Low-temperature carbonatization of metal oxides

Danny Müller*a, Christian Knollb, Georg Gravoglabc, Werner Artnerd, Andreas Wernere, Jan M. Welchf, Michael Harasekb, Ronald Miletichc, Peter Weinbergera

a Institute of Applied Synthetic Chemistry, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria.
b Institute of Chemical, Environmental & Biological Engineering, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria.
c Institut für Mineralogie und Kristallographie, University of Vienna, Althanstraße 14, 1090 Vienna, Austria
d X-Ray Center, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria.
e Institute for Energy Systems and Thermodynamics, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria.
f Atominstitut, TU Wien, Stadionallee 2, 1020 Vienna, Austria.

Abstract

In the present work carbonatization of selected metal oxides was investigated at temperatures below 100 °C and CO2 pressures of 1-55 bar (25 °C) and 110 bar (60 °C) by in-situ powder diffraction, as well as experiments in a pressure reactor. Moisture was confirmed to be a crucial requirement for any successful carbonatization, as under dry conditions always the initial metal oxide was recovered. Under the applied conditions a successful carbonatization of CaO, MnO, ZnO, CoO and PbO was achieved, highlighting, that although commonly studied at high temperatures, carbonatization of metal oxides can also be successfully operated in the presence of moisture with an elevated CO2 pressure as driving force.

© 2019 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: metal oxides; low-temperature carbonatization; non-ambient conditions; in-situ P-XRD; thermochemical energy storage

1. Introduction

In the recent past, the excessive use of fossil fuels to satisfy global energy demands has resulted in increased awareness, not only of their limited availability but also the associated increase in anthropogenic atmospheric CO2. Whereas the limited availability stimulated the research on alternative energy sources and energy efficiency [1], the increased CO2 release gave rise to political measures restricting CO2 emissions [2, 3], as well as to ambitious research programs on CO2 fixation. [4]

One major issue is that power plants continue to be operated with fossil fuels. Measures dealing with this topic target avoidance of CO2 release, its separation from flue gas or other gases and subsequent storage as form of
deposition. The avoidance of CO₂ release is hampered by the economic attractiveness of fossil fuel power plants. Therefore, as compromise research on an effective separation and subsequent storage or conversion of CO₂ from flue gas has intensified. In this context, separation of CO₂ incurs notable financial penalties for power plant and a concomitant reduction of energy output. [5] A conceivable approach to these challenges and the energy expenditure of CO₂ separation could be the concept of thermochemical energy storage (TCES) when operating with the separated CO₂ and thereby, allowing for recovery of a portion of the energy invested in CO₂ capture.

Research on thermochemical energy storage has been inspired by the ready availability of waste energy and the notable temporal shifts in energy production and consumption. The goal of such technology is to re-utilize waste heat and thereby contribute to balancing the discrepancies between energy availability and demand. [1, 6, 7] According to this approach (thermal) energy is stored by means of reversible chemical reactions: An endothermic decomposition reaction charges the storage material, whereas by recombination of the former decomposition products the exothermic reaction discharges the stored energy and restores the material. [8, 9]

Carbonates have been established as suitable materials for TCES-processes (see Eq.1) [10], although to date they have predominantly been investigated for medium- and high-temperature applications, especially in combination with concentrating solar power plants. [11, 12]

\[
\text{MeCO}_3 + \Delta\text{H} \leftrightarrow \text{MeO} + \text{CO}_2
\]  

(1)

For TCES-systems CaCO₃, PbCO₃ and, recently, SrCO₃ have been considered. [12] Most efforts focused on CaCO₃, especially due to its potential for atmospheric CO₂ sequestration. [13]

CaCO₃ provides reversible decarbonization / carbonatization with an energy storage potential of 178 kJ mol⁻¹. [12] Although fully reversible, an initial drawback was the limited cycle stability which could be overcome by dotation of the material with CaTiO₃. [14] Subsequent studies focused on improving the of reactivity by using CaO nanoparticles [15] or composite materials with Si. [16] Recently, zirconia-stabilized SrO / SrCO₃ was reported readily reversible and cyclable material for high-temperature TCES for temperatures around 1200 °C. [17] Also Cerussite (PbCO₃) offers attractive cycle stability [18, 19] with an energy content of 88 kJ mol⁻¹ [12], due to the inherent toxicity of the materials involved, for technological applications environmentally more benign materials are required.

On the basis of attempts to decrease greenhouse gas emissions by carbon dioxide fixation via the carbonatization of metal oxides, [20-22] and the highly promising mineralization of CO₂, [4] we considered a novel approach to TCES-processes using CO₂: instead of applying high temperatures, moderate temperatures combined with higher pressures should result in carbonatization of metal oxides.

In this case, CO₂ separated from fossil-fuel power plant waste gas could be stored in form of carbonates, which release thermal energy on their formation due to exothermic carbonatization reactions. Only compression of gas separated would be needed, which is in many cases could be easily accomplished with the available infrastructure. The use of environmentally harmless oxide / carbonate pairs would also allow for relatively simple disposal of the separated carbon dioxide.

For this purpose, in the present work, a systematic database survey was undertaken to identify potentially suitable carbonate materials complementing the currently known examples. [23] The feasible candidates were selected according to their energy content and their theoretical equilibrium temperature. The selected materials were investigated with respect to their carbonatization behavior at temperatures below 100 °C and at pressures of 55 bar and 110 bar to show the feasibility of the low temperature carbonatization systems. The current in-situ powder X-Ray diffraction (P-XRD) study and following carbonatization experiments in a reactor demonstrated that in the presence of moisture higher pressures can replace high temperatures for successful carbonatization of pure metal oxides.

2. Experimental Methodology

2.1 Material

The metal oxides used for carbonatization were prepared by thermal decomposition of the corresponding metal carbonates at the temperatures determined by thermogravimetric analysis (see table A1). This approach was selected to avoid potential influence of sample history on the carbonatization process.
2.2 X-Ray Powder Diffraction

The powder X-ray diffraction measurements were carried out on a PANalytical X’Pert Pro diffractometer in Bragg-Brentano geometry using Cu Kα1,2 radiation and an X’Celerator linear detector with a Ni-filter. For the in-situ experiments an Anton Paar XRK 900 reaction chamber was used. The sample consists of a 4 mm thick layer of oxide-powder-sample with a diameter of 10 mm and is mounted on a hollow ceramic powder sample holder, allowing for complete perfusion of the sample with the reactive gas. The reaction chamber allows operation between 25 °C and 900 °C and pressures up to 10 bar. For the carbonization experiments the pressure in the sample chamber was adjusted to 8 bar, maintaining a constant flow through the chamber of 0.2 L CO2 min⁻¹. To investigate the carbonatization in the presence of moisture, the CO2 was passed through an external moisturiser. The CO2 is bubbled through a 20 cm high water tank followed by a droplet-separator before contacting the sample in the reaction chamber. At the entry of the reaction chamber the gas had a dew-point temperature of 23.2 °C. Considering the gas temperature of 25 °C, this corresponds to a water vapour loading of 0.25 g h⁻¹.

The sample temperature is controlled directly by a NiCr-NiAl thermocouple and direct environmental heating, operable at heating-rates between 0.1 K min⁻¹ and 150 K min⁻¹. The reactive gas flow was set to 0.2 L min⁻¹, unless otherwise stated. The diffractograms were evaluated using the PANalytical program suite HighScorePlus v3.0d. A background correction and a Kα2 strip were performed. Phase assignment is based on the ICDD-PDF4+ database, the exact phase composition was obtained by Rietveld-refinement in the program suite HighScorePlus v3.0d.

2.3 Carbonatization in the reactor

For the carbonatization of metal oxides in a reactor at higher CO2 pressures, a small amount of the metal oxide (around 50 mg) was placed in a glass-vial with perforated cap to avoid cross-contamination. The reactor was pressurized with CO2 at 55 bar unless otherwise stated, controlling the internal pressure with the reactor’s integrated manometer. The carbonatization was aborted after the specified reaction time by release of CO2 pressure.

For the reactions at elevated temperatures the reactor was loaded with the samples, placed in an oven having the desired temperature and kept there for 1 h to equilibrate. Then 55 bar of CO2 were charged and the reactor kept for the specified reaction time in the oven. Due to the thermal expansion a final internal pressure of 110 bar was reached. Again, the carbonatization was aborted by release of CO2.

For all experiments requiring moisture approximately 0.1 ml H2O was sprayed into the sample vials.

3. Results and Discussion

The carbonate systems for the intended low-temperature carbonatization study under elevated CO2 pressure were selected from the HSC chemistry database using a systematic search algorithm[23] and are listed in table 1.

Table 1. Selected carbonate materials, ranked according to their theoretical energy density

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Theoretical equilibrium temperature [°C]</th>
<th>Theoretical energy density [GJ m⁻³]a</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaMg(CO₃)₂ → CaO + MgO + 2 CO₂</td>
<td>1152</td>
<td>4.52</td>
</tr>
<tr>
<td>CaCO₃ → CaO + CO₂</td>
<td>1433</td>
<td>4.49</td>
</tr>
<tr>
<td>MgCO₃ → MgO + CO₂</td>
<td>851</td>
<td>3.58</td>
</tr>
<tr>
<td>MnCO₃ → MnO + CO₂</td>
<td>890</td>
<td>3.22</td>
</tr>
<tr>
<td>ZnCO₃ → ZnO + CO₂</td>
<td>668</td>
<td>2.94</td>
</tr>
<tr>
<td>CoCO₃ → CoO + CO₂</td>
<td>728</td>
<td>2.90</td>
</tr>
<tr>
<td>FeCO₃ → FeO + CO₂</td>
<td>720</td>
<td>2.69</td>
</tr>
</tbody>
</table>

a The numerical values are based on the HSC Chemistry database.
To study the carbonatization reaction of those materials, the corresponding metal oxides (see materials and methods) were treated with CO2 under various conditions initially small samples were monitored by in-situ P-XRD and larger samples were subsequently treated in a larger reactor to understand the carbonatization behavior under higher pressures than were possible in the P-XRD cell.

3.1 In-situ carbonatization in the P-XRD

The well-known carbonatization of calcium oxide [5, 13] was utilized to establish the viability of monitoring carbonatization reaction progress by in-situ P-XRD. Applying 8 bar CO2 (under dynamic conditions the maximum pressure possible in the reaction chamber) and temperatures between room-temperature and 600 °C revealed that for dry CO2 no carbonatization reaction occurred. As described in many cases in the literature, hydroxides are used for carbonatization studies and even the low-temperature carbonatization of Ca(OH)2 was only successful in the presence of moisture. [24] The impact of moisture on the carbonatization of metal oxides can be attributed to traces of liquid water on the oxide surface, enhancing carbonatization by dissolution of the CO2, as well as by formation of hydroxyl groups on the oxide surface promoting the carbonatization step. [25, 26] Therefore, for all further reactions a moisturizer was implemented in the setup between CO2 tank and reaction chamber.

Using wet CO2, having a dew-point temperature of 23.2 °C for the carbonatization, for a pressure of 1 bar CO2 no carbonatization, but conversion of the CaO to Ca(OH)2, was observed (see Fig.2). The rapid hydration of CaO in the presence of moisture has been extensively studied. [27] At pressures of 3 bar and 8 bar after a reaction time of 120 minutes 11.8 % and 33.8 % CaCO3 in the presence of Ca(OH)2 were obtained. The change in the phase composition over the 120 minutes reaction time is plotted in figure 1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Theoretical equilibrium temperature [°C]</th>
<th>Theoretical energy density [GJ m⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCO₃ → NiO + CO₂</td>
<td>655</td>
<td>2.31</td>
</tr>
<tr>
<td>PbCO₃ → PbO + CO₂</td>
<td>858</td>
<td>2.07</td>
</tr>
</tbody>
</table>

For the reaction under 3 bar CO2 the intermediate hydroxide formation occurred faster than for the same experiment using 8 bar CO2, indicating a notable impact of the water partial pressure on the formation of the hydroxide intermediate. At 8 bar the initial hydroxide formation is retarded, affecting also the carbonatization rate. To increase the completeness of the reaction longer carbonatization times were considered. Nevertheless, after 24 h the final phase composition was comparable to those observed after 2 h. This suggests the system is approaches an equilibrium state under these conditions.

Since the final composition of the product contains a significant amount of Ca(OH)2 in spite of the application of a large excess of reactant (CO2) it seems likely, that a passivating carbonate layer forms on the surface of the particles and prevents further carbonatization. In literature, issues with conversion and surface passivation have been described. These effects could be circumvented by modification of the particle morphology or reactor setup. [12] Similar approaches or a different setup could be considered to increase the overall carbonatization yield. However, although repetition of the reaction at 100 °C did not significantly increase the final conversion, the formation of an excess of Ca(OH)2 could be suppressed.
Based on the promising initial results described above, the prospective metal oxides to be examined were subjected to in-situ carbonatization in the P-XRD cell. An overview of the outcomes of these in-situ experiments is given in figure 2.

Aside from CaO, only MnO and PbO showed any reactivity towards CO$_2$ under the conditions applied. Interestingly, for neither MnO nor PbO was any intermediate hydroxide formation observed. Whether or not the carbonatization process in these cases does not involve a hydroxide phase or the reaction of the intermediate hydroxide with CO$_2$ is faster than the P-XRD timescale, will be the subject of future investigations. Carbonate yields of 15.2 % (MnO) and PbO (17.5 %) were limited to 25 °C, as for 100 °C only the metal oxide could be found. Compared to the partially successful monitoring of carbonatization of CaO by in-situ P-XRD the reactivity of the other metal oxides towards carbonatization under these conditions was disappointing.
3.2 Carbonatization in the reactor

To investigate the carbonatization behavior of metal oxides under higher CO₂ pressures, a reactor setup allowing pressures up to 55 bar (25 °C) and 110 bar (60 °C) under static conditions was chosen. The resulting phase composition was determined after the reaction by P-XRD. For each of the selected oxides, 4 different experiments were performed, establishing the effect of moisture and temperature on the carbonatization process. In figure 3, the resulting phase compositions are reported.

Similarly to the in-situ P-XRD experiments, at higher pressures moisture was also identified as a crucial component for successful carbonatization. Under dry conditions the initial phase composition was retained. Whereas most of the materials test were not carbonatized in the in-situ P-XRD setup, in the case of higher pressures in the reactor only MgO, FeO and NiO failed to react. These results are in good agreement with other carbonatization studies, in which

---

b Based on the appearance of the diffractograms the presence of any amorphous material – which should give rise to a higher background or line broadening effects – could be excluded.
MgO has been carbonatized at high temperature [28], or for a longer time. [29, 30] Also in reports on basaltic-CO₂ fixation, FeO present in olivine- was inert under the carbonatization conditions applied. [30]

A sample of dolomite was nearly unaffected by carbonatization with moisture at room-temperature, but at 60 °C full carbonatization of the CaO fraction occurred. Concomitantly, the MgO was hydrated to Mg(OH)₂, still indifferent towards carbonatization. Carbonatization of CaO at 55 bar, 25 °C was highly successful, as after 2 h complete conversion was achieved. In this case, an increase in temperature was obstructive, preventing complete carbonatization of the intermediately formed Ca(OH)₂.

In the case of MnO, 55 bar CO₂, 25 °C led to a carbonatization yield of 86 %. In contrast, an increased temperature led to the unprecedented and reproducible formation of 62.4 % Mn₃O₄ after 2 h, presumably as product of MnO oxidation by CO₂. Aside from CaO, the 86 % yield of MnCO₃ was the highest observed in the series.

For the carbonatization of ZnO at 25 °C the double-salt ZnCO₃·2Zn(OH)₂·H₂O was identified as an intermediate phase. At higher temperatures only ZnCO₃ was found, due to immediate conversion of the intermediate carbonate-hydroxide phase.

CoO and PbO also revealed significant carbonatization behavior on increased temperature, yielding 68.3 % of CoCO₃ and 81.6 % of PbCO₃, respectively. At 25 °C no conversion was observed for CoO, and for PbO only a small amount of the carbonate phase (14.8 %) could be observed evidenced.

In comparison to the in-situ experiments monitored by P-XRD, in all cases improved reactivity was achieved by carbonatization in the reactor. For the carbonatization of PbO at 55 bar and 25 °C a lower carbonate content was observed compared to experiments in the P-XRD setup. Considering that moisture plays a crucial role in all carbonatization experiments, it seems comprehensible that lower pressures can effectively promote the carbonatization process.

4. Conclusion

Material and feasibility studies on the carbonatization of metal oxides at elevated CO₂ pressure and temperatures below 100 °C both in presence or absence of moisture have been carried out. The reactions were performed in-situ in the P-XRD (8 bar, variable temperatures) and in a pressure reactor (55 bar, 25 °C; 110 bar, 60 °C). For all used materials and conditions moisture revealed as crucial for carbonatization, as under dry conditions always the initial oxide-phase composition was retained.

Only for CaO, MnO and PbO could the formation of a carbonate phase be observed in relatively small amounts under in-situ P-XRD conditions. In contrast, higher pressures (55 bar, 25 °C and 110 bar, 60 °C) enabled carbonatization of CaO in dolomite, CaO, MnO, ZnO, CoO and PbO within 2 h. Of the selected metal oxides, only for CaO at 55 bar, 25 °C was complete carbonatization achieved. Comparably high carbonatization yields were obtained for MnO (86 % MnCO₃) at 55 bar, 25 °C, as well as for CoO (CoCO₃ 68.3 %) and PbO (81.6 % PbCO₃), both at 110 bar, 60 °C.

Based on these initial carbonatization results, intensified contact between metal oxide and moisture should allow for even higher carbonatization yields. Investigations regarding calorimetric data of the carbonatization and reaction rates for CaO, MnO, CoO and PbO under the applied conditions are the subject of on-going studies.

5. Acknowledgement

This work was financially supported by the Austrian Research Promotion Agency (FFG Forschungsförderungsgesellschaft), project 845020, 841150 and project 848876. The X-Ray center (XRC) of the Vienna University of Technology provided access to the powder X-Ray diffractometer.

6. Appendix

<table>
<thead>
<tr>
<th>Carbonate</th>
<th>Decomposition temperature to MeO*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>785 °C</td>
</tr>
</tbody>
</table>
MgO has been carbonatized at high temperature [28], or for a longer time [29, 30]. Also in reports on basaltic CO$_2$ fixation, FeO present in olivine- was inert under the carbonatization conditions applied [30]. A sample of dolomite was nearly unaffected by carbonatization with moisture at room temperature, but at 60 °C full carbonatization of the CaO fraction occurred. Concomitantly, the MgO was hydrated to Mg(OH)$_2$, still indifferent towards carbonatization. Carbonatization of CaO at 55 bar, 25 °C was highly successful, as after 2 h complete conversion was achieved. In this case, an increase in temperature was obstructive, preventing complete carbonatization of the intermediately formed Ca(OH)$_2$.

In the case of MnO, 55 bar CO$_2$, 25 °C led to a carbonatization yield of 86 %. In contrast, an increased temperature led to the unprecedented and reproducible formation of 62.4 % Mn$_3$O$_4$ after 2 h, presumably as product of MnO oxidation by CO$_2$. Aside from CaO, the 86 % yield of MnCO$_3$ was the highest observed in the series.

For the carbonatization of ZnO at 25 °C the double-salt ZnCO$_3$∙2Zn(OH)$_2$∙H$_2$O was identified as an intermediate phase. At higher temperatures only ZnCO$_3$ was found, due to immediate conversion of the intermediate carbonate-hydroxide phase.

CoO and PbO also revealed significant carbonatization behavior on increased temperature, yielding 68.3 % of CoCO$_3$ and 81.6 % of PbCO$_3$, respectively. At 25 °C no conversion was observed for CoO, and for PbO only a small amount of the carbonate phase (14.8 %) could be observed evidenced.

In comparison to the in-situ experiments monitored by P-XRD, in all cases improved reactivity was achieved by carbonatization in the reactor. For the carbonatization of PbO at 55 bar and 25 °C a lower carbonate content was observed compared to experiments in the P-XRD setup. Considering that moisture plays a crucial role in all carbonatization experiments, it seems comprehensible that lower pressures can effectively promote the carbonatization process.

4. Conclusion

Material and feasibility studies on the carbonatization of metal oxides at elevated CO$_2$ pressure and temperatures below 100 °C both in presence or absence of moisture have been carried out. The reactions were performed in-situ in the P-XRD (8 bar, variable temperatures) and in a pressure reactor (55 bar, 25 °C; 110 bar, 60 °C). For all used materials and conditions moisture revealed as crucial for carbonatization, as under dry conditions always the initial oxide-phase composition was retained.

Only for CaO, MnO and PbO could the formation of a carbonate phase be observed in relatively small amounts under in-situ P-XRD conditions. In contrast, higher pressures (55 bar, 25 °C and 110 bar, 60 °C) enabled carbonatization of CaO in dolomite, CaO, MnO, ZnO, CoO and PbO within 2 h. Of the selected metal oxides, only for CaO at 55 bar, 25 °C was complete carbonatization achieved. Comparably high carbonatization yields were obtained for MnO (86 % MnCO$_3$) at 55 bar, 25 °C, as well as for CoO (CoCO$_3$ 68.3 %) and PbO (81.6 % PbCO$_3$), both at 110 bar, 60 °C.

Based on these initial carbonatization results, intensified contact between metal oxide and moisture should allow for even higher carbonatization yields. Investigations regarding calorimetric data of the carbonatization and reaction rates for CaO, MnO, CoO and PbO under the applied conditions are the subject of on-going studies.

5. Acknowledgement

This work was financially supported by the Austrian Research Promotion Agency (FFG Forschungsförderungsgesellschaft), project 845020, 841150 and project 848876. The X-Ray center (XRC) of the Vienna University of Technology provided access to the powder X-Ray diffractometer.

6. Appendix

<table>
<thead>
<tr>
<th>Carbonate</th>
<th>Decomposition temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$</td>
<td>370 °C</td>
</tr>
<tr>
<td>Dolomite</td>
<td>815 °C</td>
</tr>
<tr>
<td>FeCO$_3$</td>
<td>550 °C</td>
</tr>
<tr>
<td>MnCO$_3$</td>
<td>450 °C</td>
</tr>
<tr>
<td>MgCO$_3$</td>
<td>480 °C</td>
</tr>
<tr>
<td>NiCO$_3$</td>
<td>375 °C</td>
</tr>
<tr>
<td>PbCO$_3$</td>
<td>375 °C</td>
</tr>
<tr>
<td>ZnCO$_3$</td>
<td>370 °C</td>
</tr>
</tbody>
</table>

* The given decomposition temperature refers not to the peak onset, but to the final flattening, stating complete decarbonation yielding the respective metal oxides MeO.

Figure A1. Diffractograms for in-situ re-carbonation forming Dolomite

Figure A2. Diffractograms for in-situ carbonation of CaO into CaCO$_3$

Figure A3. Diffractograms for in-situ carbonation of MgO into MgCO$_3$

Figure A4. Diffractograms for in-situ carbonation of MnO into MnCO$_3$
Figure A5. Diffractograms for in-situ carbonation of ZnO into ZnCO$_3$

Figure A6. Diffractograms for in-situ carbonation of CoO into CoCO$_3$

Figure A7. Diffractograms for in-situ carbonation of FeO into FeCO$_3$

Figure A8. Diffractograms for in-situ carbonation of NiO into NiCO$_3$

Figure A9. Diffractograms for in-situ carbonation of PbO into PbCO$_3$

Figure A10. Diffractograms for reactor re-carbonation forming Dolomite
Figure A5. Diffractograms for in-situ carbonation of ZnO into ZnCO₃

Figure A6. Diffractograms for in-situ carbonation of CoO into CoCO₃

Figure A7. Diffractograms for in-situ carbonation of FeO into FeCO₃

Figure A8. Diffractograms for in-situ carbonation of NiO into NiCO₃

Figure A9. Diffractograms for in-situ carbonation of PbO into PbCO₃

Figure A10. Diffractograms for reactor re-carbonation forming Dolomite

Figure A11. Diffractograms for reactor carbonation of CaO into CaCO₃

Figure A12. Diffractograms for reactor carbonation of MgO into MgCO₃

Figure A13. Diffractograms for reactor carbonation of MnO into MnCO₃

Figure A14. Diffractograms for reactor carbonation of ZnO into ZnCO₃

Figure A15. Diffractograms for reactor carbonation of CoO into CoCO₃

Figure A16. Diffractograms for reactor carbonation of FeO into FeCO₃
6. References