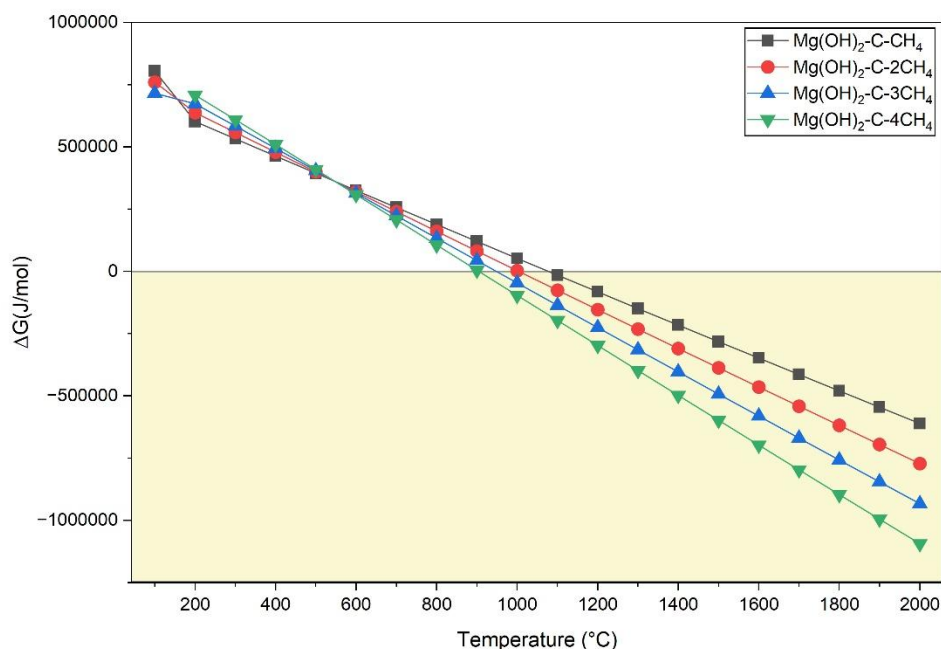


Figure B.4 Thermodynamic stability domain for $\text{Mg(OH)}_2\text{-C-CH}_4$ system at 1 atm and various temperatures.

B.4.2 Temperature profile in microwave reactor

Microwave heating efficiency is governed by the interaction between electromagnetic fields and the dielectric and conductive properties of the materials in the feed. As shown in Figure B.5, the equimolar graphite- Mg(OH)_2 mixture exhibited strong microwave interaction. Under an input power of 880 W, the bed temperature increased rapidly, reaching around 1200 °C within 3 min and stabilizing near this value during continued irradiation. This effective microwave absorption is primarily attributed to the high dielectric loss and electrical conductivity of graphite. In microwave fields, oscillation of the electric field induces electron motion in graphite, and resistive (Joule) heating results from electron scattering within the carbon lattice [20, 340]. In contrast, Mg(OH)_2 and methane exhibit negligible microwave absorption under the applied conditions. Therefore, graphite acts as the dominant microwave susceptor and heat-generation medium in our process.

In addition to bed temperature, the quartz reactor wall temperature was monitored during irradiation (Figure B.5). A substantial temperature gradient was observed between the reacting bed and the reactor wall. While the bed inventory reached around 1200 °C, the wall temperature

remained near 400 °C, corresponding to an 800 °C difference. This behavior reflects the volumetric and selective nature of microwave heating. Unlike conventional furnaces, where heat is first transferred from an external source to the reactor wall and then to the bed via convection and conduction, microwave energy penetrates directly into the microwave-absorbing phase. Heat is generated internally within the graphite particles and subsequently transferred outward to the surrounding solids and reactor environment. Consequently, during short irradiation times, the bed temperature significantly exceeds that of the reactor wall.

From a metallurgical perspective, this pronounced temperature gradient offers an important advantage. In conventional carbothermal systems, Mg vapor condensation often occurs gradually in hot zones where CO₂ generated via the Boudouard reaction can promote reoxidation [31]. In contrast, the relatively cooler reactor wall under microwave heating facilitates rapid quenching of Mg vapor, thereby reducing the likelihood of reoxidation during condensation. This selective and volumetric heating behavior contributes to improved control over Mg vapor stability and product purity.

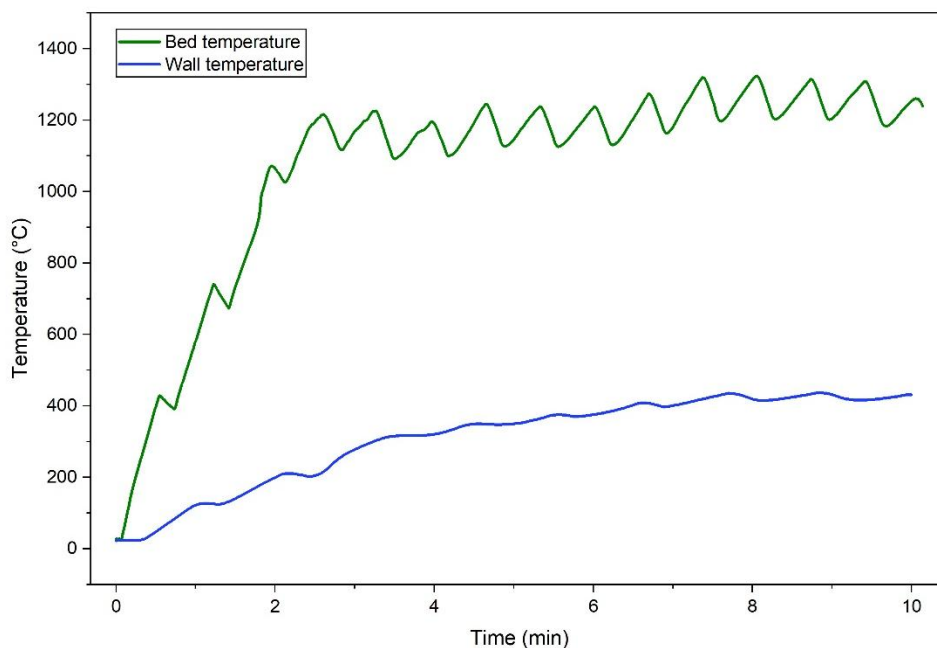


Figure B.5 Bed and reactor's wall temperature profiles for a mixture of Mg(OH)₂-graphite at input power 880.

B.4.3 Methanothermic reduction

Methanothermic reduction of $\text{Mg}(\text{OH})_2$ was evaluated under microwave irradiation at 880 W for 30 min with a fixed $\text{Mg}(\text{OH})_2$:graphite molar ratio of 1:1 and a bed temperature of approximately 1200 °C. The influence of methane concentration in the Ar carrier gas (10-50 vol% CH_4) was systematically investigated, and the results are presented in Table B.1.

As CH_4 concentration increased from 10 vol% to 50 vol%, the Mg reduction efficiency increased significantly from 31% to 56%, while the H_2 :CO molar ratio rose from 1.8 to 4.5. Since operating conditions (i.e., microwave power, reaction time, and bed temperature) were kept constant, this enhancement is primarily attributable to the increased methane partial pressure, which in turn led to greater in situ H_2 and CO generation. The higher concentration of reducing gases lowers the effective oxygen partial pressure, promoting Mg vapor formation under atmospheric conditions [385].

Beyond the chemical contribution of methane, microwave heating itself plays a critical role in enhancing the efficiency of the MTR process. As demonstrated in our previous work on microwave-assisted CTR of $\text{Mg}(\text{OH})_2$, the thermal effect of microwave irradiation enables selective and volumetric heating of carbonaceous phases, leading to rapid temperature rise and efficient steam-carbon gasification during $\text{Mg}(\text{OH})_2$ decomposition. This promotes the complete conversion of $\text{Mg}(\text{OH})_2$ to MgO , CO, and H_2 prior to metal reduction, thereby establishing a highly reducing local atmosphere. In addition to thermal effects, microwave irradiation may introduce non-thermal contributions associated with enhanced polarization phenomena, localized electric-field interactions, and defect formation. In our earlier CTR studies, evidence of water splitting and oxygen vacancy generation was observed, which can facilitate oxygen removal from MgO and accelerate reduction kinetics. Under methanothermic conditions, such defect-assisted pathways may further enhance Mg formation by lowering the local activation barrier for oxygen extraction.

Overall, the combined effects of methane-derived reducing species and microwave-induced thermal and non-thermal phenomena synergistically enhance Mg production, enabling high reduction efficiency and the generation of hydrogen-enriched syngas under atmospheric pressure.

Table B.1 Comparison of $\text{Mg}(\text{OH})_2$ methanothermic reduction in the presence of graphite under microwave heating at different methane gas concentrations.

CH_4 vol% in Ar gas flow	$\text{Mg}(\text{OH})_2$:Graphite molar ratio	Microwave input power (W)	Reaction time (min)	Bed temperature ($\pm 50^\circ\text{C}$)	Reduction efficiency ($\pm 5\%$)	H_2 :CO (mole/mole)
10	1:1	880	30	1200	31	1.8
30	1:1	880	30	1200	44	3.2
50	1:1	880	30	1200	56	4.5

The XRD patterns of the initial feed, post-reaction residue, and condensed products are presented in Figure B.6. Figure B.6(a) shows the diffraction pattern of the graphite- $\text{Mg}(\text{OH})_2$ feed mixture prior to methanothermic reduction. The dominant peak at 2θ of 26.5° corresponding to the (002) plane confirms the presence of crystalline graphite with a hexagonal structure (JCPDS No. 04-016-0554). Additional reflections at 2θ of 32.5° , 32.5° , 37.9° , 50.8° , 58.7° , 62.1° , 68.8° , and 72° are indexed to the (001), (100), (101), (102), (110), (111), (200), and (201) planes of $\text{Mg}(\text{OH})_2$, consistent with the hexagonal $\text{P}\bar{3}\text{m}1$ structure (JCPDS No. 00-044-1482). These results confirm the coexistence of well-crystallized $\text{Mg}(\text{OH})_2$ and graphite in the starting material.

After microwave-assisted methanothermic reduction, the solid residue (Figure B.6(b)) exhibits diffraction peaks corresponding to MgO and residual graphite. The reflections at 2θ of 37.1° , 42.9° , 62.3° , 74.6° , and 78.6° are assigned to the (111), (200), (220), (311), and (222) planes of cubic MgO with $\text{Fm}\bar{3}\text{m}$ symmetry (JCPDS No. 04-009-5447). The disappearance of $\text{Mg}(\text{OH})_2$ peaks confirms complete dehydration during the reaction, while the presence of MgO indicates that $\text{Mg}(\text{OH})_2$ first decomposed to MgO prior to metal reduction, in agreement with the proposed thermodynamic pathway.

The XRD pattern of the separated and refined condensate (Figure B.6(c)) shows distinct peaks at 2θ of 32.3° , 34.4° , 36.6° , 47.8° , 57.5° , 62.3° , 67.8° , 69.5° , 72.6° , and 77.5° , corresponding to the (100), (002), (101), (102), (110), (103), (200), (201), (004), and (202) planes of hexagonal Mg metal ($\text{P}6_3/\text{mmc}$, JCPDS No. 01-073-3812). The absence of MgO or $\text{Mg}(\text{OH})_2$ peaks in the

condensate confirms successful vapor-phase reduction and subsequent condensation of metallic Mg with high phase purity.

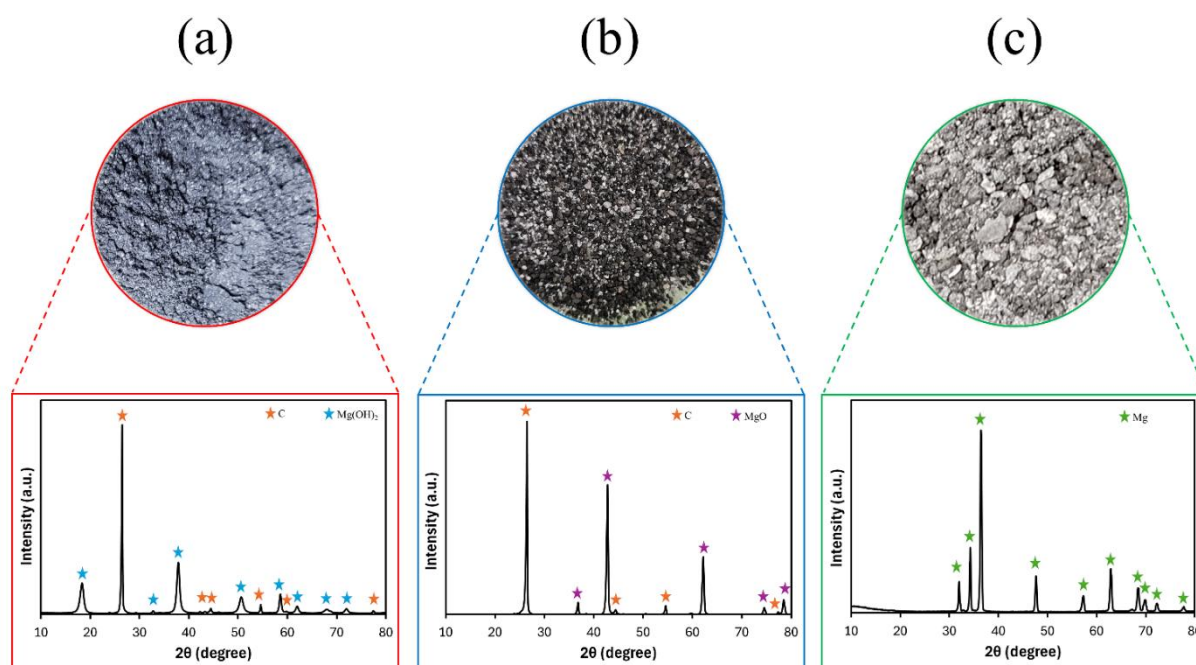


Figure B.6 XRD patterns of (a) Mg(OH)₂-mixture before reaction, (b) residue of MTR, and (c) separated condensate

B.5 Conclusion

This research presented a hydrogen-enabled, electrified method for magnesium production using microwave-assisted methanothermic reduction of waste-derived Mg(OH)₂ under atmospheric pressure. Thermodynamic analysis confirmed that, while conventional MgO carbothermal reduction requires a high-vacuum environment, Mg(OH)₂ benefits from an entropy increase driven by dehydration and the in situ formation of syngas. Methane acts as a hydrogen carrier, producing H₂ and CO in the reaction zone and shifting the reduction mechanism toward gas-solid interactions, which lowers the effective oxygen potential. Using 880 W microwave energy at roughly 1200 °C, magnesium metal was generated in 30 min, achieving a maximum reduction efficiency of 56% as CH₄ concentration in Ar gas increased from 10 to 50 vol%. In addition, the process produced hydrogen-rich syngas, with an H₂:CO ratio reaching up to 4.5 mol/mol. Our approach combines hydrogen metallurgy, electrified heating, and secondary-resource valorization, offering a promising pathway to low-carbon magnesium production. Future efforts will focus on optimizing the process, scaling up reactors, managing carbon, and assessing life-cycle decarbonization.

B.6 Acknowledgments

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