Comparative Study: Impacts of Ca and Mg Salts on Iron Oxygen Carriers in Chemical Looping Combustion of Biomass

Duygu Yilmaz,* Britt-Marie Steenari, and Henrik Leion

ABSTRACT: Chemical looping combustion (CLC) is one of the most promising methods for carbon capture and storage (CCS). An oxygen carrier, i.e., a mineral that can be oxidized and reduced, is used to convert the fuel in the process. The produced CO$_2$ is inherently separated from the air components that enables easier CCS. The use of biomass-based fuels is desirable since it can lead to negative CO$_2$ emissions. On the other hand, alkali compounds from the biomass may interact with the oxygen carrier causing problems, such as deactivation of the oxygen carrier. The most common oxygen carriers contain iron, since iron-based ores and industrial waste materials are readily available and cost-efficient. Therefore, the interaction between the iron oxygen carriers and the biomass ash-forming compounds needs to be investigated. Since Ca/Mg are abundant in biomass, it is important to clarify how their compounds interact with the oxygen carrier. In this study, the effect of Ca/Mg carbonates, chlorides, nitrates, sulfates, and phosphates along with synthetic biomass-derived ash on iron oxides was investigated. Redox reactions were investigated at 950 °C during 5 h under both oxidizing and reducing atmospheres. The results showed that the effect of Ca/Mg salts on the oxygen carrier varied depending on the anion of the salt. Generally, the nitrate- and phosphate-based salts of both Ca and Mg showed the harshest effect regarding agglomeration of the oxygen carriers. It was shown that the Ca/Mg-based compounds interacted differently with iron oxides, which was an unexpected result.

1. INTRODUCTION

Chemical looping combustion (CLC) is one of the most promising methods to reduce the cost of CO$_2$ capture to tackle the climate change.$^{1}$ CLC enables us to separate CO$_2$ from other combustion products; therefore, there is no energy consumed for the gas separation.$^2$ A CLC process consists of two interconnected fluidized beds: a fuel reactor and an air reactor.$^3$ In the fuel reactor, the fuel is oxidized by a solid oxygen carrier, which gets reduced. In the air reactor, the oxygen carrier is oxidized by air. Generally, the oxygen carriers are chosen from oxides of Cu, Fe, Mn, and their oxide-based combinations or ores.$^4$−$^7$ Even though gaseous fuels are most commonly used in CLC systems, solid fuels can be favorable since they are less expensive and more abundant.$^8$−$^9$ Recently, the use of biomass in CLC has attracted great attention since it gives a possibility to achieve "negative CO$_2$ emission" goals.$^{10,11}$ There is no doubt that the use of biomass in CLC systems brings a lot of advantages.$^{12,13}$ However, biomass-derived ash consists of highly reactive species such as alkali metal compounds and compounds of alkaline earth elements,$^{13,14}$ which may cause partial sintering or agglomeration of the oxygen carriers.$^{15}$

If the interaction mechanism between ash-forming matters and the oxygen carrier can be understood, selection of the most appropriate biomass source as a fuel for CLC applications can be made. Ash-forming species may exist as different compounds, and their composition in a biomass may vary depending on the source of biomass.$^{14,15}$ In the literature, studies focused on the interaction of alkali-metal-based ash-forming matters and oxygen carriers have been published.$^{17,18}$ Especially, the effect of alkali metal salts/alkaline earth salts has been focused on by researchers, as the salts can affect the oxygen carriers in various ways.$^{16,20}$ Among these salts, the interaction of Ca- and Mg-based ones with the oxygen carrier has not been investigated in detail, since their effect on the oxygen carriers was expected to be similar.$^{21}$ A recent study showed, however, that their impact might differ depending on which oxygen carrier was used.$^{22}$ The Ca compounds showed higher reactivity toward iron oxides than the Mg compounds did, and the formation of Ca–Fe-based oxides was observed.
On the contrary, no formation of Mg−Fe oxides occurred.\(^{25}\) It is known that the Ca/Mg ratio in biomass can vary from one biomass to another (Table 1). From this point of view, it is important to clarify more the effects of Ca- and Mg-based species on iron oxygen carriers, since iron oxides are one of the most commonly used oxygen carriers in combustion of biomass.\(^{26}\) In this way, the right fuel selection can be made among the several biomass sources available. In addition to this, it is important to reveal the interaction mechanisms of the alkaline earth compounds with the other ash-forming matters. Combinations of alkali metal compounds and silica, for example, can cause serious agglomeration since alkali metal silicates may have melting points that are lower than the operation temperature of the combustor.\(^{13,16,27-30}\) In addition to the risk of agglomeration due to ash melts, there is a risk of deactivation of oxygen carriers via the formation of new compounds during CLC operation. Moreover, thermodynamic and kinetic characteristics of the redox reactions may be different depending on which oxygen carrier is used.\(^{11,33}\)

So far, there is no study published that presents data from investigations of the high-temperature interactions between alkaline earth element compounds common in biomass ash-forming matter and pure Fe oxygen carriers, individually. Therefore, it was considered important to investigate these interactions to make it possible to select the best oxygen carrier and type of biomass to be used in real applications. In this way, problematic sintering and formation of unwanted compounds can be avoided.

In the present study, the interactions between pure Fe oxides and Ca/Mg-based compounds (representing reactive biomass ash species) were investigated. Two synthetic model ashes consisting of either Ca- or Mg-based compounds were also prepared and used in experiments with Fe oxides to investigate the overall effect of the alkaline earth metal species on the Fe oxides. Thermodynamic equilibrium calculations were used for theoretical evaluation of the chemical systems and comparison with the compounds obtained in the experiments. Agglomeration and sintering of the oxygen carriers caused by the alkaline earth compounds was studied by visual observation and determination of the surface area of the samples after the experiments.

### 2. RESULTS AND DISCUSSION

#### 2.1. Effect of Ca/Mg Hydroxides on the Pure Fe Oxygen Carriers

Table 2 shows the results of the experiments (Figure 1) and thermodynamic equilibrium calculations. When Ca(OH)\(_2\) was used as an alkaline earth compound representative in the mixture, the formation of new compounds, such as CaFe\(_2\)O\(_4\) and Ca\(_2\)Fe\(_2\)O\(_5\), was observed under both reduction and oxidation conditions most likely via reactions 1 and 2. These reactions are only solid-state reactions and do not involve reduction of the iron. As both new compounds formed have been reported as potential oxygen carriers for energy-related applications, their formation as such was not considered as a problem.\(^{34,35}\) However, a serious agglomeration was observed, particularly during the oxidation step, most likely due to solid-state formation of these compounds. It is known that CaFe\(_2\)O\(_4\) is stable under oxidizing atmosphere, and it may dissociate into Ca\(_2\)Fe\(_2\)O\(_5\) and Fe\(_3\)O\(_4\) under reducing atmosphere (reaction 3). This was also observed in the X-ray diffraction (XRD) analysis of the reduced Ca(OH)\(_2\)−Fe\(_2\)O\(_3\) mixture.

![Figure 1. XRD patterns of the iron oxides—Ca(OH)\(_2\) and Mg(OH)\(_2\) mixtures after the experiments (AR: after reduction, AO: after oxidation).](image-url)
Similarly, the presence of Mg(OH)$_2$ also caused an agglomeration of the sample. However, the observed agglomeration was milder in this case. There was no significant Mg- and Fe-based oxide formation observed based on the XRD analysis of the reaction product. This is not surprising since reaction 4 is thermodynamically favorable only below 700 °C. Above 700 °C, MgFe$_2$O$_4$ may dissociate into MgO and Fe$_2$O$_3$ under oxidizing atmosphere.

$$\text{CaO} + 2\text{Fe}_2\text{O}_3 \rightarrow \text{CaFe}_2\text{O}_4, \Delta G_{1223K}^{\circ} = -34 \text{ kJ}$$

(1)

$$2\text{CaO} + \text{Fe}_2\text{O}_3 \rightarrow \text{Ca}_2\text{Fe}_2\text{O}_5, \Delta G_{1223K}^{\circ} = -63 \text{ kJ}$$

(2)

$$6\text{CaFe}_2\text{O}_4 + \text{H}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$$

$$\rightarrow 3\text{Ca}_2\text{Fe}_2\text{O}_5 + \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O}(\text{g}), \Delta G_{1223K}^{\circ} = -87 \text{ kJ}$$

(3)

2.2. Effect of Ca-Based Salts on the Pure Fe Oxygen Carriers. Some types of biomass sources such as bark and forest residue can contain a high amount of Ca-based species. Since alkaline earth metal compounds can easily interact with the other ash-forming matters present in biomass, their effect on the oxygen carriers has attracted the attention of researchers. Therefore, it is important to reveal the interaction between the alkali-earth-based salts and Fe oxygen carriers. The alkaline earth elements are mainly present in the biomass ashes as chlorides, carbonates, sulfates, and phosphates. Especially calcium carbonates were found as deposits in biomass-fired power plants. Thermodynamic equilibrium calculations showed that CaFe$_2$O$_4$ and Ca$_2$Fe$_2$O$_5$ were expected along with iron oxides in redox reactions of calcium carbonate–iron oxide mixtures (Table 3). XRD analysis results (Figures 2 and 3 for reduction and oxidation, respectively) showed the presence of CaFe$_2$O$_4$ both after the reduction and oxidation experiments with the CaCO$_3$–Fe oxide mixtures. This result was expected since CaCO$_3$ is stable up to 750 °C and can interact with Fe oxides to form CaFe$_2$O$_4$ through reaction 5. Most likely, reactions 6 and 1 occurred above 750 °C to form CaFe$_2$O$_4$. Along with the CaFe$_2$O$_4$ formation, a strong agglomeration was observed when CaCO$_3$ interacted with the Fe oxides both under oxidizing and reducing atmospheres. This agglomeration most likely occurred due to the CaFe$_2$O$_4$ formation by solid-state reactions. It is known that the dwell during the redox reactions can cause sintering via grain growth. In addition to that, calcium ferrites were detected in the sintered matrix of the iron ores in different studies.

$$\text{CaCO}_3 + \text{Fe}_2\text{O}_3 \rightarrow \text{CaFe}_2\text{O}_4 + \text{CO}_2(\text{g}), \Delta G_{1223K}^{\circ} = -42 \text{ kJ}$$

(5)

$$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2(\text{g}), \Delta G_{1223K}^{\circ} = -8 \text{ kJ}$$

(6)

When the impact of chloride ions on oxygen carrier was investigated earlier by researchers, the results showed that HCl formation may cause a deactivation of the oxygen carriers due to the formation of gaseous products from reaction between oxygen carrier and Cl-based species. However, high steam concentration in the CLC process was successful to prevent this reaction and formation of HCl was observed instead. In the investigation of the effect of CaCl$_2$ as a Cl source on the iron oxygen carriers in the present work, the theoretical
was most likely due to the fact that the melting point of CaCl2 but no such products were observed in the experiments. This Ca(NO3)2 experiment and a low-viscosity melt Ca19Fe2(PO4)14 was observed under both oxidizing and reducing atmospheres such as H2 and CO. However, reductive potential (PH2/pH2O) is known to be one of the most important parameters to decide the decomposition mechanism of CaSO4.47 Since steam was also present under reducing atmosphere in this study, although the amount was very small, CaSO4 could be observed in the system after the reduction. No new Ca–Fe-based oxide or other reaction product was observed in the experiments, which is also consistent with the results provided by Thermodynamic Equilibrium Calculations (TEC).

To summarize, the most dramatic effects regarding the agglomeration formation were observed in the mixtures of iron oxide carriers and Ca carbonate, nitrate, and phosphates. If the formation of Fe-based new compounds is taken into consideration, calcium phosphate generated the harshest conditions for the Fe oxygen carrier. From this point of view, the best biomass for Fe-based oxygen carriers can be chosen from the biomasses with the highest CaO/P2O5 value, such as wood-derived biomass,33 to limit the formation of Ca–Fe–P-based oxides. Calcium phosphates can also interact with the other compounds present in the biomass, especially with alkali metal compounds.48 However, it is worth noting that the melting temperatures of calcium phosphates may be close to the operation temperature, which shows that there is a risk for agglomeration of the bed material.49

2.3. Effect of Mg-Based Salts on Pure Fe Oxygen Carriers. The concentrations of Mg compounds are generally lower than those of the Ca compounds in biomass.50 However, there are some biomass sources such as chlorella, spirulina, coffee residue, and bean curd, which contain more Mg than Ca.51 Therefore, it is important to have a better understanding on the interaction of Mg-based salts and the oxygen carriers. It is known that the decomposition temperature of alkaline earth carbonates to oxides decreases down the group in the periodic table.52 When MgCO3 was used as a salt compound in the Fe oxide–salt mixture, no formation of new Fe compounds was observed in any of the experiments (Figures 4 and 5). The decomposition of MgCO3 to MgO is thermodynamically favorable above 400 °C (reaction 8). Therefore, MgCO3 will exist in the mixture as MgO above 400 °C, and it may interact with Al2O3 rather than Fe oxide as indicated by thermodynamics (reactions 9 and 10). The system was assumed as a closed system in TEC, and no interaction with the Al2O3 crucible was considered. Therefore, the modeling results differed from the experimental ones (Table 4).

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\begin{align*}
\text{CaSO}_4 & \text{ is a comparably stable salt under operation conditions, and it has a higher melting point than other Ca-based salts used in the study. CaSO}_4 \text{ can be reduced to CaS in the presence of reducing atmospheres such as H}_2 \text{ and CO. However, the reduction potential (PH}_2/pH}_2O) \text{ is known to be one of the most important parameters to decide the decomposition mechanism of CaSO}_4. \\
\text{Since steam was also present under reducing atmosphere in this study, although the amount was very small, CaSO}_4 \text{ could be observed in the system after the reduction. No new Ca–Fe-based oxide or other reaction product was observed in the experiments, which is also consistent with the results provided by Thermodynamic Equilibrium Calculations (TEC).}
\end{align*}
\]

Figure 3. XRD patterns of the mixtures of iron oxygen carriers and Ca salts after the oxidation. The chemical formula of the calcium salt is used for the identification of the respective product diffraction data.
Ca- or Mg-based salts as described in the Materials and Methods section, were studied. The detailed chemical composition that was used to prepare the synthetic ash can be found in Section 4. The experimental results can be found in Figure 6 for the reduction experiments, and in Figure 7 for the oxidation experiments. In addition to this, thermodynamic calculation results are given in Table 5 for comparison between the experimental results and theoretical equilibrium compositions. The most significant result was the formation of Ca–Fe-based oxides in the cases where only Ca-based salts (combination of Ca carbonate, chloride, nitrate, phosphate, and sulfate) were used as a salt component of the synthetic ash. The formation of Ca–Fe-based oxides was observed both under reducing and oxidizing atmospheres, even though there was no such formation indicated by TEC results. Along with Ca–Fe oxides, calcium silicate and calcium aluminum silicate formation were also observed, which is very common to form during the combustion of biomass fuels. When the combination of Mg-based salts was used in the synthetic ash, there was no formation of Mg–Fe oxides observed. This result is important since it shows that there was no direct chemical interaction between the Mg-based salts and the Fe oxygen carrier. However, a harsher agglomeration occurred than in the case of Ca compounds, most likely due to the lower melting temperatures of the Mg salts than those of the Ca salts. Except the formation of Ca–Fe oxides, there was no problematic new solid-phase formation observed, which may cause deactivation of the oxygen carriers.

The thermodynamic calculation results differed from the experimental results for both reducing and oxidizing atmospheres. This may be expected since the volatile species are assumed to stay in the system in the theoretical modeling of the systems. However, the flowing gas in the experimental system (air for the oxidation experiments and H₂/Ar/H₂O mixture for the reduction experiments) can sweep away the volatile species (mainly easily volatilized salts in this work) and change the chemistry. In addition to this, XRD has a detection limit around ca. 1–2% by volume, and this limit depends on the density, atomic number of the elements in the sample, and the crystal structure of the present phases. If the amount of the phase is lower than this limit, the peaks belonging to the phase will not be detected in the diffraction pattern or will remain under the background.

Another important information that these experiments can give is where in or on the oxygen carrier particles the Ca- and Mg-based species are located. The formation of bridges consisting of more or less melted silicates between oxygen carrier particles causes serious agglomeration problems in the CLC process. Therefore, the elements and compounds that may contribute to such bridge formation in the reaction systems studied here were investigated more in detail. To reveal the independent effects of Ca- or Mg-based salts in the synthetic ash, elemental mapping by scanning electron microscopy—energy-dispersive X-ray spectroscopy (SEM–EDX) was made of the samples after the redox experiments. Figure 8 shows the elemental mapping and SEM micrograph of the cross section of the sample consisting of Ca-salt-based synthetic ash and iron oxide after the experiment. An agglomerated oxygen carrier particle was chosen here. It was found that a silicon dioxide particle was stuck to the iron oxide via a bridge phase of the type which was mentioned before. The silicon oxide was surrounded by a thin layer containing K and Ca. This layer most likely belongs to a potassium silicate—
potassium calcium silicate mixture phase, which is the common phase where the ash contains a high amount of Ca. Moreover, the outer layer of the bridge phase, which was closer to the iron oxides, consisted of Na, P, and Ca, which indicates the formation of an alkali phosphate. The most significant effect of Ca-based salts in this case was the formation of Ca−Fe oxides, which could easily be observed in the elemental mapping. When the same analysis was carried out for Mg-based ash, the results were significantly different (Figure 9). A silicon-rich particle was stuck to the iron oxide like in the Ca case; however, there was no relation between the outer phase layer of the silicon-based particle and Mg. As expected, potassium silicate was the bridge phase, which caused the agglomeration of the oxygen carrier. Moreover, there was no correlation between Mg and Fe oxides, which was different from the Ca case. To verify this distinctive interaction mechanism between Fe oxides and Ca- or Mg-based salts, one more experiment was carried out. In the experiment, Fe oxygen carriers were mixed with a synthetic ash consisting of both Ca- and Mg-based salts. A significant agglomeration was observed in the mixture, which was expected due to the use of both Ca- and Mg-based salts along with alkali metal compounds (Figure 10). Silicon oxide particles were observed within the darker parts of the cross section and found to be attached to the iron oxides. Fe oxides were surrounded by Ca- and Na-based oxides along with Si. However, there was no significant interaction observed for the interaction of Mg and Fe oxides. Likewise, there was no similar interaction observed between Mg or Ca with other ash-forming matters, indicating selective phase formation. This result was quite surprising since Ca- and Mg-based salts are supposed to interact within a similar interaction mechanism with the other ash-forming matters.

To summarize the overall effect of the Ca-/Mg-based salts on the iron oxygen carriers in a visual manner, the samples were inspected after the experiments (Table 6). The inspection was based on the visually observable agglomeration behavior, and the effect was graded according to how easy or difficult it was to remove the samples from the crucibles after the experiments. It is known that some agglomeration can break down within the redox cycles, or the formed melt phase may affect the other phases rather than the oxygen carriers. In our experiments, some samples were stuck to the crucible due to the interaction between alkali metal salt melts and the crucible material. Therefore, it was difficult to measure the agglomeration of the oxygen carriers without the possibility to measure the surface area of the particles. Among Ca-based compounds, CaCO₃, Ca(NO₃)₂, and Ca₃(PO₄)₂ showed the

| magnesium salts | oxidation Fe₂O₃ as starting material | reduction Fe₂O₃ as starting material | visual inspection | thermodynamic calculations |
|-----------------|-------------------------------------|-------------------------------------|------------------|---------------------------|
| MgCO₃           | Fe₂O₃                               | Fe₂O₃                               | high-grade agglomerates | Fe₂O₃ Fe₂O₃ |
|                 |                                    | Fe₂O₃                               | amorphous phase    | MgO Mg₂Fe₆O₁₃ x < 2       |
| MgCl₂           | Fe₂O₃                               | Fe₂O₃                               | low-grade agglomerates | Fe₂O₃ Fe₂O₃ |
|                 |                                    | Fe₂O₃                               |                  | MgO Mg₂Fe₆O₁₃ x < 2       |
| Mg(NO₃)₂        | Fe₂O₃                               | Fe₂O₃                               | high-grade coarse agglomerates | Fe₂O₃ Fe₂O₃ |
|                 |                                    | Fe₂O₃                               |                  | MgO Mg₂Fe₆O₁₃ x < 2       |
| Mg₃(PO₄)₂       | Fe₂O₃                               | Fe₂O₃                               | high-grade coarse agglomerates | Fe₂O₃ Fe₂O₃ |
|                 |                                    | Fe₂O₃                               |                  | MgO Mg₂Fe₆O₁₃ x < 2       |
| MgSO₄           | Fe₂O₃                               | Fe₂O₃                               | high-grade coarse agglomerates | Fe₂O₃ Fe₂O₃ |
|                 |                                    | Fe₂O₃                               |                  | MgO Mg₂Fe₆O₁₃ x < 2       |
The harshest agglomeration effect on the Fe oxygen carriers. When the surface area analysis was carried out, the smallest surface area was obtained for the sample consisting of Ca₃(PO₄)₂ and Fe oxygen carriers. Based on the results, Ca-based compounds reduced the surface area of the oxygen carriers 13.3−50.6% from the surface area 4.21 m²/g of the pure Fe oxygen carriers.

Table 5. Obtained Results of Interaction between Fe Oxygen Carriers and the Synthetic Ash Containing either Ca- or Mg-Based Salts as Alkali Earth Content

| used salt combination | experimental results | visual inspection | thermodynamic calculations |
|-----------------------|----------------------|------------------|-----------------------------|
| Ca-based              |                      |                  |                             |
| Fe₂O₃                 | Fe₂O₃                | severe agglomerates | Fe₂O₃                      |
| Ca–Fe oxides          | Fe₂O₃                |                  | Ca₃Si₂O₆                   |
| Ca₂SiO₄               | Ca–Fe oxides         |                  | CaFe₂O₄                    |
| SiO₂                  | Ca–Al–Si oxides      |                  | K(Na)Al₃O₄                 |
| Ca–Al–Si oxides       | SiO₂                 |                  | K₂SO₄                      |
| Al–Si oxides          | amorphous phases     |                  | K(Na)Al₃SiO₄               |
| Mg-based              |                      |                  |                             |
| Fe₂O₃                 | Fe₂O₃                | severe agglomerates | Fe₂O₃                      |
| Fe₃O₄                 | MgSiO₃               |                  | MgSiO₄                      |
| Al₂SiO₅               | Mg₂SiO₄              |                  | NaAlSiO₄                    |
| MgAl₂O₄               | Mg–Al–Si oxides      |                  | KCl (liq.)                  |
| SiO₂                  | Al–Si oxides         |                  | Na₂PO₄                      |
| amorphous phases      | Mg₈₋₆Al₆O₆, x < 0.5 SiO₂ |            | K₂SO₄                      |

Figure 8. SEM micrograph (BSE) and elemental mapping of the cross section of the sample consisting of Ca-salt-based synthetic ash and iron oxide after the experiment.
The results were similar for Mg-based compounds; however, MgCO3 showed a milder effect on the Fe oxides than CaCO3 did. Mg(NO3)2 and Mg3(PO4)2 showed the highest decrease of the surface area. Interactions between the Fe oxides and these salts reduced the surface area of the oxygen carriers by 48.2−59.4%.

When the agglomeration effect of Ca- or Mg-based synthetic ashes was investigated, the ash consisting of Mg-based salts was found to be more aggressive than that containing Ca-based salts. From this point of view, a biomass containing a large amount of Mg, N, and P such as algae or some agricultural residues may not be the best candidates to be used as a fuel, where the Fe-based oxides will be used as the oxygen carriers. It is worth noting that a biomass containing a large amount of Ca could also create problems, since the reactivity of the oxygen carriers may decrease due to the formation of Ca−Fe-based solid compounds. However, some of the Ca−Fe-based reaction products, particularly Ca2Fe2O5, have been reported to be promising oxygen carriers for fuel conversion, so the formation of new compounds may also be positive.

3. CONCLUSIONS

In the study, the interaction between Fe oxides and alkaline-earth-based ash-forming matters was investigated to distinguish the different effects of Ca- and Mg-based salts. Iron oxide, one of the most used oxygen carriers, was used as an oxygen carrier, and a biomass composition was targeted to simulate the biomass-derived ash. It is vital to understand the nature of interaction between the ash-forming matters and oxygen carriers, since ash-forming matters may result in the deactivation of the oxygen carriers. There are a lot of studies focused on this interaction; however, these are mostly related to the alkali-metal-based ash-forming matters, since the alkali metal compounds can cause serious agglomeration issues due to the silicate-based formations. Alkaline earth species can also contribute to complex silicate phase formations, such as calcium or magnesium silicates. Moreover, recent studies reported that Ca- and Mg-based species may have different impacts on the oxygen carriers, even though they are supposed to have a similar chemical nature. This study presents only the effect of Ca/Mg-based ash-forming matters on the Fe oxides. Thermodynamic calculations were also carried out to reveal the possibly formed phases under the equilibrium conditions. The resulting phases provided by the calculations were consistent with those found in the experiments. This consistency is very important when an oxygen carrier would be chosen for a defined type of fuel, as the ash composition of fuels varies. The most significant result of the study was the formation of Ca−Fe-based oxides, when the synthetic ash consisting of Ca-based salts was used in the experiments. However, no formation of salt consisting of Fe and Mg oxides was observed, where the Mg-based salts were used as ash-forming matters in the experiments. The harshest salts in terms of the agglomeration were carbonates, nitrates, and phosphates. Their one-to-one interaction with the oxygen carriers resulted in serious agglomerations. In addition to this, the use of Mg-based salts in the synthetic ash caused more serious agglomeration than the use of Ca-based salts.
4. MATERIALS AND METHODS

The starting materials were provided by Alfa Aesar as pure Fe$_2$O$_3$ and Fe$_3$O$_4$. Ash-forming matter representatives (Ca and Mg compounds) were all provided by Sigma-Aldrich. The iron-based oxygen carriers were prepared by the wet granulation technique to provide particle size distributions that are normal for oxygen carrier materials. The prepared oxygen carrier particles were then sieved to the size range of 125–180 μm. Hydroxides, chlorides, carbonates, nitrates, phosphates, and sulfates of Ca and Mg were used to represent ash-forming matters from the fuel. The mixtures consisting of Fe oxygen carriers and alkaline earth compound representatives were prepared to reveal the one-to-one interactions between the oxygen carriers and the model ash compounds. A previous experiment was taken as a reference to decide the composition of the mixtures. A representative sample was taken from the partially sintered body for BET analysis.

**Table 6. Summary of Visual Inspection/Surface Area of the Samples after Experiments**

| used compound in Fe oxides-ash-forming matter-based mixture | oxidation | reduction | surface area (m$^2$/g) |
|------------------------------------------------------------|-----------|-----------|------------------------|
| Ca(OH)$_2$                                                 | 3         | 4         | 3.54                   |
| CaCO$_3$                                                   | 2         | 1         | 3.09                   |
| CaCl$_2$                                                   | 2         | 2−3       | 3.16                   |
| Ca(NO$_3$)$_2$                                              | 1         | 2         | 2.11                   |
| Ca$_3$(PO$_4$)$_2$                                         | 1         | 2         | 2.08                   |
| CaSO$_4$                                                   | 2         | 4         | 2.84                   |
| Mg(OH)$_2$                                                 | 4         | 4         | 3.68                   |
| MgCO$_3$                                                   | 2         | 3         | 3.16                   |
| MgCl$_2$                                                   | 3         | 4         | 3.51                   |
| Mg(NO$_3$)$_2$                                              | 2         | 1         | 2.18                   |
| Mg$_3$(PO$_4$)$_2$                                         | 2         | 1         | 2.09                   |
| MgSO$_4$                                                   | 2         | 2−3       | 3.03                   |
| Ca-based synthetic ash                                      | 0         | 1         | 0.41                   |
| Mg-based synthetic ash                                      | 0         | 0         | 0.38                   |

1: High amount of coarse agglomerates. 2: Low amount of coarse agglomerates. 3: High amount of small agglomerates. 4: Low amount of small agglomerates. 0: Partially sintered. A representative sample was taken from the partially sintered body for BET analysis.

**Figure 10.** SEM micrograph (BSE) and elemental mapping of the cross section of the sample consisting of both Ca- and Mg-salt-based synthetic ash and iron oxide after the experiment.

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| Ca$_3$(PO$_4$)$_2$                                         | 1         | 2         | 2.08                   |
| CaSO$_4$                                                   | 2         | 4         | 2.84                   |
| Mg(OH)$_2$                                                 | 4         | 4         | 3.68                   |
| MgCO$_3$                                                   | 2         | 3         | 3.16                   |
| MgCl$_2$                                                   | 3         | 4         | 3.51                   |
| Mg(NO$_3$)$_2$                                              | 2         | 1         | 2.18                   |
| Mg$_3$(PO$_4$)$_2$                                         | 2         | 1         | 2.09                   |
| MgSO$_4$                                                   | 2         | 2−3       | 3.03                   |
| Ca-based synthetic ash                                      | 0         | 1         | 0.41                   |
| Mg-based synthetic ash                                      | 0         | 0         | 0.38                   |

1: High amount of coarse agglomerates. 2: Low amount of coarse agglomerates. 3: High amount of small agglomerates. 4: Low amount of small agglomerates. 0: Partially sintered. A representative sample was taken from the partially sintered body for BET analysis.

Despite the fact that the ratio of the oxygen carrier to fuel-derived ash is higher in a real application, the mixture was prepared with a higher ash amount to represent the worst-case scenario for the oxygen carrier. Åbo Chemical Fractionation Database and the related studies were taken as a reference to determine the composition of the salt representatives in the synthetic ashes. The chemicals were mixed in an agate mortar with a pestle. To obtain a homogeneous mixture, acetone was used as a dispersing agent and the materials were mixed until a dry mixture was obtained.

**Figure 10.** SEM micrograph (BSE) and elemental mapping of the cross section of the sample consisting of both Ca- and Mg-salt-based synthetic ash and iron oxide after the experiment.
Table 7. Chemical Composition of the Synthetic Ashes

| compound                        | amount (wt %) |
|---------------------------------|---------------|
| SiO₂                            | 31            |
| combination of Ca⁺⁺ or Mg-based salts   | 36            |
| KOH                             | 12.5          |
| NaOH                            | 12.5          |
| Al₂O₃                           | 4             |
| Fe₂O₃                           | 2             |
| MnO                             | 1             |
| TiO₂                            | 1             |

“The mixture consists of an equivalent amount (∼7.2 wt % of each) of CaCO₃, CaCl₂, Ca(NO₃)₂, Ca₃(PO₄)₂, and CaSO₄. The mixture consists of an equivalent amount (∼7.2 wt % of each) of MgCO₃, MgCl₂, Mg(NO₃)₂, Mg₆(PO₄)₂, and MgSO₄.

The oxidation experiments took place in a tube furnace where an air atmosphere was used to simulate the air reactor, and a tube furnace was also used for the reduction experiments with reducing atmosphere consisting of 5 vol % H₂ in Ar together with steam (50 vol %). The mixtures consisting of the oxygen carriers (Fe₂O₃ for reduction experiments and Fe₃O₄ for oxidation experiments) and one of the alkaline earth compound representatives were inserted in an alumina crucible, and heat treatments were carried out at 950 °C for 5 h. The same procedure was also performed for the synthetic ash/oxygen carrier mixtures. The gas flow rate was applied as 100 mL/min, and the heating/cooling rate was set to 10 °C/min in each experiment.

The samples obtained after each experiment were analyzed by X-ray diffraction (XRD) for identification of crystalline compounds. A Bruker D8 diffractometer was used with the characteristic Cu Kα radiation and settings 40 kV, 40 mA to collect diffraction data in the 2θ range of 15–80° with a step size of 0.01. Elemental mapping by scanning electron microscopy (SEM)—energy-dispersive X-ray spectroscopy (EDX) (JEOL JSM-7800F Prime) was also used to localize Ca and Mg compounds in the sample particles. Cross sections of the agglomerated particles were investigated via elemental mapping to reveal the agglomeration formation mechanism. To be able to see the cross section, the particles were embedded in an epoxy mold and the surface of the epoxy was polished to create a cross section. The specific surface area, as measured by BET-Micromeritics TriStar 3000, along with visual inspection of the mixtures after the experiments was also used to determine the extent of agglomeration.

FactSage 7.2-Equilibrium/Reaction Modules were used to evaluate the thermodynamic equilibria. The calculations were performed for 950 °C, and Pure Substance (FactPS)-Oxide (FToxid) databases were used under the presumption of an isothermal and standard state. The Gibbs energy minimization method was applied for the equilibrium module calculations. Calculated gaseous species present at less than 0.001 mol were ignored for the sake of simplicity. When the TEC results were reported in this study, only the phases that were present in amounts higher than 2.5 wt % in the resulting mixture were taken into consideration for both the sake of clarity and simplicity. This also helped us to compare the TEC with the experimental results.

**AUTHOR INFORMATION**

**Corresponding Author**

Duygu Yilmaz — Chemistry and Chemical Engineering, Chalmers University of Technology, 412 96 Gothenburg, Sweden; orcid.org/0000-0002-4142-4788; Email: duygu@chalmers.se

**Authors**

Britt-Marie Steenari — Chemistry and Chemical Engineering, Chalmers University of Technology, 412 96 Gothenburg, Sweden

Henrik Leon — Chemistry and Chemical Engineering, Chalmers University of Technology, 412 96 Gothenburg, Sweden; orcid.org/0000-0002-9716-2553

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02138

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was carried out with funding from Swedish Research Council, project “Biomass combustion chemistry with oxygen carriers”, contract 2016-06023.

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