Article

Solar Metallurgy for Sustainable Zn and Mg Production in a Vacuum Reactor Using Concentrated Sunlight

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Abstract: Solar carbothermal reduction of volatile metal oxides represents a promising pyro-metallurgical pathway for the sustainable conversion of both metal oxides and sunlight into metal commodities and fuels in a single process. Nevertheless, there are several scientific challenges in discovering suitable metal oxides candidates for the ease of oxygen extraction from metal oxides to enhance the reaction extent and in designing reactors for the efficient absorption of incident solar radiation to minimize losses. In this study, ZnO and MgO were considered as volatile metal oxides candidates, and their reaction behaviors were studied and compared through gas species production rate, metal oxides conversion, and yield. A solar reactor prototype was developed to facilitate solar carbothermal reduction of ZnO and MgO with different reducing agents comprising activated charcoal and carbon black. The process was operated in a batch operation mode under vacuum and atmospheric pressures to demonstrate the flexibility and reliability of this system for co-production of metals (Zn/Mg) and CO. As a result, decreasing total pressure enhanced conversion of ZnO and MgO, leading to increased Zn and Mg. However, in the case of ZnO, CO yield decreased with decreasing total pressure at the expense of favored CO₂ as a result of the decrease of residence time. In contrast, CO₂ formation was negligible in the case of MgO, and CO yield thus increased with decreasing pressure. Using activated charcoal as the reducing agent exhibited better conversion of both ZnO and MgO than carbon black thanks to the higher available specific surface area for chemical reactions. MgO and ZnO conversion above 97% and 78%, respectively, and high-purity Mg and Zn content were accomplished, as evidenced by the recovered products at the reactor outlet and filter containing pure metal. In addition, Mg product exhibited strong oxidation reactivity with air, thus requiring inert atmosphere for the handling of Mg-rich powders to avoid direct exposure to air.

Keywords: solar thermochemical; concentrated sunlight; solar reactor; carbothermal reduction; zinc; magnesium; extractive metallurgy

1. Introduction

Harnessing the plentiful, clean, and renewable solar energy resource via solar thermochemical conversion processes is a promising avenue to convert intermittent solar radiation into chemical fuels and commodities [1]. In particular, solar carbothermal reduction (CTR) routes for extracting oxygen from volatile metal oxides using solid carbon as a reducing agent in order to produce metals and CO have attracted attention [2]. These processes have the potential to both lower the thermodynamic barrier via utilization of solid carbon reductants and produce metals and CO in a single reaction while

storing solar energy into chemicals, thereby providing an attractive pathway towards sustainable fuel production. Various metal oxide redox pairs have been discovered for solar-driven thermochemical processes involving chemical looping methane reforming [3], chemical looping gasification [4], two-step thermochemical $\text{H}_2\text{O}/\text{CO}_2$ splitting cycles [5,6], and carbothermal reduction [7]. In general, they can be categorized into two groups according to their phase change.

On the one hand, non-volatile oxides such as ceria ($\text{CeO}_2/\text{Ce}_2\text{O}_3$) [8], iron oxides ($\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$, ferrites [9]), and perovskites (e.g., $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$) [10] exhibit solid state reactions throughout the entire process. Hence, only oxygen is discharged from their metal oxide structure, circumventing the recombination issue. For these reasons, non-volatile oxides are suitable to be used as oxygen carriers, e.g., for chemical looping reforming [11] and chemical looping gasification [12]. Nevertheless, their disadvantages are related to the issues of non-stoichiometric reactions such as ceria or perovskites [13], and sintering such as iron oxides [14]. On the other hand, volatile metal oxides such as ZnO/Zn [15], SnO_2/SnO [16,17], and MgO/Mg [18] usually offer high oxygen exchange capacity and high entropy variation, as they can be completely reduced to their metallic elements (Zn and Mg), thus enhancing fuel production capacity. However, they come at the expense of an issue of recombination with oxygen (O_2) during thermal reduction, since both products (metal and O_2) are simultaneously released in the gaseous phase. In this study, ZnO and MgO have been considered as attractive volatile metal oxide candidates for solar carbothermal metallurgical processes towards Zn and Mg commodities production. The overall carbothermal reduction reactions of ZnO and MgO are represented in Equations (1) and (2), respectively.

The possible solid–gas side reactions taking place during ZnO reduction with solid carbonaceous feedstock are related to Equations (3) and (4). In addition, during MgO reduction, reaction 4 is also possible but not reaction 3 (reaction of MgO with CO) according to thermodynamics.

The ZnO or MgO conversion (X_{ZnO} or X_{MgO}) represents the net fraction of ZnO or MgO converted to Zn or Mg (also corresponding to Zn or Mg yield). It can be calculated based on outlet gas analysis using an oxygen mass balance, according to Equation (5).

$$X_{\text{ZnO}}(X_{\text{MgO}}) = \frac{n_{\text{CO}} + 2n_{\text{CO}_2}}{n_{\text{ZnO}}(n_{\text{MgO}})} \quad (5)$$

where n_{CO} and n_{CO_2} indicate the mole amounts of produced CO and CO_2 obtained by time integration of their production rates over the reaction duration.

Conventionally, Zn is extracted from ores via smelting and refining processes [19], while Mg is produced by Pidgeon, Magnetherm, and electrolytic methods [20]. Both Zn and Mg production processes discharge large amounts of greenhouse gases, particularly CO_2 , responsible for global warming, thereby contributing to climate changes [21]. Regarding Zn and Mg applications, Zn product can be used in various industrial sectors such as food, pharmaceutical, galvanizing, electrical batteries, and mechanical engineering [22], while Mg product can be used as a structural material involving magnesium-based alloys [23,24] and power generation in magnesium-based combustion engines. In addition, both Mg and Zn powders are highly reactive for oxidation with $\text{H}_2\text{O}/\text{CO}_2$ to generate high-purity H_2/CO [25]. In this case, the metal oxide (ZnO or MgO) is also produced, which can be recycled back to the solar carbothermal step, thus closing the cycle.

According to Equations (1) and (2), the enthalpy change of Zn formation is moderate, implying low operating temperature requirement, easy for scaled-up reactor operation, while that of Mg is quite high, indicating high potential for the storage of solar energy at the expense of higher operating temperature requirement. Therefore, different advantages arise between CTR of ZnO and MgO, which makes these systems attractive for further detailed investigation. Besides, to increase the reduction extent as well as decrease the reduction temperature, vacuum operation has been proposed [26–32], at the expense of pumping energy requirement. For example, Chubukov et al. [33] investigated CTR of MgO with carbon black in the pressure range 0.1–100 kPa and temperature range 1350–1650 °C using a graphite furnace and found that the MgO reduction rate increased with decreasing pressure. In addition, Brkic et al. [34] conducted CTR of ZnO under pressures of 1100 and 960 hPa in a drop tube reactor, and reported that Zn production was higher at 100 hPa compared to ambient pressure thanks to the reduced pressure. However, reaction at 1 hPa was inhibited due to insufficient particle residence time. Regarding the CTR of ZnO and MgO, most previous works were related to thermodynamics [18] and experimental studies [33,35] for each metal oxide, and a comparative study of CTR of MgO and ZnO on product yields in a solar reactor has not been done yet.

This paper addresses the solar thermochemical reduction of ZnO and MgO using carbon-based feedstocks in a directly-irradiated cavity-type solar reactor for the clean production of energy-intensive fuels and materials. Using solar energy for process heat in place of fossil fuels is a means to reduce the dependence of pyro-metallurgical processes on conventional energy resources and to avoid emissions of CO₂ and other pollutants, for the production of high-value chemical fuels and metals (both Zn/Mg and CO). The new solar process is thus a sustainable alternative option outperforming the conventional metallurgical processes currently used for Zn and Mg production. Therefore, the present work aims to further explore the on-sun experimental study and comparison of solar CTR of ZnO and MgO in a novel prototype solar reactor. The objective of this study was to demonstrate the feasibility of the Zn and Mg production process with high ZnO and MgO conversion in the new prototype solar reactor. Experiments were conducted with different reducing agents including activated charcoal (AC) and carbon black (CB) in a batch mode under vacuum and atmospheric pressures. The flexibility, reliability, and robustness of this scalable pyro-metallurgical process for solar Zn and Mg production with high yields were demonstrated. In addition, a comparative study of CTR of ZnO and MgO concerning the influence of pressure and solid carbon reductant on CO production rate, products yield (CO and Mg/Zn), and morphology was conducted. This study demonstrates the solar process performed in a high-temperature solar reactor under atmospheric or vacuum operation, and shows the feasibility of solar Zn and Mg production with high yields as a function of different operating temperatures, pressures, and carbon feedstocks.

2. Materials and Methods

A prototype solar vacuum reactor (1.5 kW_{th}) was designed and assembled, based on the concept of a directly-irradiated cavity-type solar reactor (Figure 1). It was operated using a vertical-axis solar furnace at PROMES-CNRS, Odeillo, France. A facedown parabolic dish (2 m diameter with a concentration ratio up to 10,551 suns) was employed to concentrate sunlight. This reactor was focused especially on the vacuum pressure operation at high reduction temperatures up to ~1650 °C (required for MgO). The reactor consists of the cylindrical cavity receiver (47 mm ID, 56 mm OD, and 70 mm height, 0.121 L volume), made of alumina surrounded by a layer of porous ceramic insulation, thereby enabling rapid solar heating to the desired temperature. Its bottom is closed with an alumina plate punctured at its center for allowing the injection of carrier nitrogen (0.2 NL/min) inside the cavity receiver. The insulated cavity is placed in a water-cooled cylindrical stainless-steel shell (170 mm OD, 150 mm ID, and 151 mm height, volume: 2.67 L). Inert alumina particles (2 mm diameter) with a ~10 mm bed thickness were positioned on a layer of alumina wool at the cavity bottom to support the solid reactants. The top of the cavity receiver is closed with an alumina cap with a 17 mm-diameter aperture to absorb concentrated solar radiation. Lastly, a hemispherical transparent glass window is

employed to cover the top of reactor and operate in a controlled atmosphere. The temperature within the cavity receiver (in the center of the packed bed) was measured with a type-B thermocouple (T_1) and compared to the uppermost sample surface temperature measured with a solar-blind optical pyrometer. The cavity pressure (P) was measured by a pressure transducer. N_2 flow rates were controlled with electronic mass flow controllers (Brooks, model SLA5850S, range 0–5 NL/min $\pm$ 0.2% full scale).

Figure 1. Schematic diagram of the 1.5 kW_{th} directly irradiated solar reactor and its external components. Source: author.

Regarding reacting materials, MgO (particle size: 1–2 μm , 99.8% chemical purity) and ZnO (particle size: 1–5 μm , 99.0% chemical purity) were purchased from PROLABO. Table 1 shows the physical properties of activated charcoal (AC) and carbon black (CB) used as the solid carbon reducers. They were provided from Sigma Aldrich and Asahi Carbon (Japan), respectively. Their specific surface area values, measured via N_2 adsorption method, were consistent with those obtained from the data sheet. Metal oxides powders (either MgO or ZnO) and solid carbon were mechanically mixed with a C/metal oxides molar ratio of 1.5, which represents 50% excess carbon, to favor CO production and complete conversion of MgO or ZnO.

Table 1. Physical properties of solid carbonaceous materials.

Material	Purity (%)	Average Particle Size (μm)	Specific Surface Area (m^2/g) (Data Sheet)	Specific Surface Area (m^2/g) (Measured)
Activated charcoal (AC) Darco®	99.9	<149	732	811
Carbon black (CB), SB905 powder	99.9	15.10^{-3}	210	181

The vacuum solar reactor was heated with highly concentrated sunlight, while the solar heat rate supply was manually regulated by the degree of shutter opening. Note that the shutter is positioned between the solar reactor and the sun tracking heliostat, thus enabling the control of the incoming solar intensity before its concentration. During heating, N₂ protective gas (2 NL/min) was introduced through two stainless-steel tubes (6 mm O.D. and 4 mm I.D.) towards the transparent window area. Subsequently, it flowed down through the aperture and then exited the reactor along with product gases, thus protecting the window from product deposition. Once the temperature reached ~650 °C for CTR of ZnO and ~900 °C for CTR of MgO, the reactor was sucked by using a rotary vane vacuum pump (Alcatel) to the targeted vacuum pressures in the range of 0.11–0.40 bar. Atmospheric pressure corresponds to ~0.90 bar at the experimental site elevation. The reduction reaction occurred from the temperatures of ~750 °C (for ZnO) and ~1000–1200 °C (for MgO, depending on total pressure), as evidenced by the CO and CO₂ production and rates evolution detected from online gas analysis. Solar heat supply rate was maintained constant (~50% shutter opening for CTR of ZnO and 100% shutter opening for CTR of MgO). A stream of product gases was sucked with a secondary membrane pump to an online syngas analyzer for gas products analysis, while the mainstream of product gases was vented. The molar flow-rate of CO and CO₂ product species (F_i) was determined using their outlet mole fraction (y_i) and the inlet N₂ molar flow-rate (F_{N_2}) as reference: $F_i = F_{N_2} \cdot y_i / y_{N_2}$. Finally, the solid products in the outlet components (zone A: alumina tube and collector and zone B: ceramic filter, according to Figure 1) were quantified and then analyzed by calibrated X-ray diffraction (XRD) for phase identification. Particle morphology analysis was characterized via a field emission scanning electron microscope (FESEM).

Additionally, a non-destructive analytical calibration method was employed to estimate Mg and Zn mass fraction in accordance with XRD peak intensity patterns. Concerning CTR of ZnO, standard samples were prepared by mechanically mixing the known amounts of commercial pure Zn and ZnO as reference with Zn mass fractions of 50%, 60%, 70%, 80%, and 90%. They were subsequently characterized by XRD, and the intensity ratios of the main peaks of Zn (43.2°) to ZnO (31.7°) were evaluated and plotted against Zn mass fraction (wt%) in Figure 2a. Concerning CTR of MgO, commercial pure Mg and MgO were mixed with Mg mass fractions of 15%, 30%, 45%, 60%, 75%, and 90% and the intensity ratios of the main peaks of Mg (36.53°) to MgO (42.71°) were calculated and plotted versus Mg mass fraction (wt%) according to Figure 2b.

Figure 2. Calibration curve for (a) Zn and (b) Mg mass fraction quantification from XRD patterns of the collected solid products. Source: author.

3. Results and Discussion

3.1. Syngas Production Rates

On-sun CTR of ZnO and MgO was carried out under non-isothermal operation at both reduced (0.11, 0.15, and 0.40 bar) and atmospheric (0.90 bar) pressures. The two metal oxides with respect to ZnO (2 g) and MgO (2 g) were considered, and each one was mechanically mixed with different solid carbon types including activated charcoal (AC) and carbon black (CB) with a defined C/(ZnO or MgO) molar ratio of 1.5 (stoichiometric excess). Note that according to previous study, an excess in solid carbon reductant in regard to the stoichiometry (C/ZnO or $C/MgO = 1$) is essential to complete the metal oxide conversion.

The transient CO and CO₂ species production rates along with reactor temperatures (T_1 and $T_{pyrometer}$) as a function of pressure were plotted for CTR of ZnO (Figure 3) and CTR of MgO (Figure 4). The maximum operating temperature ranges (referred to T_1) were 1437–1668 °C for CTR of MgO and 974–1248 °C for CTR of ZnO. Overall, a significant influence of the temperature on the evolution of gas species production rates for both CTR of MgO and CTR of ZnO was observed, demonstrating a strong temperature dependence on the endothermic reaction.

Figure 3. CO and CO₂ production rates along with reactor temperatures for ZnO carbothermal reduction over (a–c) AC and (d–f) CB at different total pressures ($C/ZnO = 1.5$). Source: author.

Figure 4. CO and CO₂ production rates along with reactor temperatures for the carbothermal reduction of MgO over (a) CB and (b–d) AC at different total pressures (C/MgO = 1.5). Source: author.

Concerning CTR of ZnO (Figure 3), the peak CO₂ production rates increased significantly with decreasing total pressure, but the peak CO trends were found to be not significantly different for both AC and CB. Evolutions in the gas species production rate for CTR of ZnO using AC were less obvious than those for CTR of ZnO using CB, because of a fluctuation in solar power input caused by clouds' passage (Figure 3b,f). When decreasing the total pressure, an increase in the slope of CO production rates along with a decline of the reaction duration was evidenced, especially for CB reductant, demonstrating a beneficial impact of decreasing pressure on reduction kinetics.

Concerning CTR of MgO (Figure 4), the CO₂ production rate was extremely low and remained stable despite lowering the pressure to 0.16 and 0.11 bar, while the peak rate of CO production increased slightly, significantly in contrast with the CTR of ZnO. In comparison, the CO₂ production rate for CTR of ZnO was significantly higher than that for CTR of MgO regardless of pressure. Differences in the thermochemical reaction mechanism and the effect of pressure between the CTR of ZnO and CTR of MgO were thus highlighted.

3.2. Syngas Yield

CO and CO₂ yields along with ZnO conversions were plotted as a function of total pressure for CTR of ZnO (Figure 5a) and CTR of MgO (Figure 5b). Regarding CTR of ZnO (Figure 5a), on the one hand, decreasing pressure lowered CO yield because of increased CO₂ production. For example, CO and CO₂ yields for AC were 6.12 and 1.50 mmol/g_{ZnO} at 0.90 bar compared to 4.22 and 2.59 mmol/g_{ZnO} at 0.15 bar, respectively. This is because the gas residence time is decreased with decreasing pressure, and then the produced CO₂ from Equation (3) has not enough time to react with C in the powder bed according

to Equation (4), thereby leading to increased CO_2 at the outlet. On the other hand, ZnO conversion increased slightly, e.g., from 74.2% at 0.90 bar to 76.5% at 0.15 bar for AC, suggesting that decreasing total pressure enhanced ZnO conversion at the expense of lowered CO yield, in agreement with previous study [34]. Note that incomplete net ZnO conversion was attributed to Zn diffusion into insulation layers and Zn recombination at the outlet tip [35], and ZnO conversion for CB at 0.15 bar was lower than that at 0.40 bar due to an adverse effect of the unstable solar power input caused by clouds' passage, as previously mentioned. Considering the impact of the reducing agents (AC and CB) on CO and CO_2 yields, using AC showed superior CO yield, which in turn increased the total gas yield, thanks to the favorable physical properties of AC promoting solid conversion (Table 1). As ZnO conversion increased slightly, but CO_2 increased significantly with decreasing total pressure, operating CTR of ZnO at an intermediate pressure of 0.40 bar is recommended.

Figure 5. CO and CO_2 yields of carbothermal reduction with AC and CB in batch mode as a function of total pressure: (a) ZnO ($\text{C}/\text{ZnO} = 1.5$) and (b) MgO ($\text{C}/\text{MgO} = 1.5$). Source: author.

Concerning CTR of MgO (Figure 5b), as expected, mainly CO was produced regardless of the reductants. In contrast to CTR of ZnO, a decrease in the total pressure significantly increased CO yield, e.g., from 20.10 mmol/g_{MgO} at 0.90 bar to 23.80 mmol/g_{MgO} at 0.11 bar for AC, in turn resulting in MgO conversion increasing from 82.0% to 97.8%. In comparison, the total gas yields obtained from CTR of MgO (Figure 5b) were much higher than those obtained from CTR of ZnO (Figure 5a).

This is because: (i) the released oxygen is in the form of CO for MgO whereas a significant part is released in CO₂ in addition to CO for ZnO, and (ii) the molecular weight of MgO is around twice lower than that of ZnO (40.30 g/mol (MgO) vs. 81.38 g/mol (ZnO)). In contrast to the CTR of ZnO (Figure 5a), CO₂ yields were found to be negligible (e.g., 0.12–0.23 mmol/g_{MgO} for AC) even if they tended to rise with decreasing pressure. The formation of CO₂ would be caused by the Boudouard equilibrium (Equation (4)), because the solid–gas reaction between MgO and CO is thermodynamically unfavorable within the considered temperature range ($\text{MgO} + \text{CO} \rightarrow \text{Mg} + \text{CO}_2$, $T(\Delta G^0 = 0) > 2000^\circ\text{C}$), whereas the solid–gas side reaction of ZnO with CO (Equation (3)) is thermodynamically favorable [34]. This indicates that MgO is mostly reduced with solid carbon (Equation (2)). Therefore, the difference in the reduction behavior between CTR of ZnO and CTR of MgO can be evidenced. Similar to the results obtained from the CTR of ZnO, using AC as reducing agent for MgO resulted in higher CO and CO₂ yields. For example, at 0.11 bar, CO and CO₂ yields were 23.80 mmol/g_{MgO} and 0.23 mmol/g_{MgO} for AC compared to 20.76 mmol/g_{MgO} and 0.04 mmol/g_{MgO} for CB, respectively. From these results, it was confirmed that AC is more efficient than CB, thanks to significantly higher available surface area accessible for particle contact between MgO and AC (Table 1) to favor the solid–solid reaction.

In summary, the main difference between ZnO and MgO carbothermal reduction is the formation of CO₂ by-product in the case of ZnO (via the reaction of ZnO with CO) that lowers the CO yield, whereas the amount of CO₂ is negligible for MgO (reaction of MgO with CO thermodynamically unfavorable). Thus, the decrease of the CO₂ formation to enhance the CO yield in the case of ZnO should be investigated, for instance by increasing the gas residence time (solid–gas contact time) in the ZnO/C powder bed in order to favor the CO₂ consumption by carbon (Equation (4)).

3.3. Characterization of Zn and Mg Products

The outlet components where solid products deposited were divided into two zones: (1) zone A gathered product from the outlet alumina tube and connector and (2) zone B represents product gathered from the ceramic filter, according to Figure 1. To quantify the amount of solid products, the outlet components were weighed with a digital balance (0.01 g readability) before and after each experiment. Then, the collected samples were characterized via XRD and FESEM analysis.

XRD patterns of the solid products as a function of pressure at zone A and zone B were plotted for CTR of ZnO (Figure 6a,b) and CTR of MgO (Figure 6c,d). Regarding XRD patterns for CTR of ZnO (Figure 6a,b), the effect of pressure on products composition was negligible and only Zn patterns were identified with clearly defined peaks and high intensity, whatever the pressure (both zone A and zone B), as compared to the commercial pure Zn reference pattern. This demonstrates high-purity Zn production in both zones, in agreement with the high net ZnO conversion in the range 66.8–78.2% (Figure 5a). Nevertheless, some crystallized gray-chunks deposits were observed, located only at the condensation zone of the outlet tip (~1 cm length in zone A where the outlet temperature dropped below Zn boiling point, 907°C), which resulted from partial Zn recombination, thereby explaining the incomplete global net ZnO conversion. At zone B (downstream filter), the condensed Zn particles as fine droplets were transported by the gas product and inert carrier gases flowing through the filtering unit, and their temperature dropped fast enough to avoid recombination, thus recovering pure Zn powder in the filter. Pure Zn (no detection of any other species) was observed in both zone A and zone B, according to the weight fraction of condensed Zn (wt%) in the collected solid products calculated by calibrated XRD (Figure 2a).

Figure 6. XRD patterns of the collected solid products in zone A and zone B as a function of total pressure: (a,b) ZnO (AC/ZnO = 1.5) and (c,d) MgO (AC/MgO = 1.5). Source: author.

In contrast to the results shown in Figure 6a,b, XRD patterns of both Mg and MgO were observed in both zones (Figure 6c,d), indicating partial Mg oxidation and/or recombination. Furthermore, Mg intensity was greater when decreasing the total pressure, in agreement with the increased CO yield (Figure 5b). Basically, ex-situ XRD analysis of products samples implies the collection and transfer of the produced powder from the reactor to the XRD equipment, with an inherent and inevitable contact of the powder with air occurring during solid particles handling. Importantly, during collecting and transferring the solid products, Mg oxidation with air was observed with a potential pyrophoric issue at ambient temperature due to the very fine and dispersed powder (composed of agglomerates of nanoparticles). For these reasons, MgO content in the solid products after the collecting process was drastically increased and did not reflect the real products composition after the solar reduction reaction, which explains the presence of MgO pattern in all the XRD patterns of samples from zones A and B. However, high net MgO conversion values up to 97.8% (Figure 5b) confirmed that complete MgO conversion was accomplished, and high Mg production yields were reached. The Mg mass fraction calculated by XRD calibration curve (Figure 2b) was in the range of 6.4–18.8% for zone A and 5.3–32.8% for zone B, thus showing low Mg content in the solid products after their exposure to air caused by the strong Mg oxidation with air at room temperature (after opening the reactor). In brief, high MgO conversion validated that high Mg production yield above 97% was achieved, but the collection and safe handling of the pyrophoric Mg-rich powder would need to be performed in inert atmosphere to avoid its rapid oxidation with ambient air.

The particle morphology in the solid products at the reactor outlet (zone A) and filter (zone B), analyzed by FESEM, is presented for CTR of ZnO (Figure 7a,b) and CTR of MgO (Figure 7c,d). Regarding CTR of ZnO, Zn product deposit collected on the alumina wall was condensed in the

form of sheet layers at the condensation zone (zone A). At zone B, condensed Zn particles featured large-scattered droplets with a clear hexagonal crystal structure, characteristic of the Zn structure. In addition, the condensed Zn particles were covered with a small amount of fine solid carbon in both zone A and zone B (Figure 7a,b). Regarding CTR of MgO, the condensed Mg exhibited a spherical shape attributed to the droplet condensation during cooling as clearly seen at zone B. Mg morphology in zone A was less visible than that in zone B, caused by the issue of Mg oxidation with air during the solid product collecting process. In addition, solid carbon or MgO was also observed around Mg droplets, as seen in the filter (Figure 7d). In comparison, differences in the particle morphology between Mg and Zn were obvious. For example, the Zn particles' size was bigger than Mg and their shapes were also different.

Figure 7. Representative FESEM micrographs of solid products from the outlet tube (zone A) and filter (zone B): (a,b) ZnO (CB/ZnO = 1.5) and (c,d) MgO (AC/MgO = 1.5). Source: author.

4. Conclusions

On-sun carbothermal reduction of ZnO and MgO has been experimentally compared and conducted in a prototype solar reactor with different reducing agents including activated charcoal (AC) and carbon black (CB) in a batch mode under vacuum and atmospheric pressures, thus demonstrating flexibility and reliability of this thermochemical reactor for both Zn and Mg production. CO and CO₂ species production rates along with gas yields, metal oxides (ZnO and MgO) conversion, and metals (Zn and Mg) yields were investigated and evaluated according to the reactor operating temperature, pressure, and carbon feedstock.

Regarding ZnO reduction, a decrease in pressure enhanced the ZnO reduction rate as well as the ZnO conversion with the maximum value up to 78.2%, thereby increasing Zn production yield. However, decreasing total pressure significantly decreased CO yield because of increased CO₂ yield caused by shortened residence time. Using AC as reductant exhibited higher ZnO conversion

than CB because AC displays larger specific surface area, which led to favored solid–solid reaction. Regarding MgO reduction, decreasing pressure considerably enhanced the MgO reduction rate and MgO conversion with the maximum value up to 97.8% at a pressure of 0.11 bar. In contrast to ZnO reduction, when decreasing pressure, the CO yield from MgO carbothermal reduction increased significantly and reached the highest value of 23.80 mmol/g_{MgO} at the lowest pressure, while the CO₂ yield was negligible regardless of pressures, thus pointing out the differences of reaction mechanism between MgO and ZnO carbothermal reduction. In agreement with ZnO reduction, employing AC as reducing agent offered the best MgO conversion thanks to effective solid-to-solid contact. Considering the goal to increase ZnO and MgO conversion, lowering the total pressure is necessary, and an intermediate reduced pressure of 0.40 bar would be recommended to promote the reduction rate while alleviating the required energy needed for pumping. In the case of ZnO, in addition to CO production, CO₂ by-product is formed via the reaction of ZnO with CO, which downgrades the CO yield. Thus, the decrease of the CO₂ formation to enhance the CO yield should be further investigated, for instance by increasing the gas residence time (solid–gas contact time) in the ZnO/C powder bed in order to promote the CO₂ consumption by carbon.

Regarding the characterization of Zn and Mg products, high-purity condensed Zn production with 100% Zn content was demonstrated. Zn structure was well crystallized and clearly exhibited the shape of hexagonal crystal structure in micrometric particle size. Condensed Mg particles were observed in spherical shape attributed to the droplet condensation during cooling. Mg-rich fine powder exhibited high reactivity and oxidation with air, thus resulting in low Mg content after exposure to air based on ex-situ solid products analysis. The solar prototype vacuum reactor was proved to be efficient and reliable in producing both metallic Mg and Zn along with CO as a valuable co-product and key component of syngas for fuel production. Carbon feedstock sources are varied and boundless and they can further be renewable if based on bioresources (charcoal). Such a solar-driven carbothermal reduction concept represents a sustainable and renewable thermochemical path toward green metallurgical processes.

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