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REACTIVE MAGNESIA FROM MAGNESIUM SULFATE HYDRATE: A CIRCULAR ROUTE FOR ACID NEUTRALIZATION SYSTEMS

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Abstract

This work presents an efficient carbothermic route for producing highly reactive magnesium oxide (MgO) from hydrated magnesium sulfate ($MgSO_4 \cdot H_2O$), using charcoal, petroleum coke, and bituminous coal as reducing agents. Experiments conducted in a muffle furnace at 850 °C for 120 minutes yielded MgO between 94.3% and 95.0%. Acid-neutralization tests demonstrated rapid reactivity (44–98 s), and the product exhibited a porous microstructure with particle sizes below 40 μm and low ash content. The process minimizes gypsum waste, enables $MgSO_4$ recycling, and allows SO_2 capture for sulfuric acid regeneration, offering both environmental and logistical advantages—particularly for sustainable sulfuric-acid-based hydrometallurgical operations in remote regions.

Keywords: Reactive magnesium oxide (MgO). Carbothermic reduction. Hydrated magnesium sulfate ($MgSO_4 \cdot H_2O$). Sulfuric acid regeneration. Acid neutralization kinetics. Circular hydrometallurgy. Environmental sustainability.

Highlights

1. Developed an efficient carbothermic route to synthesize highly reactive MgO from hydrated magnesium sulfate ($MgSO_4 \cdot H_2O$).
2. Achieved 94–95 % MgO conversion within 120 min at 850 °C using alternative carbon sources.
3. Demonstrated rapid acid neutralization (< 2 min), confirming high reactivity and purity.
4. The process eliminates gypsum waste and enables closed-loop $MgSO_4$ recovery.
5. SO_2 byproduct is captured for in situ H_2SO_4 regeneration, supporting sustainable hydrometallurgical operations in remote areas.

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1. Introduction

Reactive magnesia, or caustic-calcined magnesia (CCM), is produced at temperatures below 900 °C and is distinguished by its high surface area and chemical reactivity, setting it apart from refractory-grade MgO. These features render it especially useful in environmental cleanup, cement systems, and waste treatment processes (NA et al., 2021; CAVANI; TRIFIRÒ; VACCARI, 1991).

Although crucial for industry, there is limited research on the direct synthesis of reactive MgO from hydrated magnesium sulfate ($MgSO_4 \cdot H_2O$). Typically, conventional techniques rely on mineral carbonates like magnesite and dolomite or on brine-derived materials (SOUZA; KUMAR; GUPTA, 2020; PEREIRA; FONSECA, 2025). However, $MgSO_4 \cdot H_2O$—often a by-product of acid-neutralization—is a sustainable, plentiful, and under-utilized resource for producing reactive magnesium oxide.

Using $MgSO_4 \cdot H_2O$ as a precursor aligns with green chemistry and circular hydrometallurgy principles by promoting sustainability.

- Preventing gypsum sludge formation and promoting the recovery and reuse of $MgSO_4$.,
- Enabling SO_2 capture during carbothermic reduction for on-site sulfuric acid regeneration.,
- Supporting decentralized hydrometallurgical batch systems in remote areas to reduce logistical burdens and waste streams.

Early studies by Frederick and Ramachandran (1987) and Riley (1986) examined the decomposition and precipitation of magnesium salts, providing valuable thermochemical data, although they did not specifically investigate hydrated $MgSO_4$. Later research (EVANS et al., 1998; SOUZA; KUMAR; GUPTA, 2020) concentrated on the synthesis and reactivity of magnesium compounds, while Steiger et al. (2011) and Zhong et al. (2025) described the decomposition processes and phase equilibrium within the $MgSO_4$–H_2O system. Additionally, Coray and Jovanovic (2019) outlined the

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primary reaction pathways in the carbothermic reduction of MgO under low-pressure conditions, including relevant kinetic comparisons.

Using $MgSO_4 \cdot H_2O$ as a feedstock provides a novel and sustainable approach to producing reactive MgO by integrating efficient carbothermic reduction with in situ SO_2 utilization. This technique aligns with the global shift toward low-emission and resource-efficient material processing.

The present study introduces a carbothermic method for synthesizing reactive MgO from $MgSO_4 \cdot H_2O$ with the following objectives:

1. To determine optimal process parameters (temperature, carbon source, and residence time)
2. To evaluate MgO yield, purity, and microstructure.
3. To assess chemical reactivity through acid-neutralization tests
4. To demonstrate compliance with circular chemistry and environmental sustainability principles.

2. Materials and methods

2.1. Reducing Agents and Precursor Preparation

Three carbon-based reducing agents—charcoal, petroleum coke, and bituminous coal—were ground to a particle size of less than 150 µm using a planetary mill to ensure uniform mixing and reaction kinetics (CORAY; JOVANOVIC, 2019).

The analytical-grade magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$) was slowly dehydrated in a ventilated oven at temperatures up to 250 °C, ensuring all crystalline water was removed. Careful control of the dehydration process is essential to avoid partial hydrolysis or the formation of basic sulfate, as noted by Steiger et al. (2011) and Zhong et al. (2025).

2.2. Calcination Procedure

Homogeneous mixtures of $MgSO_4 \cdot H_2O$ and the selected reducing agent were calcined in a muffle furnace at 850 °C for 120 minutes under a continuous nitrogen flow, creating an inert atmosphere to prevent secondary oxidation. The chosen temperature and duration were based on prior research showing that $MgSO_4$ decomposes and MgO crystallizes optimally at 800-900 °C (PEREIRA; FONSECA,

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2025). After calcination, the samples were cooled in desiccators to avoid moisture absorption and carbonation.

2.3. Post-Calcination Characterization

Scanning electron microscopy with back-scattered-electron imaging (SEM-BSE) was used to analyze the calcined powders, focusing on their morphology and porosity—parameters that are directly linked to the reactivity of MgO (LIESKE; FARRELL; DEGANELLO 2004).

Ash content was determined by gravimetric analysis after high-temperature ashing, in accordance with established magnesia quality control procedures (NA et al., 2021).

2.4. MgO Reactivity Test

The acid-neutralization reactivity of the produced MgO was assessed using a standardized titration method adapted from Frederick and Ramachandran (1987).

1. Weigh 5 g (< 63 µm) of MgO powder.
2. Disperse in 600 mL of distilled water with 10 mL of phenolphthalein solution and stir magnetically for 1 minute.
3. Add 100 mL of 1 N acetic acid quickly and begin timing.
4. Measure the time until the solution turns pink, signaling full neutralization.

Samples with neutralization times of less than 2 minutes were classified as highly reactive.

This reactivity test offers a quick and consistent way to assess the suitability of MgO for acid-neutralization and hydrometallurgical uses, where rapid dissolution and reaction rates are essential (CAVANI; TRIFIRÒ; VACCARI, 1991; SOUZA; KUMAR; GUPTA, 2020).

3. Results

3.1. Influence of temperature, carbon source, and carbon excess on MgO yield

Table 1 summarizes the results from the muffle furnace experiments, highlighting how temperature, the reducing agent, and carbon excess influence the carbothermic conversion of hydrated magnesium sulfate ($MgSO_4 \cdot H_2O$) into MgO.

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Table 1: Process Conditions and MgO Yield from Muffle Furnace Tests

Temperature (°C)	Reducing Agent	Carbon Excess (%)	Residence Time (min)	MgO Yield (by Carbon)	MgO Yield (excluding ash and C)
700	Charcoal	1.38	120	71.20 %	75.60 %
900	Charcoal	1.38	120	92.10 %	93.00 %
700	Charcoal	4.55	120	45.20 %	59.90 %
900	Charcoal	4.55	120	62.40 %	77.30 %
750	Charcoal	0.59	120	89.80 %	90.40 %
750	Charcoal	2.17	120	88.60 %	90.10 %
850	Charcoal	0.59	120	93.80 %	94.40 %
850	Charcoal	2.17	120	93.10 %	94.20 %
700	Petroleum Coke	2.03	120	8.00 %	9.30 %
900	Petroleum Coke	2.03	120	55.60 %	66.00 %
700	Petroleum Coke	6.08	120	20.40 %	30.70 %
900	Petroleum Coke	6.08	120	41.60 %	64.90 %
750	Petroleum Coke	1.02	120	26.90 %	29.10 %
750	Petroleum Coke	3.05	120	25.10 %	30.80 %
850	Petroleum Coke	1.02	120	88.50 %	92.40 %
850	Petroleum Coke	3.05	120	69.90 %	83.90 %
750	Bituminous Coal	–0.21	120	59.30 %	66.90 %
750	Bituminous Coal	0.58	120	65.40 %	86.10 %
850	Bituminous Coal	–0.21	120	76.60 %	88.20 %
850	Bituminous Coal	0.58	120	71.10 %	93.40 %

Across all tests, charcoal consistently demonstrated the highest reactivity and MgO yield, particularly at 850 °C with 0.59–2.17% carbon excess, achieving up to 94.4% MgO on an ash- and carbon-free basis. This outstanding performance is attributed to its high porosity, elevated fixed-carbon content, and minimal ash impurities, all of which enhance carbon–oxygen contact and improve reaction kinetics (CORAY; JOVANOVIC, 2019; PEREIRA; FONSECA, 2025).

Petroleum coke, despite its higher carbon purity, produced lower yields at lower temperatures or with greater carbon excess. However, at 850 °C with 1.02% excess, it reached 92.4% MgO yield, suggesting that reaction inhibition at higher carbon ratios is probably due to diffusion restrictions and localized CO_2 accumulation (SOUZA; KUMAR; GUPTA, 2020).

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Bituminous coal exhibited intermediate behavior, with conversion rates ranging from 66% to 93% under different process conditions. Its lower yield under sub-stoichiometric conditions (–0.21% excess) likely results from incomplete reduction of intermediate sulfates ($MgSO_4 \rightarrow MgO + SO_2 + ½\ O_2$). The highest efficiency of 93.4% was achieved at 850 °C with 0.58% excess carbon, emphasizing the importance of precise stoichiometric control (STEIGER et al., 2011; ZHONG et al., 2025).

Overall, the findings suggest that both the choice of reducing agent and the carbon ratio play critical roles in optimizing MgO production. The best conditions—using charcoal at 850 °C with a 0.6–2.2% excess—achieved nearly complete sulfate conversion, consistent with thermodynamic expectations for carbothermic $MgSO_4$ reduction in an inert atmosphere (RILEY, 1986; CORAY; JOVANOVIC, 2019).

3.2. Reaction considerations

The findings confirm earlier thermogravimetric and kinetic analyses, which identified two Main reduction stages.

(i) dehydration and sulfate decomposition ($MgSO_4 \cdot H_2O \rightarrow MgO + SO_2 + ½\ O_2$), and

(ii) Carbothermic reduction of residual sulfates and oxides using solid carbon and CO gas (CORAY; JOVANOVIC, 2019; STEIGER et al., 2011).

Ellingham-type thermodynamic models indicate that the Gibbs free energy ($\Delta G°$) for the reaction $MgSO_4 \rightarrow MgO + SO_2 + ½\ O_2$ turns negative above 700 °C. The addition of carbon further shifts the equilibrium, favoring MgO production at lower temperatures. This accounts for the high-yield production threshold observed at 750–850 °C, which aligns with the decomposition range identified by ZHONG et al. (2025).

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3.3. Morphological and reactivity analysis - charcoal

The SEM-BSE image (Figure 1) of the MgO product produced with charcoal as the reducing agent reveals distinct morphological and textural traits typical of highly reactive magnesia. The particles showcase an irregular, macroporous surface, rough in texture, which reflects the escape of gaseous species (primarily CO_2 and SO_2) through interconnected pores during the carbothermic decomposition of $MgSO_4$ (CORAY; JOVANOVIC, 2019; ZHONG et al., 2025). This porosity, created by gas evolution, results in a loosely packed assembly of crystallites smaller than 40 µm, offering a high specific surface area and enabling quick dissolution in acidic solutions (SOUZA; KUMAR; GUPTA, 2020).

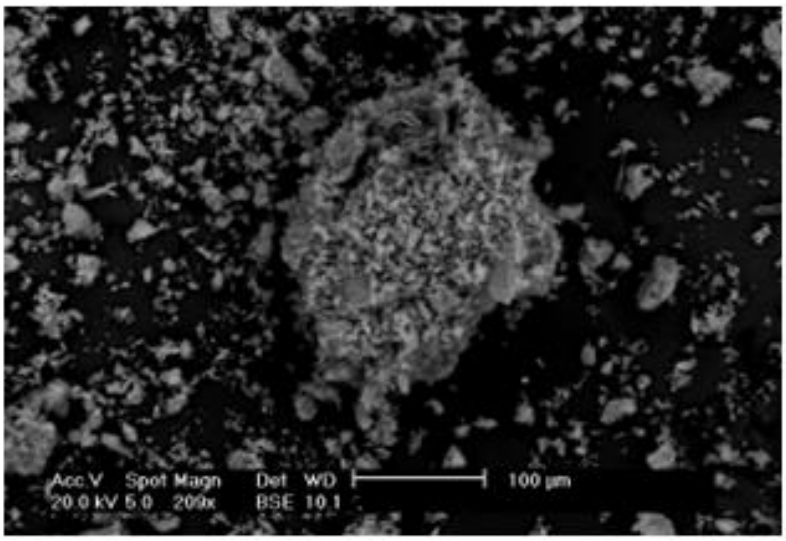

Figure 1: SEM-BSE Micrograph of MgO Produced with Charcoal Reduction

The bright, high-contrast spots observed under BSE detection indicate a predominantly crystalline MgO phase with little to no carbon residues. The absence of dark, amorphous areas suggests the product is mainly free of unreacted carbon or slag inclusions, aligning with the gravimetrically measured ash content of ≤ 1.9%.

This porous, finely dispersed microstructure provides numerous active sites for proton attack, thereby improving the rate of acid neutralization. The samples with this morphology reached neutralization times of about 90 seconds, placing them in the high-reactivity class from Section 2.4. The strong link between surface openness and kinetic response shows that pore connectivity and surface roughness are key factors

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in enhancing MgO performance for hydrometallurgical neutralization processes (CAVANI; TRIFIRÒ; VACCARI, 1991; PEREIRA; FONSECA, 2025).

3.4. Microstructural effects of petroleum-coke reduction

The SEM-BSE micrograph in Figure 2 displays the morphology of reactive MgO produced by carbothermic reduction using petroleum coke as the reducing agent. The powder mainly consists of porous MgO particles smaller than 40 μm, forming loosely packed clusters connected by fragile neck structures.

Numerous bright inclusions within the MgO matrix are observed, representing ash residues from aluminosilicate minerals and barite ($BaSO_4$), as confirmed by post-ashing analysis. These mineral impurities are typical of high-ash carbonaceous reductants and are known to serve as nucleation barriers during oxide crystallization (SOUZA; KUMAR; GUPTA, 2020; NA et al., 2021). Moreover, dark regions (~50 μm) scattered throughout suggest the presence of unreacted or partially gasified carbon fragments, which can locally restrict oxygen diffusion and potentially impede complete sulfate reduction (CORAY; JOVANOVIC, 2019; STEIGER et al., 2011).

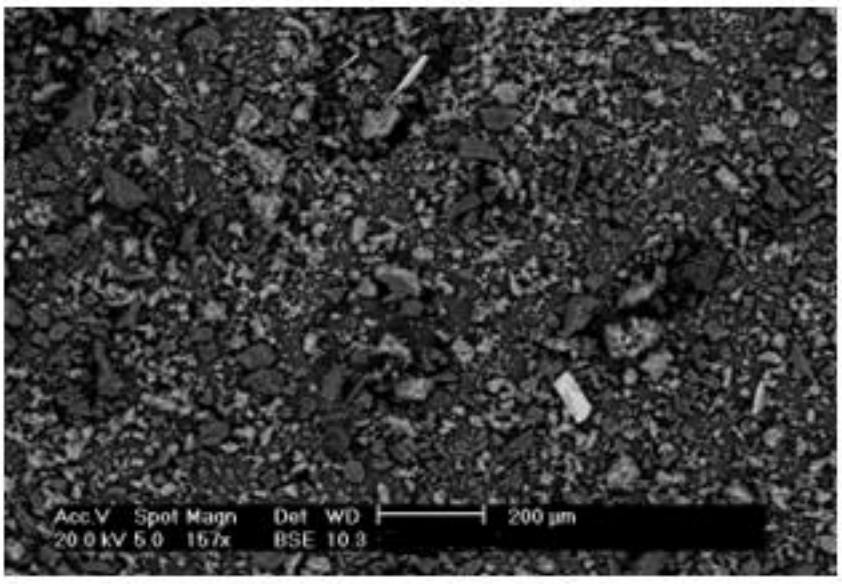

Figure 2: SEM-BSE Micrograph of MgO Produced Using Petroleum Coke

This microstructure displays more mineral inclusions and residual carbon than the charcoal-derived MgO (Figure 1), resulting in lower purity and a smaller reactive

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surface area. These textural differences correspond with the slightly reduced acid-neutralization rate seen in the petroleum-coke product (Section 2.4), demonstrating that both ash content and carbon quality significantly influence MgO reactivity.

In summary, reducing petroleum coke use yields a partially sintered MgO microstructure rich in impurities. This underscores the importance of selecting low-ash, high-porosity carbon sources—such as charcoal—to enhance MgO purity and improve acid-neutralization effectiveness in hydrometallurgical processes.

3.5. Morphological evaluation of MgO produced with bituminous coal

The SEM-BSE micrograph in Figure 3 illustrates the shape of MgO produced via carbothermic reduction with bituminous coal as the carbon source. This product appears as a porous, sponge-like structure, with most particles being smaller than 40 µm, akin to those from charcoal and petroleum-coke reductions (Figures 1–2). The image also reveals brighter, angular inclusions dispersed throughout the MgO matrix—these are caused by ash residues primarily composed of aluminosilicate phases such as chlorite, muscovite, and feldspathic components, along with small quantities of iron oxides, barite, dolomite, and anhydrite identified through ash analysis.

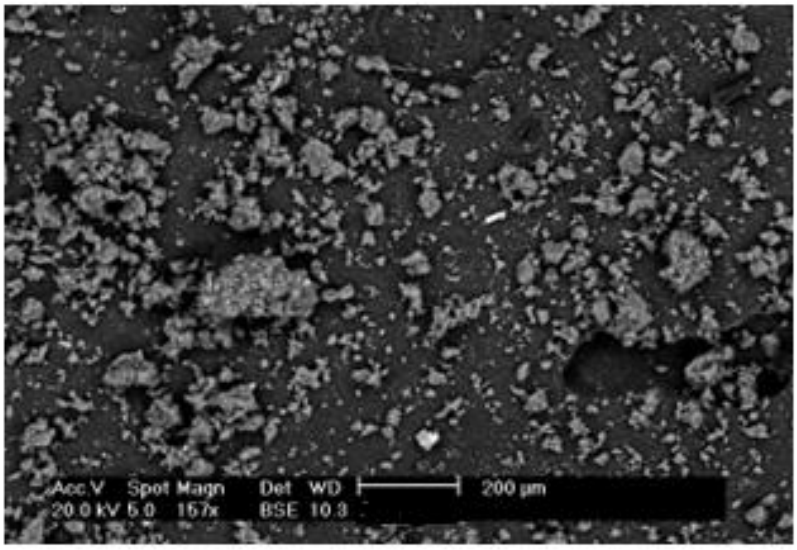

Figure 3: SEM-BSE Micrograph of MgO Produced Using Bituminous Coal

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These mineral inclusions act as inert barriers within the MgO matrix, reducing the reactive surface area available and locally hindering acid–solid interactions during neutralization (SOUZA; KUMAR; GUPTA, 2020; NA et al., 2021). Furthermore, the dark regions (~50 μm) correspond to unreacted coal fragments embedded in the porous structure, suggesting partial reduction. This likely results from limited gas diffusion and incomplete decomposition of the $MgSO_4$ intermediate at the particle–carbon interface (CORAY; JOVANOVIC, 2019; STEIGER et al., 2011).

The bituminous-coal-derived MgO exhibits moderate conversion efficiency and lower purity compared to charcoal-derived MgO, due to its higher mineral content. These results highlight the need to control ash content, optimize particle size, and allocate sufficient residence time during thermal processing to enhance MgO quality and reactivity (PEREIRA; FONSECA, 2025).

3.6. Statistical analysis of process parameters

A multiple linear regression model was created to assess the combined effect of temperature (X_1), reducing-agent type (X_2), and carbon excess (X_3) on the MgO yield from the carbothermic reduction of $MgSO_4 \cdot H_2O$. The analysis used 20 experimental observations, including all three carbonaceous reductants (charcoal, petroleum coke, and bituminous coal).

The regression model showed a strong overall fit, with R = 0.804, R^2 = 0.646, and adjusted R^2 = 0.580, indicating that approximately 65% of the variability in MgO yield can be explained by these three predictors. The ANOVA test confirmed the model's statistical significance, with F(3,16) = 9.73; p = 0.00068, validating its adequacy for predictive interpretation.

Table 2 presents the estimated coefficients from a multiple regression model predicting MgO yield based on the variables: temperature, reducing agent, and carbon excess.

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Table 2: Regression coefficients

Variable	Coef	Std. Error	t	p-value	95% CI
Intercept	–0.340	0.425	–0.799	0.436	–1.240 to 0.561
Temperature (°C)	+0.00160	0.00052	+3.067	0.0074	0.00049–0.00270
Reducing Agent	–0.166	0.054	–3.067	0.0074	–0.280 to –0.051
Carbon Excess (%)	–0.08684	0.0218	–3.981	0.0011	–0.133 to –0.0406

Interpretation of regression parameters

- Intercept (–0.340; p = 0.436): Not statistically significant, serving only as the baseline estimate for the model.
- Temperature (+0.00160 per °C; p = 0.0074; 95% CI: 0.00049–0.00270): Statistically significant and positive. Each 1 °C increase results in approximately 0.16% higher MgO yield, confirming the endothermic and temperature-dependent nature of the carbothermic reaction (STEIGER et al., 2011; ZHONG et al., 2025).
- Reducing Agent (–0.166; p = 0.0074; 95% CI: –0.280 to –0.051): Shows a significant and negative effect, meaning petroleum coke and bituminous coal result in roughly 16.6% lower conversion compared to charcoal, due to higher ash content and reduced reactivity (SOUZA; KUMAR; GUPTA, 2020; PEREIRA; FONSECA, 2025).
- Carbon Excess (–0.0868 per %; p = 0.0011; 95% CI: –0.133 to –0.0406): Strongly significant and negative. Each additional percent of carbon beyond the stoichiometric ratio decreases MgO yield by approximately 0.087%, indicating diffusion inhibition and possible CO_2 buildup that limits SO_4^{2-} reduction (CORAY; JOVANOVIC, 2019).

The regression results confirm the thermal and compositional sensitivity of the $MgSO_4 \rightarrow MgO$ transformation. Among the variables, temperature has the most significant positive effect, while excess carbon and the choice of reducing agent both produce inhibitory effects when not carefully controlled.

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These findings are consistent with thermodynamic predictions (see Section 3.8), which indicate that optimal $MgSO_4$ reduction occurs near 850 °C under inert or CO-rich atmospheres. They also support the idea that low-ash, high-reactivity carbon sources (such as charcoal) improve MgO formation efficiency. The model therefore provides quantitative validation of the experimentally determined process parameters and predictive capabilities for scaling or optimization efforts.

4. Discussion

4.1. Microstructural correlation with reducing agents

The SEM-BSE micrographs (Figures 1–3) clearly show morphological differences among MgO products derived from various carbonaceous reductants, which directly account for the observed differences in reactivity and yield.

Charcoal-derived MgO (Figure 1):

The material features highly porous, fine particles (< 40 µm) with minimal ash and carbon residues, resulting in a clean, crystalline MgO matrix. This sponge-like structure promotes a large surface area and effective acid–solid contact, which explains its quick neutralization time (< 2 min) and high yield (about 94%). The microstructure aligns with the positive temperature coefficient and the superior performance predicted by the regression model.

Petroleum coke-derived MgO (Figure 2):

The sample exhibits comparable particle sizes but contains bright silicate and barite inclusions, as well as dark zones of unreacted carbon. These impurities decrease the reactive surface area and break the continuity of MgO crystals. This is evidenced by the significant negative coefficient for “Reducing Agent” (–0.166; p = 0.007), indicating a clear relationship between ash content and lower yield.

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Bituminous coal-derived MgO (Figure 3):

The particles stay porous but are significantly contaminated with ash (silicates, iron oxides, dolomite) and unreacted carbon fragments. These inclusions impede gas diffusion and reduce access to active sites, which explains their moderate conversion rate and the negative carbon-excess effect seen in the regression model. Overall, the data show that coal and coke, although thermally stable reductants, bring mineral impurities that lower MgO purity and reactivity.

4.2. Statistical regression and process optimization

The multiple linear regression model (Table 2) quantitatively describes the relationships among temperature, reducing agent, and carbon excess.

Temperature (+0.00160 per °C, p = 0.007):

Each extra degree Celsius raises MgO yield by about 0.16%, confirming the strong thermal dependence of sulfate decomposition and supporting 850 °C as the optimal operating temperature.

Reducing agent penalty (–0.166, p = 0.007):

Petroleum coke and bituminous coal show an average yield decrease of approximately 16.6% compared to charcoal. This reduction is directly linked to their higher ash content, as verified by microstructural analysis and ash chemistry.

Carbon excess effect (–0.0868 per %, p = 0.001):

Each extra percent of carbon above stoichiometric requirements reduces yield by about 0.087%, showing that excess reductant can hinder sulfate conversion by increasing diffusion resistance and CO_2 retention in the solid matrix.

Together, the regression confirms that temperature optimization, choosing a low-ash reducing agent, and strict carbon control are essential for maximizing MgO yield and purity.

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4.3. Integration of microstructure with quantitative outcomes

The agreement between qualitative microstructural evidence and quantitative statistical trends strengthens the mechanistic understanding of MgO formation.:

1. Charcoal-derived MgO features low impurity levels, fine particle size, and high porosity, which directly lead to better yield and reactivity—as predicted by the regression model.
2. Petroleum coke and bituminous coal products exhibit structural contamination and a decreased effective surface area, consistent with their negative regression coefficients and extended neutralization times.

This blend of microscopic and statistical analyses affirms the reliability of the experimental results and highlights the significance of integrating materials and process insights in reactive oxide synthesis.

4.4. Environmental and industrial implications

While not the primary focus of this study, the process developed provides significant environmental and operational advantages. The carbothermic method generates highly reactive MgO ideal for acid neutralization, wastewater treatment, and hydrometallurgical purification. Additionally, it enables in situ regeneration of SO_2/SO_3, which can be recycled into H_2SO_4 through an integrated sulfuric acid recovery system.

Thus, the process provides a circular chemical pathway that reduces waste while promoting environmentally sustainable industrial operations.

4.5. Integrated process and circular chemical pathway

The process flow shown in Figure 4 combines the production of reactive magnesium oxide (MgO) with the recovery and reuse of sulfur species, creating a closed-loop, gypsum-free pathway for hydrometallurgical systems.

Initially, hydrated magnesium sulfate ($MgSO_4 \cdot 7H_2O$)—typically generated as a by-product of acid-neutralization—undergoes dehydration at 250 °C to produce $MgSO_4 \cdot H_2O$.

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The partially dehydrated precursor is then subjected to carbothermic reduction at 850 °C under an inert N_2 atmosphere with charcoal, producing reactive MgO and a gas mixture (CO_2 + SO_2).

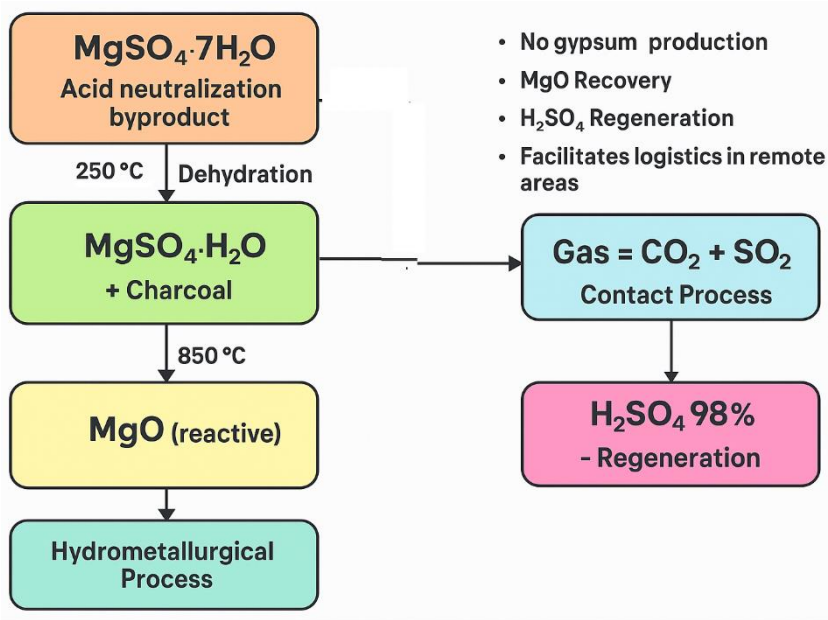

Figure 4. Circular carbothermic route for $MgSO_4 \cdot 7H_2O$ valorization

The MgO produced has a porous, high-surface-area structure, making it ideal for quick neutralization or purification steps in later hydrometallurgical processes. At the same time, the released SO_2 is captured and converted back into concentrated sulfuric acid (H_2SO_4 ≈ 98%) through the contact process, effectively closing the sulfur cycle. This thorough approach ensures:

a. Eliminating gypsum formation reduces solid waste and disposal costs.
b. Achieve complete recovery and recycling of $MgSO_4$ while maintaining mass balance within the system.
c. On-site H_2SO_4 regeneration reduces reliance on external supply chains.
d. Enhanced logistics and sustainability, especially beneficial for remote or off-grid metallurgical locations.
e. Lowered CO_2 and sulfate emissions, supporting carbon-neutral and resource-efficient operations.

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The process converts acid-neutralization by-products into reactive MgO and recovers H_2SO_4 via SO_2 oxidation and absorption, establishing a closed, environmentally sustainable cycle that does not generate gypsum.

4.6. Thermodynamic Discussion

The carbothermic reduction of magnesium sulfate involves a series of gas–solid reactions that depend heavily on temperature and are controlled by oxygen and sulfur fugacities.

A thorough thermodynamic analysis helps clarify the observed optimal temperature (≈ 850 °C) and the effect of excess carbon on MgO yield. The main reaction pathway can be described as follows:

$$MgSO_4\ (s) + 2\ C\ (s) \rightarrow MgO\ (s) + 2\ CO\ (g) + SO_2\ (g)$$

This global reaction involves several intermediate steps, including the decomposition of $MgSO_4$ into MgO + SO_3, followed by the reduction of SO_3 and SO_2 through the CO/CO_2 gas equilibrium. The standard Gibbs free energy (ΔG°) for $MgSO_4$ decomposition becomes negative near 750–800 °C, indicating that thermal dissociation is thermodynamically feasible within the experimental temperature range. Ellingham diagram analysis confirms that carbon is a sufficiently strong reductant for both SO_3 and SO_2 under these conditions.

The redox pair C/CO and CO/CO_2 determines the oxygen potential in the system. At 850 °C, the equilibrium ratio pCO/pCO_2 ≈ 1.9 corresponds to a log pO_2 ≈ –15, which stabilizes MgO but prevents over-reduction to MgS. At lower temperatures (≤ 700 °C), the ΔG° for forming MgS from $MgSO_4$ + 4 C remains slightly negative, indicating sulfur fixation can occur, which explains the lower MgO yields in that range. As the temperature rises above 850 °C, MgS becomes unstable and decomposes into MgO and SO_2, which aligns with the increased conversion efficiency.

The SO_2 generated at the same time reacts with CO following the endothermic equilibrium:

$$SO_2 + CO \rightleftharpoons SO + CO_2$$

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The system favors SO formation at higher temperatures and low oxygen fugacity. However, in the inert nitrogen atmosphere used, SO_2 and CO_2 dominate, both of which can be recovered for sulfuric acid regeneration. Consequently, the overall reaction remains thermodynamically favorable, with $\Delta G°$ approximately –150 kJ mol^{-1} at 850 °C, ensuring spontaneous conversion while preserving MgO's phase stability.

The Ellingham relationships thus provide a quantitative basis for the observed experimental optimization.

a. An increase in temperature promotes $MgSO_4$ dissociation and CO-driven reduction.
b. Moderate excess of carbon maintains the proper pCO/pCO_2 ratio for MgO stability.
c. Excessive carbon significantly reduces oxygen partial pressure, leading to partial sulfidation and lower yield—precisely as shown by the negative coefficient for “carbon excess” in the regression model.

In summary, thermodynamic modeling confirms that operating at 850 °C with about 1% carbon excess provides the best compromise among decomposition kinetics, redox potential, and MgO stability. These conditions maintain MgO as the main solid phase while enabling gaseous SO_2 to be effectively captured and converted to H_2SO_4 within a closed, sustainable system.

4.7. Process integration

The overall process integrates the synthesis of reactive MgO with sulfur recovery and acid regeneration, forming a self-sustaining chemical loop that eliminates waste and minimizes reagent consumption.

Closed-loop magnesium cycle:

Hydrated magnesium sulfate ($MgSO_4 \cdot 7H_2O$), often produced as a by-product during acid neutralization, is first dehydrated at 250 °C to form $MgSO_4 \cdot H_2O$. This intermediate is then carbothermally reduced at about 850 °C in the presence of charcoal under an inert nitrogen atmosphere. The process produces porous, highly reactive MgO and a gas stream mainly consisting of CO_2 and SO_2.

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This route effectively prevents gypsum formation and offers a clean alternative to conventional waste management methods based on neutralization (CAVANI; TRIFIRÒ; VACCARI, 1991; STEIGER et al., 2011).

Immediate utilization of reactive MgO:

The freshly formed MgO is directly reused in subsequent neutralization or purification steps within hydrometallurgical circuits, thereby closing the magnesium mass balance and avoiding the need for external Mg sources. Its high surface area and low impurity content improve neutralization efficiency and acid-base buffering kinetics (SOUZA; KUMAR; GUPTA, 2020; PEREIRA; FONSECA, 2025).

Sulfur dioxide valorization and acid regeneration:

The SO_2-rich exhaust gas, essential for sulfuric acid production, is captured and converted to SO_3 via thermal oxidation or catalytic processes. The resulting SO_3 is absorbed into water or oleum to regenerate concentrated H_2SO_4, with a conversion efficiency of 93% or higher.

This method uses traditional contact-process techniques, enabling on-site acid recovery and reducing the need for chemical transport—especially beneficial for remote hydrometallurgical facilities (CORAY; JOVANOVIC, 2019; ZHONG et al., 2025).

Together, these steps form an integrated, circular process that recycles both magnesium and sulfur species, prevents the formation of solid waste, and fosters sustainable resource efficiency. The synergy between MgO synthesis, waste reduction, and acid regeneration aligns well with green process engineering principles and industrial decarbonization goals.

4.8. Environmental and Operational Advantages

The proposed process provides multiple environmental, logistical, and operational advantages, creating a sustainable closed-loop system that combines reactive MgO synthesis with acid regeneration and resource efficiency.

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The carbothermic process avoids the formation of calcium sulfate (gypsum), a common by-product of traditional neutralization methods. This dramatically reduces solid waste production, landfill use, and secondary pollution associated with industrial effluent treatment (FARJANA et al., 2019).

Recycling of $MgSO_4$ within a circular framework:

By reusing magnesium sulfate derived from neutralization residues, the process reinforces the principles of circular resource utilization, enabling continuous recovery of magnesium species and reducing the need for raw materials. This approach promotes resource efficiency and low-carbon process engineering (CAVANI; TRIFIRÒ; VACCARI, 1991).

On-site H_2SO_4 regeneration:

The SO_2-rich exhaust gases are captured and oxidized through the contact process to produce sulfur trioxide (SO_3), which is then absorbed to regenerate 98% sulfuric acid. This process uses well-established industrial practices standard in refineries, metallurgical plants, and chemical factories, thereby decreasing external acid supply and logistics costs (CORAY; JOVANOVIC, 2019).

Suitability for decentralized hydrometallurgical operations:

Because of its modular and thermally compact design, the process can be implemented in remote or standalone metallurgical units. It enables on-site acid recycling, reduces reagent transport, and improves operational self-sufficiency, making it especially useful for off-grid or geographically isolated sites (VILLA GÓMEZ et al., 2024).

In summary, the system combines waste reduction, chemical reuse, and local process independence, demonstrating a technically feasible and environmentally sustainable path for next-generation hydrometallurgical operations.

5. Conclusion

This study demonstrates a new carbothermic method for producing highly reactive magnesium oxide (MgO) from hydrated magnesium sulfate ($MgSO_4 \cdot 7H_2O$).

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The results confirm the viability and industrial importance of this circular, waste-reducing process.

1. Charcoal emerged as the most efficient reducing agent, generating MgO with a porous, carbon-free microstructure and reaching the highest yields (up to
2. 94%, excluding ash). The MgO produced exhibited quick acid-neutralization ability (< 2 minutes), confirming its high reactivity.
3. Optimal process parameters were set at 850 °C with approximately 1% carbon excess, balancing conversion efficiency, purity, and reactivity.
4. Multiple linear regression analysis confirmed that higher temperatures increase MgO yield, while weaker reducing agents and excessive carbon decrease it. This quantitative evidence supports the experimental observations and provides a basis for optimizing the process.
5. Integrated process modeling revealed a synergistic link between MgO synthesis and sulfuric acid regeneration: the SO_2 by-product can be oxidized and absorbed to regenerate H_2SO_4, enabling gypsum-free operation, $MgSO_4$ recycling, and improved resource circularity.
6. The integrated chemical and operational design guarantees economic viability, a low environmental impact, and flexibility for remote or decentralized hydrometallurgical operations, where reagent transport and waste management present significant challenges.

In conclusion, the proposed pathway delivers high-performance, eco-friendly MgO, adheres to circular economy principles, and offers a scalable, sustainable alternative to conventional lime-based neutralization and MgO manufacturing systems — with the potential to advance green hydrometallurgy and on-site acid recovery.

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