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Use of natural ores as oxygen carriers in chemical looping combustion: A review

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Abstract

Chemical looping combustion (CLC) has gained considerable ground in energy production due to its inherent carbon capture with a minimal energy penalty. The choice of metal oxide used as an oxygen carrier (OC) in CLC has a substantial weight on the overall efficiency of energy production as well as the ultimate cost per MW. While much work has gone into manufacturing synthetic OCs with high fuel conversions, harsh operating conditions and process limitations cause some unavoidable loss of the oxygen carrier. With low production costs and minimal conditioning required, natural ores have grown in interest as cheap alternative oxygen carriers. This work provides a substantial literature review of recent works studying the use of natural ores in CLC. Iron-based, manganese-based, copper-based and calcium based ores were found to be the main ores researched, along with mixtures of these ores and natural ores with minor additional compounds. Typical parameters have been collected for each study including; fuel conversion, stability, physical characteristics, and carbon capture efficiency. Natural ores are compared with purified metal oxides to highlight strengths and weaknesses of each ore and recommendations for future studies are made.

Keywords: Chemical looping combustion, Sustainable energy, Carbon capture, Natural ore, Oxygen carrier

1. Introduction

Chemical looping combustion (CLC) is one method of electricity generation being developed to address the concerns of growing levels of atmospheric CO₂. CLC is a unique form of fuel combustion that can use most fuels (renewable or fossil based) and exhibits inherent CO₂ capture. CLC utilizes the redox cycle of a metal oxide to split the combustion reaction into two distinct processes; fuel combustion and metal oxide reformation. Oxygen required for the combustion of fuel is supplied by a metal oxide

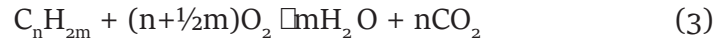
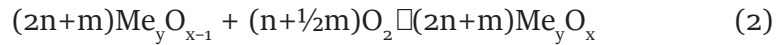
oxygen carrier (OC) rather than air, preventing the dilution of the flue gas with atmospheric N_2 . Hence the off gas from combustion contains primarily CO_2 and water vapor which, after condensation, can produce a nearly pure CO_2 stream for sequestration. The second step of the cycle reforms the metal oxide by reaction with air.

The center of this process is the metal oxide itself. Important considerations are required in the choice of oxygen carrier in CLC including fuel conversion potential, recyclability through multiple redox cycles, mechanical strength, fluidization properties, environmental impact, and also importantly cost. There has been much research into the methods of OC technology to provide improved reaction and mechanical properties. However many of these methods increase production costs for the OC and therefore decrease the economic feasibility of such systems (Porrizzo et al., 2016; Abad et al., 2007). The use of raw metal ores has been investigated by numerous groups as a method of providing a readily available and cheap oxygen carrier for the chemical looping process (Demirel et al., 2015; Wang et al., 2015a; Adanez et al., 2012; Imtiaz et al., 2013). The objective of this paper is to compile the latest work involving the use of natural ores as OCs in CLC processes. We provide an updated literature review of iron, copper, manganese and calcium based ores that have been studied for their use in CLC. A comparison of the results found for these different ores is conducted and compared to conventional (purified) metal oxide OCs. This work may provide a better understanding of ore use in CLC, clarify current research demands and help distinguish the benefits of certain ores in comparison with purified metal oxides.

2. Background

2.1. Chemical looping combustion

Chemical looping combustion is a novel method of energy production that modifies conventional fuel combustion to inherently include carbon capture. This modification comes from the utilization of a metal oxide (MeO) as the source of oxygen in the combustion reaction. The use of this metal oxide oxygen carrier effectively splits the combustion reaction into two major steps and couples it to the reduction-oxidation cycles shown in Reactions (1) and (2), respectively.



Reaction (1) is usually an endothermic reaction ($\Delta H_1 > 0$); however, it can be either exothermic or endothermic depending on the choice of metal oxide and fuel used. Reaction (2) is highly exothermic ($\Delta H_2 \ll 0$). The net reaction of an entire cycle is simply a conventional combustion reaction (Reaction (3)) and is highly exothermic ($\Delta H_1 + \Delta H_2 < 0$). Fig. 1 shows a schematic for use of chemical looping technology in electricity production. Most CLC processes utilize fluidized bed technologies to mix the OC and the fuel. Fixed bed reactors with periodically changing feed streams as seen in Fig. 1b are also considered. These reactors contain the mixed OCs with fuel (Noorman et al., 2007). For solid fuels atmospheric operation is common, although some CLC units have been operated under pressurized conditions (Xiao et al., 2012). The flue gas from the fuel combustion in fuel reactor contains primarily CO_2 and H_2O without nitrogen. A gas cleaner can be used, as gases exiting the fuel reactor can include unburnt compounds (CH_4 , CO , H_2) from incomplete combustion of the fuels.

Gaseous fuel is easier to work with in CLC because it produces very little char, no ash and does not require solid-solid separations. However the large supply of coal dictates that investigation into CLC with solid fuels is also important. Indeed, the use of solid fuels has extended during the last years, and an extensive work has been done in the use of solid fuels (Demirel et al., 2015; Wang et al., 2015a; Adanez et al., 2012). When using gaseous fuels, the fuel can be fed directly to the fuel reactor as the fluidization agent. However with solid fuels three schemes are applied; *ex-situ* gasification (eG-CLC), *in-situ* gasification (iG-CLC), and chemical looping with oxygen uncoupling (CLOU). eGCLC involves the gasification of the solid fuel outside of the loop. The resultant gasification products are fed to the FR and combusted. iG-CLC involves a direct feed and gasification of the solid fuel in the fuel reactor and fluidization through the addition of steam, CO_2 or a mixture of these gases. CLOU uses unique OCs that readily release gaseous oxygen and rather than gasifying with additional CO_2 or steam, gasification takes place in the FR using this released O_2 (Adanez et al., 2012; Imtiaz et al., 2013; Mattisson et al., 2014; Cormos, 2017). While each of these processes has strengths and weaknesses the

real task in the CLC process is carried out by the oxygen carrier itself. Fuel conversion, reoxidation ability, kinetics, thermodynamic limitations, char conversion etc. all depend of the choice of the metal oxide used as an oxygen carrier in the process.

2.2. Oxygen carriers

Ryden et al. (2010) presents some characteristics of good oxygen carriers as follows; OCs must have a high reactivity towards fuels (solid, CH_4 or syngas), be thermodynamically capable of converting fuels to CO_2 and H_2O , have a high oxygen transport capacity, have positive physical characteristics (low attrition/fragmentation, low agglomeration), be thermally stable, prevent carbon formation in the fuel reactor, be environmentally sound and be cost effective. In order to meet these characteristics, many metal oxides have been tested (Adanez et al., 2012). Most OCs consist of metal oxides such as CuO , Fe_2O_3 , NiO , Mn_3O_4 or CoO . However, the MeOs in their pure state normally have poor stability and mechanical properties. Therefore they are typically bound to inert supports such as Al_2O_3 , MgAl_2O_4 , SiO_2 , TiO_2 , ZrO_2 or stabilized ZrO_2 , which improve the physical characteristics of the pure metal oxide. Additional modifications can also be made to oxygen carriers to further increase its ability to perform in the CLC process. These include spray-drying or impregnating OCs with additional compounds or metal oxides that can benefit the OC (Mattisson et al., 2014). A variety of methods of synthesis including sol-gel, mechanical mixing and combustion synthesis have been explored to further improve the lives and properties of artificial oxygen carriers. However, with each additional step and modification the cost of producing the metal oxide may increase. With inevitable losses due to attrition, fragmentation, deactivation and OC/ash separation losses the cost of the metal oxide replacement can be a contributing factor to the overall economic feasibility of a CLC process (Porrizzo et al., 2016). It is obvious that a balance between processing cost and make-up cost must be achieved to yield an economically viable CLC OC. It is for this reason that many researchers have begun exploring cheap alternative OCs. Raw metal ores are a natural choice for this alternative OC. While likely not as stable (and requiring higher make-up costs) natural ores present a cheap alternative to synthetic OCs requiring little processing cost. Natural ores contain metal oxides and most are inherently bound to materials like Al_2O_3 , TiO_2 and ZrO_2 much like supported synthetic OCs. This allows them to operate in CLC processes

with the added physical toughness of supported materials without costly manipulations. The pretreatment of natural ores used as OCs consists of only crushing, sieving and calcination. Some ores contain trace amounts of compounds that have shown catalytic effects in char gasification, water gas shift promotion and gas conversions.

As a member of oxygen carriers family, natural ores attract more and more attention in the CLC systems due to its vast resources and cheap price compared with the conventional oxygen carries. Basically, oxygen carriers must have some crucial characteristics such as high fuel conversion to CO_2 and H_2O in CLC, resistance to attrition, high or acceptable oxygen transport capacity and so on. As an oxygen carrier, the ability of transporting oxygen is the most considerable. Oxygen transport capacity is the factor that describes an oxygen carrier's ability of carrying the oxygen in a CLC process.

Oxygen transport capacity (R_{O_2}) can be defined by Adanez et al. (2012)

$$R_{\text{O}_2} = w_{\text{OC}} R_{\text{O}} \quad (4)$$

where, w_{OC} is the fraction of active material for oxygen carrier and R_{O} is called the oxygen transport capability which is defined as

$$R_{\text{O}} = (m_{\text{o}} - m_{\text{r}})/m_{\text{o}} \quad (5)$$

where m_{o} and m_{r} are the mass of fully oxidized and reduced OC, respectively. The value of R_{O_2} depends on the final oxidation state after reduction.

In general, the oxygen transport capacity of natural ores is not higher than that of conventional oxygen carriers. The reason is that there are considerable amounts of impurities in the natural ores. However, considering the pre-treatment of conventional oxygen carriers and the cost, natural ores are still highly competitive. On the other hand, most natural ores contain more than one active compound. In that case, the oxygen transport capacity can be achieved by simply adding the R_{O_2} of each active compound in the mixed natural ores.

Below we present the results of a comprehensive literature search into the use of natural ores in chemical looping combustion processes. We present results from numerous studies showing the ability for ilmenite, iron ores (hematite, wustite, etc.), manganese ores, copper ores and calcium ores to perform in CLC operations. We also discuss the use of mixed ore systems and the addition of minor compounds to ores for further enhanced performance.

3. Natural ores as oxygen carriers

Natural ores contain valuable elements especially including metals. Abundant ore resources makes them easily attained at a minor cost. With the considerable content of metal oxides and the acceptable price, natural ores can be competitive when compared with traditional oxygen carriers. Table 1 gives some natural ores with active components listed. The active components of an ore vary based on mining site and ore quality. Based on the active metal components, natural ores can be divided by different species. Iron-based, manganese-based, copper-based, calcium-based and mixed ores are the most commonly studied examples for oxygen carriers.

3.1. Iron-based ores

3.1.1. Ilmenite

Ilmenite is a naturally occurring important ore of titanium, with an idealized composition of FeTiO_3 . On an oxygen carrier basis it can be comparable to an iron oxide fixed to a titanium support. Its most commercial use is in the production of titanium and titanium oxides. Ilmenite is one of the most studied and used minerals as an OC. Its support can be linked to its low cost, \$165/ton (2014) and high crush strength (Azis et al., 2010; Liu et al., 2013; Leion et al., 2009a; Bedinger, 2015). Ilmenite is nontoxic, radioactive or hazardous and its only environmental impact would come from its mining operation (Moldenhauer et al., 2012). It is mined in two forms, mineral sands and hard rock and is found nearly everywhere in the world with most production coming from Australia, South Africa, China and Canada (Bedinger, 2015). Minor modifications are required to natural ilmenite ore before use as an OC. Besides crushing, ilmenite must be calcined before use which brings it to its fully oxidized state. Most procedures include a prolonged heating of the ore (900–1200 °C) in air. This has also been shown to reduce sulfur emissions from the ilmenite in CLC operation (Schwebel et al., 2012). However even in its raw state ilmenite can be used as an oxygen carrier (Azis et al., 2010; Leion et al., 2009a; Adanez et al., 2010).

In terms of stability, ilmenite performs rather well. Interestingly even after calcination, it shows an increased activation after multiple redox cycles in many studies. This improved activation typically stabilizes after several cycles and reaches a maximum value (Cuadrat et al., 2012a).

This activation is associated with an increased porosity of the particles over multiple cycles (Schwebel et al., 2012; Adanez et al., 2010; Cuadrat et al., 2012a, 2011a). While this porosity does improve fuel conversions it could lead to a diminished particle strength, eventually causing attrition. However this effect has yet to be fully studied (Leion et al., 2009a). There has been some concern of a decreased oxygen transport capacity (R_{O_2}) with multiple cycles (Adanez et al., 2010; Cuadrat et al., 2012a, 2011c). This has been attributed to a segregation of the Fe from the TiO_2 and a shell of iron being formed along the perimeter of the particles. R_{O_2} values have shown to decrease from 4 to 2.4 after 100 cycles. Even with this decrease, the values of oxygen that can be transferred to the fuel reactor are still high enough to provide sufficient fuel conversions (Cuadrat et al., 2012a).

Ilmenite shows a higher activity for H_2 conversion than CO conversion but typical syngas conversions are between 90 and 99%. Results show that higher amounts of iron in the mineral may cause improved CO conversions (Azis et al., 2010). Rock based minerals are found to exhibit higher fuel conversions when compared to sand based ilmenite. Rock ilmenite was also found to be more stable and exhibit less agglomeration (Cuadrat et al., 2011c). CH_4 conversions of ilmenite are low for most studies (Leion et al., 2009a; Proll et al., 2009). The conversion of solid fuels varied from study to study and largely depended on experimental reactor setups and operating conditions. The limiting factor in most solid fuel operations is conversion that can be improved at suitable operating conditions or highly reactive fuels (Cuadrat et al., 2012b). In other cases, high fuel conversion values can be achieved by using a carbon stripper in the CLC unit (Markstrom et al., 2014). After the conversion from solids to gas, ilmenite performs very similarly to combustion using previously prepared syngas (Bidwe et al., 2011). Higher conversions were observed for higher temperatures in many studies, leading to reduced oxygen demands and increased carbon capture efficiencies (CCE) (Cuadrat et al., 2011c; Bidwe et al., 2011; Berguerand and Lyngfelt, 2009). This was attributed to increased gasification rates and higher char conversions at increased temperatures (Cuadrat et al., 2011a; Berguerand and Lyngfelt, 2009). Numerous studies have been found detailing the use of ilmenite as an oxygen carrier in CLC operations. These studies present a variety of reactors, operating conditions, fuels and ores. A collection of results from these works can be found in Table 2.

3.1.2. Hematite and other iron ores

The majority of iron ore comes from different mines in China, Australia and Brazil and is typically used in steel making. Current costs for iron ore vary based on location but a typical value is around \$92.78/ ton. Different mines produce ore with different compositions and impurities but iron ore is mainly composed of the iron oxides, Fe_2O_3 and Fe_3O_4 . Major impurities are SiO_2 , Al_2O_3 and dolomite. These impurities are largely responsible for the improved mechanical properties when compared to pure iron oxides and ilmenite (Song et al., 2012; Jerndal et al., 2011). Much like ilmenite, iron ore typically performs better when calcined at high temperatures before use. The temperature of calcination was cited to be of high importance in Song et al. (2012), however many different calcination temperatures (900–1000 °C) have shown comparable results.

Before discussing different studies it is important to clarify that due to the inherent differences in individual iron ores, results vary between studies. Even so, general inferences can be made about the feasibility of using iron ores as OCs in CLC. The reaction stability of iron ores is slightly less than that of ilmenite. Some samples show similar increases in reactivity with redox cycles which was again attributed to porosity increases in the OC (Gu et al., 2011; Xiao et al., 2010a). However decreases in porosity and surface area were also observed for other ores (Karlsson, 2014; Pans et al., 2015). Agglomeration was not found to be an issue for any of the studies found however attrition of the ore was observed in many works. Although, the iron ore particles maintained their particle size without agglomeration, the particles become more porous due to thermal stress and repeated oxidation/reduction cycles (Gu et al., 2011). Attrition rates of 0.05–0.12 wt%/h were observed (Song et al., 2012, 2013; Pans et al., 2015). However these low rates are not substantial due to the low cost of iron ore.

Iron ore typically has low oxygen transport capacity and thermodynamic constraints (Gu et al., 2011). In general though the combustion efficiency of iron ores is rather high, even when using solid fuels. Like ilmenite, increasing the temperatures of the fuel reactor helps to improve carbon capture efficiency and conversion. An added benefit of the SiO_2 impurities in iron ore is the inhibition of sintering at higher temperatures. This allows operations at >900 °C without much observed sintering (Song et al., 2012; Gu et al., 2011). An increased operational pressure was also found to beneficially effect the conversion rates of solid fuels (Xiao et al., 2012, 2010a). One major issue in using iron ore is its low reactivity for combusting CH_4 . A highly reactive iron ore is suitable to burn syngas, but

not methane (Pans et al., 2015). Therefore any CH_4 present from the solids volatilization and gasification or the natural gas would cause fuel conversion issues. Results on the general use of iron ores as OC from literature can be found in Table 3.

3.2. Manganese-based ores

Manganese oxides are considered relatively safe, with respect to handling and the environment compared to nickel and cobalt. They are also considered a cheap and abundant class of materials, and has a greater oxygen carrying capacity than iron redox systems. Typical manganese ores contain about 30–60% manganese in oxide form, Mn_2O_3 . The major impurities of Mn ore are iron, alumina and silica but these vary greatly from mine to mine. These impurities could play a large role in the properties of the OC due to their ability to combine and form additional OC materials (Sundqvist et al., 2015). The majority of manganese ore is mined in China, South Africa, Australia, Gabon and Brazil. Most U.S. consumption of manganese (80–90%) is in the production of steel however it is also used in solid state batteries. Current market prices for metallurgical-grade ore (46–48% manganese) are around \$4.61/mt, making it a very cheap alternative OC (Corathers, 2016). The ore can be used in its natural state or calcined before use, the effect this has on OC performance has not been addressed.

Manganese ores show great conversion of syngas with most conversion being 95–100% (Leion et al., 2009a; Sundqvist et al., 2015; Arjmand et al., 2014). It was found that higher potassium impurities led to a diminished gas conversions, however this was not distinctly proven (Arjmand et al., 2014). Mn OCs typically show low conversions of CH_4 . However Mn ore shows mixed conversions of CH_4 likely due to impurity differences, with max conversions approaching 80% (Sundqvist et al., 2015). While this value is still not complete combustion, additional conversions could be achieved by optimizing reactor temperatures or by increasing OC loading (Moldenhauer et al., 2012). Fuel conversions of solid fuels were also very high for all studies. This has been attributed to two distinct mechanisms; O_2 released from the Mn_3O_4 at high temperatures and catalysis of char conversion by ore impurities. Pure manganese oxygen carriers have shown the ability to perform in chemical looping oxygen uncoupling (CLOU) schemes in which fuel combustion occurs as a result of the release of gaseous oxygen from the OC. Mn ore was shown to have some

CLOU properties, however to a lower extent than synthetic OC (Sundqvist et al., 2015). However sustained CLOU capability of Mn ore is debatable. CLOU capability is lost after the first reduction because MnO is not able to be re-oxidized to Mn_2O_3 , but only to Mn_3O_4 (Zafar et al., 2007; Mei et al., 2016). Arjamand et al. (2014) concluded that the presence of alkali particles in the ore catalytically improve the conversion of char by causing cavities and channels in the fuel. Both of these effects lead to improved gasification rates, up to 4 times as fast as ilmenite (Linderholm et al., 2013). However this catalytic effect may not be sustainable as the alkali can be lost after multiple redox cycles (Mei et al., 2016).

Most of the manganese ore studied showed relatively stable conversion performance. Some deactivation was noted however this stabilized after 10 cycles (Mei et al., 2015). This could be the result of natural MnO_2 and Mn_2O_3 being converted to Mn_3O_4 due to thermodynamic limitations at oxidation conditions. Minor sintering could also be the cause for this decrease (Sundqvist et al., 2015). Physical deterioration to the manganese ore is the main stability concern for its use as an oxygen carrier. Attrition of the OC was noted to be a large concern in most studies with the production of fines. Mei et al. (2015) noted that micropores present in the original ore were expanded into macropores, leading to a decreased crush strength. The production of fines caused by this decreased structural strength makes the use of Mn ore as an oxygen carrier less feasible. However, some Mn ores have been identified with low attrition rates, which would be beneficial in order to reduce the amount of fines produced (Schmitz et al., 2016). Even still, the low cost of the ore means that even the high loss rates observed may not hinder the economic performance of this process. A collection of results from literature can be found in Table 4.

3.3. Copper-based ores

Copper-based OCs are promising in CLC based processes as they exhibit high reaction rates and oxygen transfer capacity, with no thermodynamic limitations. Purified CuO shows promise as an OC in CLOU operations as well, as it readily releases gaseous oxygen at fuel reactor operating conditions. This ultimately leads to higher solid fuel conversion and better fuel efficiencies. Many of the studies found using copper ore were to investigate their use in CLOU applications. The majority of copper ore comes from Chile, China, Peru and the United States. Ore concentrates are a typical product of mines. These concentrates have increased copper concentrations and are produced by sulfuration and flotation. Because of this

process the natural copper and iron present in the ore are converted to CuS and CuFeS. A calcination process is done in most cases to reconvert the metals into an oxidized form, typically CuO and CuFe₂O₄ (Zhao et al., 2014). Most of the studies found used the same copper ore concentrate with a copper concentration (after calcination) of 21% CuO and 70% CuFe₂O₄, with the remainder being SiO₂, CaSO₄ and Al₂O₃. The effect of this concentration process is notable as the oxygen capacity of the ore is greatly increased. Unfortunately there exists a major lack of data from the use of other copper ores in CLC processes. The price of copper ore is likely the reason for this, the price of ore depends greatly on the fluctuating copper metal price but a value of \$1.60/kg is reasonable, making this the most expensive ore studied (Tian et al., 2015).

The higher CuO content ores typically performed better in terms of fuel conversions. These ores have very high O₂ transport capacities (Tian et al., 2015; Yang et al., 2015) as is common with CuO oxygen carriers. Zhao et al. (2015) showed that with the high CuO concentrates mentioned above reach combustion levels >95% can be achieved. Carbon capture efficiencies >80% were also found using this same concentrate in a gasification scheme to produce syngas (Guo et al., 2015). However, with lower Cu content ores, lower combustion efficiencies were found (Tian et al., 2013). Copper ores do have the potential for use in CLOU processes though. Wen et al. (2012) found that in a CO₂ atmosphere 3 distinct ores could produce O₂ efficiently, showing that even lower Cu content ores can be used in CLOU.

Purified CuO shows good stability as an oxygen carrier however due to its relatively low melting point agglomeration and sintering is a concern at high temperatures. This phenomena was observed in many studies found however only minimal agglomeration was noted (Zhao et al., 2014, 2015; Tian et al., 2015). It was also found that agglomeration could be avoided by using low CuO content ores but this would also lead to higher required OC loadings (Wen et al., 2012). Conversion stability is also somewhat of concern using copper ores. The sintering of the ore leads to decreased conversions but it was also observed that a decrease in conversions did stabilize after multiple cycles. A collection of results from numerous publications can be found in Table 5.

3.4. Natural gypsum oxygen carrier

Due to the availability of large amount of natural gypsum worldwide, it is considered widely as a low cost oxygen carrier for CLC systems. Gypsum behaves environmentally benign in the oxidized state and can

transport high level of oxygen when acting as an OC (Song et al., 2008a). The composition of gypsum is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with the active compound being CaSO_4 . A large benefit of using gypsum ore is that it naturally contains a large amount of CaSO_4 (60–70%). The main impurities in gypsum (aside from the entrained water) are SiO_2 , Al_2O_3 , CaCO_3 , MgCO_3 and Fe_2O_3 (Wilder, 1918). Again a calcination step for the ore is required to remove the water from the ore. The dehydrated gypsum ore (now primarily CaSO_4) is commonly called anhydrite but the terms have been found to be synonymous in literature. Anhydrite ore also occurs in nature but is rarer than gypsum.

The main benefit of using a gypsum OC is the large oxygen transport capacity of CaSO_4 . This reduces the required OC demand and the amount of OC required to circulate the fuel and air reactors. Information on the general use of CaSO_4 as an OC in CLC can be found in literature (Guo et al., 2012). The most prolific use of Ca based ores in CLC can be found in a 3MW, solid fuels plant by Alstom. This process uses limestone (primarily CaCO_3) converted to CaSO_4 by sulfur released from coal, thus also achieving in-situ desulphurization. The process was recently reviewed by Abad et al. (2017). The reduction kinetics of CaSO_4 with CO in a differential fixed bed is studied by Zheng et al. (2011) and Xiao et al. (2010b). Song et al. (2009) investigated a CaSO_4 oxygen carrier by thermodynamic analysis and thermogravimetric analysis. It has been proved that CaSO_4/CaS is an effective oxygen carrier in a CLC system (Moghtaderi, 2012). One main concern with CaSO_4 CLC operation is low fuel conversions (Ding et al., 2011; Zheng et al., 2014). However many studies found that increasing the fuel reactor temperature conversions can be improved to reasonable levels (Song et al., 2008a; Zheng et al., 2014; Zhang et al., 2013). The downside to this increase in operating temperatures is that the emission of H_2S and SO_2 gas from the OC become unavoidable. Low CO concentration may also increase sulfur emission (Zheng et al., 2011). This may be preventable by the addition of supplementary components as will be addressed in subsequent sections. The use of CaSO_4 OCs in multiple consecutive CLC cycles has also been investigated (Zhang et al., 2013; Song et al., 2008b). Conversions were seen to slowly decrease the first 15 cycles followed by a sharp decrease after that. Large amounts of SO_2 were emitted corresponding to the decomposition of the OC which explains the decreased performance. Slight agglomeration and sintering were also noted. A collection of results can be found in Table 6.

3.5. *Mixed ores and modifications*

It is clear that different metal oxides and different ores perform very differently in CLC processes. While ores may perform well in some aspects they all have some improvements that can be made. The easiest way to alleviate these issues is to physically mix two separate ores together. By grinding and then subsequently blending two ores together additional processing costs are avoided but synergistic effects may result. Many researchers have also tried to avoid these downfalls by making small modifications to the ores themselves with the addition of different compounds. It should be noted in the case of modifications (i.e. wet mixing, impregnation, precipitation, sol-gel etc.) a natural (unprocessed) ore is no longer being used and additional costs associated with this modification would make the OC more expensive. However, most of the works focused on inexpensive methods of modification. A collection of works detailing these two modification methods can be found in Table 7. As the method of modification can influence the reactivity of an OC we have added the method of modification to Table 7b. We also acknowledge that further work is required to determine the influence of mixing methods on OC properties (Hu et al., 2014; Pour et al., 2013). Below we discuss how these mixes/modifications influence the overall OC performance.

Most of the oxygen carrier mixes contained ilmenite and an additional mineral. This is not surprising due to the overwhelming research into the use of ilmenite as an OC. Linderholm et al. (2016) present a mix of ilmenite with Mn ore to combust solid fuels. This led to an increased gas conversion efficiency from 84.2% to 91.5% as well as improvements in CCE and solid fuel conversion. This mixture exhibits CLOU properties noted with manganese OC but an improved OC lifetime of 700–800 h when compared to 50–290 h found for pure Mn ores. NiO oxygen carriers are known for their activity for hydrocarbon decompositions to CO and H₂. Rydén et al. (2010) showed that the addition of a conventionally prepared Ni-based OC to ilmenite could improve combustion efficiencies from 76% to 90%, while maintaining low CO and H₂ emissions. However, the method of mixing used for Fe/Ni OCs can greatly influence the combustion efficiency (Pans et al., 2013). One study was found using blends of hematite and copper ore to combust syngas and anthracite coal. This work suggested a synergistic effect between Cu and Fe ores, showing a non-linear increase in O₂ transport capacity with a linear increase in Cu ore (Yang et al., 2014). An optimized ratio of 8Cu:2Fe was chosen which showed improved fuel and

gas conversions while maintaining the structural stability and sintering resistance of iron ores (Yang et al., 2015).

Combination of multiple natural minerals (ilmenite with limestone or natural olivine) can be cheap, environmentally friendly oxygen carriers, and improves the hydrocarbon conversion moderately. Two studies were found using an addition of limestone (calcined and sulfured) to ilmenite. This addition showed a greater gas conversion of CO to CO₂, faster fuel conversions and reduced SO₂ emissions. The first two effects were linked to the catalytic effect that calcined limestone (CaO) has on the water-gas shift reaction and char gasification. The reduced SO₂ emissions were the result of CaSO₄ being produced and capturing released SO₂ from the fuel (Teyssie et al., 2011; Cuadrat et al., 2011b). Cement has also been added to ilmenite and CaO blends. This combination also showed an improved carbon conversions but showed a further improvement in CO₂ yield and sintering prevention. Olivine, a naturally occurring mineral with a formula of (Fe,Mg)₂SiO₄, was found to moderately improve CH₄ conversions, which was found to be a concern with ilmenite in other work (Leion et al., 2009a; Proll et al., 2009). Sulfur release was shown to be a large issue in CaSO₄ OC use (Guo et al., 2012). A mixture of natural iron ore and anhydrite ore has been tested to lessen this problem. A mixture of 7% Fe₂O₃ in natural anhydrite ore was shown to not only improve CO₂ conversion but also reduce SO₂ emission by 77% and reduce H₂S emissions to trace amounts (Zheng et al., 2014). However after multiple cycles the emissions of SO₂ may rise back to unsatisfactory levels. It is also postulated that a synergistic effect may take place between the Fe ore and anhydrite that improves char gasification and volatile combustion (Ding et al., 2015).

Chemical additions to natural ores also showed a substantial increase in OC performance. Most studies employed a wet or dry impregnation method that doped the ore with an additional compound. Two categories could be made from the works found based on the compound added being the addition of an additional oxygen carrier or alkali metal for catalytic effects. Addition of an oxygen carrier should present similar conversion effects to physical mixing of OC while actually bonding the two OCs together. Four studies were found binding Cu to Mn ore, Cu to Fe ore, Fe to Mn ore and Mn to Fe ore. When Cu is added to Mn ore a possible synergistic effect was noted and potential CLOU properties were observed. While all of the samples showed complete CO conversion, the major influence this addition had was a prolonged conversion time, likely due to an increased oxygen transport capacity (Xu et al., 2014). The addition of Cu

to Fe ore also showed a higher CO conversion as well as an increase in C conversion (Yang et al., 2014). In a dual study by Haider et al. (Haider et al., 2016) the synergy of Fe ore with Mn additions and Mn ore with Fe additions was investigated. Comparing with the simplex natural ores, both additions showed the attrition decreased and surface area increased, improving the physical characteristics of the OCs. Both additions showed an improved syngas conversions. The addition of Fe_2O_3 to anhydrite ore was shown to improve upon the characteristics see for the physical mixing of Fe ore with anhydrite. An 85% inhibition of SO_2 release was shown along with higher conversions of CO and H_2 and stability (Zhang et al., 2013).

Potassium addition to ilmenite and iron ore was investigated in two separate works. When added to iron ore carbon conversions were able to be increased from 79% to 90% with improved reaction rates and improved CO conversions. In this work the lowest loading (6%) of potassium was mentioned to be the best. However, after multiple cycles the catalytic effect of the potassium was decreased and it was observed that the added potassium was being lost with the coal ash (Gu et al., 2012). When added to ilmenite, potassium was also observed to improve the reactivity towards CO. Not only were conversions improved but an increased K loading showed an 8 times increase in reaction rate and an improved pore volume. This work also investigated Na and Ca additions but noted that K had the best effect (Bao et al., 2013). Potassium addition was also found to improve gasification rates in coal combustion when coupled with a CaSO_4 ore (Guo et al., 2014). $\text{Ca}(\text{OH})_2$ addition to various Mn ores was also investigated. This study also observed a decreased attrition rate and the ability to fully convert syngas. CH_4 conversions were also improved (Pour et al., 2013). Fossdal et al. (2011) also investigated the addition of calcium to manganese ore resulting in an oxygen capacity of 4.5 wt% and potential advantages in terms of kinetics and chemical and mechanical stability (Table 8).

3.6. Comparison of natural ores with conventional OC

We have put together a comparison matrix based on the results found for the use of ores as oxygen carriers in chemical looping combustion. Each cell in the matrix receives a plus or minus rating based on the individual OC's performance for that criteria. A – rating means the OC does not perform well in respect to this subject, a +/- means the OC has a neutral performance for this category and a score of + means the OC performs better

than most at this category. This ranking system allows us to qualitatively compare different OCs and highlight individual strengths while pointing out areas where further work is required. The purified ores are for comparison are assumed to be bound to some (Al_2O_3 , SiO_2 , CeO_2 etc.) support. Values for the conventional OCs are based off of works by Demirel et al. (2015), Cho et al. (2004) and Hedayati (2011).

Data routinely shows that synthetic OCs display better reactivity than ores (Thon et al., 2014). Interestingly Mn ores show higher conversions than purified Mn OCs. This could be the result of Mn-Fe compounds formed from iron impurities in the ore. We also observe that while ores fare comparatively well in the conversion of syngas and coal, CH_4 combustion results are prohibitively low for most ores. Typical values floated around 35% for CH_4 conversions and peaking in the low 80% for some Fe based ores. With the inclusion of cost and processing requirements the total values for ores tend to be higher than purified components. Except in the case of Ca-based OCs, as gypsum ores do not require much processing due to the natural CaSO_4 purity. Ilmenite shows the highest promise as a viable ore-based oxygen carrier and it is no surprise the majority of works using ore as an OC are based on ilmenite.

4. Future work

Chemical looping combustion technology, when compared to conventional energy production, is still in its infancy. The possibility of future innovations in this field are truly endless and this is especially true with the use of ores as oxygen carriers. Ilmenite has been a widely studied ore but investigations into the best type of ilmenite needs to be addressed. The variances in trace components could play a large role in char conversion and ultimate fuel efficiency. The mechanism explaining the activation of ilmenite with multiple redox cycles is that the pores in the ore are expanded. Investigations into the mechanical stability, including health, safety, and attrition rates, of ilmenite after activation would be a beneficial study. A wide array of iron ores has also been tested and much like ilmenite the influence of trace components in the ores is largely unknown. Further investigation into the use of iron ores in the combustion of gaseous fuels was found to be a shortcoming of current works. Mn ore and Mn_3O_4 oxygen carriers seem to have attrition and fines production issues. Despite mechanical property problems Mn ores do show good performance in terms

of solid fuel conversion. Multiple works were found comparing many ores with multiple sources. Further work optimizing reactor conditions for Mn ores showing promise could lead to a decrease in fines production and improved feasibility of using Mn ore OCs. The main limitation of works using Cu ore is the limited variety of ores studied. Over half of the studies found used the same ore. Further investigation into multiple ore sources needs to be investigated to further knowledge in this area. Cu ore shows promise in terms of fuel conversion but the low melting point of Cu causes sintering and agglomeration issues. Lower temperature studies should be conducted to investigate conversions while limiting mechanical property issues. Mn and Cu ores also show some CLOU properties and further investigations into this work would also be of benefit.

The combination of ores and minor additions to ores showed large improvements in the results of most OCs. Synergies of different ore mixes should be investigated. Nickel-based ores have been largely uninvestigated likely because of their low concentration of Ni. However the effective catalytic effect of Ni on CH₄ combustion is worth mentioning and Ni ore mixing may be a topic worth study. Calcium based oxygen carriers have also been utilized in CLC operations. Natural anhydrite ore of calcium contains up to 95% CaSO₄ and would be an ideal ore to study due to its high O₂ transport capacity. However processing conditions would need to be carefully tuned to limit SO₂ emissions. Dolomite has shown promise as a catalyst for solid fuel gasification and might be a valuable addition in solid fuel CLC (Sutton et al., 2001). As well, different compound additions using the calcination step would a valuable investigation. As the calcination process is required for most ores this would be a cheap method of modification. Catalytic additions like alkali metals, perovskite materials or additional metal oxides could be beneficial to CH₄ conversions or char gasification, which were identified as limiting for most ores studied. As the calcination process is something that most ores require, future work minimizing the energy intensity of this process would be beneficial before large scale processing is realized.

Further feasibility studies based on all ores would be required before an ultimate decision could be made on the use of ores as oxygen carriers in CLC. A large portion of the works found used either small bench scale reactors or TGA results. While an excellent low cost way to evaluate the effectiveness of an oxygen carrier expansion of these works including the use of a full scale CLC system is required to make ultimate conclusions on the use of natural ores as OCs in CLC. Much more work is required in this

area but the rise in interest in this research has led to the production of numerous full scale units used for testing. It is also important to include environmental considerations, not only technical and economic concerns in feasibility studies (Matzen et al., 2015). An OCs impact on the workers, waste water, exhaust gas, and solid waste should be evaluated. Process safety requires the evaluation of exposure and safe concentrations of OCs during handling of intensely used OCs (Geerts et al., 2017). A techno-economic analysis coupled to a life cycle assessment of the entire ore production process and use in CLC would be an effective way to investigate the true feasibility of ore use as an OC.

5. Conclusions

In this work we have conducted a review on the recent use of ores as oxygen carriers in chemical looping combustion technologies. Ores may present an exciting technology in OCs because of their cheap cost, inherent mechanical properties and lack of expensive processing required to function. From the literature studied, ilmenite presents the most likely candidate for use as an oxygen carrier, largely due to its mechanical strength and stability. These properties and reasonable fuel conversions allow ilmenite to be used as a long lived OC in CLC units without high makeup costs due to attrition, deactivation or physical losses. However, all of the ores studied (Fe-, Mn-, Cu-, and Ca- based) show promising results for use in the combustion of coal and syngas fuels. CH₄ based fuels showed low fuel conversions for all ores studied and therefore, without additional research, should not be considered viable fuel for ore based CLC. Mixed ores and ores with minor modifications show improved combustion efficiencies and present sustainable OCs. These additionally modified ores were able to make up for some of the negative aspects of ore use in CLC but much more research could be done. While current work is substantial in this field we presented many aspects and shortcomings that could use more detailed investigation. In summary while performance of natural ores in CLC was observed to be slightly lower than synthetic OCs, natural ores present a cheaper and more sustainable source of OCs for CLC.

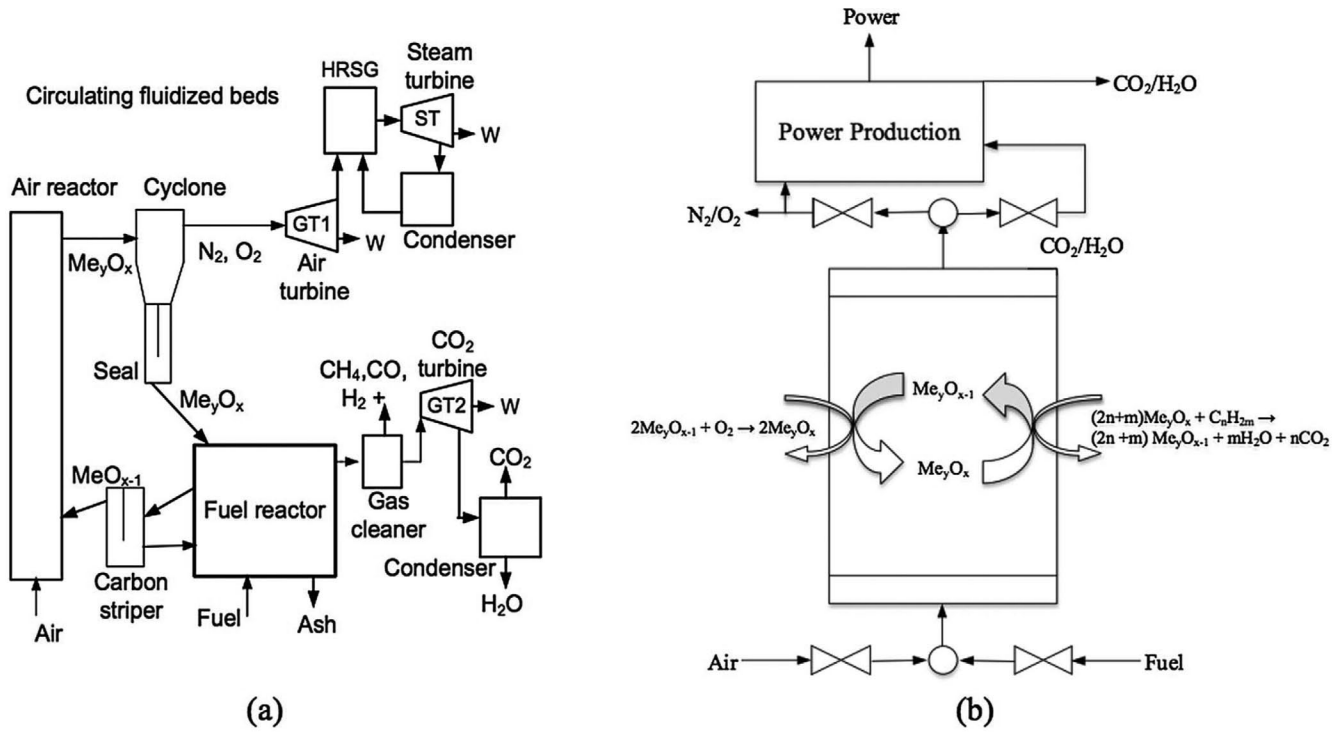


Fig. 1. Chemical looping technology: (a) Circulating fluidized bed (pressurized), (b) Fixed bed reactor with periodically changing input streams.

Table 1. Natural ores tested as oxygen carriers, showing typical component compositions (Demirel et al., 2015).

Oxygen carrier	Active component(s)	Composition (%)					
		CuO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	TiO ₂	CaSO ₄
Chrysocolla	CuO	64.41	1.34	7.73	24.59	0.93	-
Cuprite	Cu ₂ O	15.7	2.66	18.18	61.04	2.09	-
Malachite	CuO/Fe ₂ O ₃	15.08	12.12	12.82	52.64	7.08	-
Hematite	Fe ₂ O ₃	0.76	94.23	2.55	1.39	1.01	-
Ilmenite	Fe ₂ O ₃ /TiO ₂	0.76	46.01	6.26	10.84	36	-
Limonite	Fe ₂ O ₃	2.184	66.97	8.78	18.11	3.79	-
Magnetite	Fe ₃ O ₄	0.88	88.23	2.9	6.27	1.64	-
Taconite	Fe ₂ O ₃	2.51	79.46	8.55	4.5	4.83	-
Anhydrite	CaSO ₄	-	-	-	-	-	94.38

Table 2. Literature results of various tests of ilmenite as an oxygen carrier in chemical looping combustion.

Ores studied	Fuel Used	Cycles/Tested Time	Conversion/Reformation	Characteristics	Source
Rock, Sand, Synthetic (various ratios)	CO/H ₂ (50:50)	21–27 cycles	CO basis: 80–90% H ₂ basis 90–95%	Visible particle agglomeration for sand ilmenite, fairly stable conversions after 30 cycles	Azis et al., 2010
Canadian Ilmenite (Calcined)	CO in Argon	10 cycles	Oxygen transport capacity 5.52%	Stable through multiple cycles, good crushing strength	Liu et al., 2013
Ilmenite (Raw)	CH ₄ , Syngas (various ratios)	10 (CH ₄), 5 (syngas)	>90% for CO ~50% for methane	Good fluidizing properties, stable reactivity	Leion et al., 2009a
3 rock ilmenites, 2 sand ilmenites (Raw/Calcined)	CO/H ₂ , CO/N ₂ , H ₂ /N ₂	25–30 cycles	^a CO ₂ yield: 65–70% (rock), 50–35% (sand)	No agglomeration segregation or attrition observed	Schwebel et al., 2012
Ilmenite (Raw/Calcined)	H ₂ /H ₂ O, CO/CO ₂ , CH ₄ /H ₂ O	up to 100	-	Oxygen transport capacity decreases with cycles	Adanez et al., 2010
Ilmenite (Calcined)	CH ₄ , Syngas	20–30, 100 cycles	High syngas conversion (~99%)	Low attrition rates	Cuadrat et al., 2012a
Norway Ilmenite	CO/H ₂ (50:50)	85 h	CO basis: 50%–85%, H ₂ basis >95%	Minor agglomeration, slight decrease in reactivity with cycles	Moldenhauer et al., 2012
Norway Ilmenite	CO/H ₂ , CH ₄	12–16 h	CO: 55–80%, H ₂ : ~95%, CH ₄ : 30–40%	Increased load decreases conversion, defluidization of fresh ilmenite	Proll et al., 2009

b) Solid Fuels

<i>Ores studied</i>	<i>Fuel Used</i>	<i>Testing Time</i>	<i>Conversion/Reformation</i>	<i>CCE_b</i>	<i>O₂ Demand</i>	<i>Characteristics</i>	<i>Source</i>
Ilmenite (Calcined)	Columbian bituminous coal		70% (870C), 95% (950C)		5-15%		Cuadrat et al., 2011a
Ilmenite (Calcined)	Columbian bituminous coal	26, 35 h			5-15%	Decrease in R _{coz} from 4 to 3.9% observed after 26hr	Cuadrat et al., 2011c
Australian Ilmenite	German bituminous coal/syngas		Carbon conversion: 100% (syngas) 85% (Coal)			Reactivity increases over first cycles	Bidwe et al., 2011
Ilmenite	Mexican petcoke	18 h	Solid fuel conversion: 55-75%	68-87%	^a 27-36%	1000 °C for 12 h caused no problems	Berguerand and Lyngfelt, 2009
Norwegian Ilmenite	Colombian hard coal			80%	20%	Low solids circulation	Strohle et al., 2015
Australian Ilmenite	Lignite dust	39 h (CH ₄), 21 h (Coal)		>95%	19.2%		Thon et al., 2014
Ilmenite	Mexican petcoke	11 h	Solid fuel conversion: 66-78%	60-75%	25%	Very low attrition/fragmentation	Berguerand and Lyngfelt, 2008
Ilmenite	Bituminous coal/Mexican petcoke	4.75-13.5 h	Fuel Conversion: 45-84%	51-95%	21.45%		Linderholm et al., 2012

a. Values are attributed to operating conditions or reactor setup not OC performance.

b. CCE: Carbon conversion efficiency.

Table 3. Results found for use of iron ores as OC in chemical looping combustion.

<i>Ores studied</i>	<i>Fuel Used</i>	<i>Cycles/ Testing Time</i>	<i>Conversion/Reformation</i>	<i>CCE</i>	<i>Characteristics</i>	<i>Source</i>
Natural Australian Hematite	Shenhua bituminous coal (China)	10 h	Coal easily gasified	81.20%	Stable reactivity, resistant to agglomeration, attrition rate (0.0625%/h)	Song et al. (2012)
Australia Iron Ore	Sawdust/ Bituminous Mixes	-	Good Regeneration	98% (Biomass), 93-98% (BM/Coal)	No agglomeration, porosity increased w/cycles	Gu et al. (2011)
Brazil Iron Ore	Chinese Xuzhou Bituminous coal	20 cycles	-	76.48 (0.1 MPa), 84.65 (0.5 MPa)	Low sintering, no agglomeration	Xiao et al. (2010a)
Australia Iron Ore (2 types), Limonite	Victorian brown coal	9.7-11.7 h	Limonite has highest reactivity	44-92% (WA-1), 73-94% (WA-2), 75-85% Limonite	Decrease in CO ₂ conversion after 10 cycles, minor attrition,	Karlsson, 2014 no agglomeration
Natural Australian Song et al., 2013 Hematite	Bituminous coal/anthracite (China)	20 h	Carbon conversion: 81% (bituminous), 65% (anthracite)	90% (bituminous), 82% (anthracite)		Loss rate 0.12 wt%/h
Australia Iron Ore Xiao et al., 2012	Shenhua bituminous coal (China)	19 h	Combustion efficiency: 95%		84.70%	No agglomeration
Tiarga Iron Ore	Anthracite, lignite and bituminous coal	50 and 30 h	O ₂ Demand < 4%	85-94% lignite 40-57% bit. 30-45% anthracite	No reactivity changes, 0.1%/h attrition rate, stable mechanical strength	Mendiara et al., 2014
Mt. Wright Iron ore	Mexican petcoke, coal, lignite, wood char	40 cycles (25 h)	High fuel conversions > 95%			Stable or increased fuel conversions, no agglomeration Leion et al., 2009b

Magnetite, Limonite, Hematite, Taconite	Coal and CH ₄	30 cycles	% Combustion: 10–26% % Oxidation: 36–70%	Fairly stable R ₀₂ , no agglomeration observed	Tian et al., 2013
Hematite	Chinese bituminous coal and CH ₄	300 h	Combustion efficiency: 73.5–96.3%, CO ₂ yield: >85%	Resistant to sintering/agglomeration, stable reactivity	Ma et al., 2015a
Hematite	CH ₄	100 h	CH ₄ conversion: 81.3%	Improved efficiency at higher temperatures, No sintering/agglomeration, stable reactivity	Ma et al., 2015b
Spanish hematite ore	CH ₄ /syngas	50 h	Full syngas conversion, lower with CH ₄ present, R ₀₂ 2.54%	Low attrition and fluidization, porosity decrease after 56 h	Mendiara et al., 2014
Swedish Iron ore	Syngas	20 cycles	CO: 60–70% H ₂ : 90–96%	Stable conversion	Jerndal et al., 2011
Ukraine Ore and 2 Fe-Mn ores	H ₂ and CH ₄	40 cycles up to 200	Rate data	High reactivity/fast reduction at high temps, long term performance uncertain	Larring et al., 2015
Tiarga iron ore	Pine Sawdust	78 h	75–80% char conversion, O ₂ demand 5–30%	No fluidization or agglomeration problems, attrition of 0.1%/h, stable performance	Mediara et al., 2013

Table 4. Literature results using manganese oxide ores as oxygen carriers in CLC.

Ores studied	Mn Content	Fuel Used	Cycles/ Testing Time	Fuel Conversion	Characteristics	Source
3 ores: Norway (×2), Gabon	NW: 33.7, 68% GB: 63.4%	Syngas, CH ₄	10 (CH ₄), 5 (Syngas)	>95% for syngas, 40–50% initially for CH ₄	Poor fluidization, Attrition issues	Leion et al. (2009a)
Brazilian Mn Ore	38%	Mexican petcoke	10.5 h	91–97% Fuel conversion CCE: 89–98% O ₂ demand: 13–17%	Fines production problems	Linderholm et al., 2012
11 different ores	22–81%	Syngas, CH ₄	13 cycles	CH ₄ conversion 70–80%, 100% conversion syngas (for most)	Attrition rate: 2.2–8.4%/h	Sundqvist et al., 2015
6 ores: South Africa (×2), Norway, Brazil, Slovakia, Egypt	SA: 63.3, 57.2% NW: 63.3% BR: 68.8% SL: 62.3% EG: 48.8%	Mexican petcoke, wood char, CO:H ₂		100% conversion of syngas, high char gasification	Some show stable conversion, some decrease	Arjmand et al., 2014
Brazilian Mn Ore	38%	Mexican petcoke	9.2 h	90–94% Fuel conversion CCE: 68–76% O ₂ demand: 15–16%	Fines production problems	Linderholm et al., 2013
4 ores: South Africa, Gabon(×2), Brazil	SA: 39.9% GB-1: 47.1% GB-2: 56.0% BR: 50.3%	Syngas, CH ₄	35–54 h (40–58 cycles)	Rate data	No agglomeration, decrease in activity for 10 cycles then stabilizes	Mei et al., 2015

Table 5. A collection of results using copper ores as oxygen carriers in CLC.

Ores studied	Cu content (wt %)	Fuel Used	Conversion/Reformation	Characteristics	Cycles/Time	Source
Chrysocolla, Cuprite, Malachite	CuO: 64.41%	Coal and CH ₄	% combustion: 11.6–35%, % oxidation: 23.2–67.2%	Very stable conversion, no agglomeration, some loss of mechanical strength	30 cycles	Tian et al., 2013
	CuO: 15.7% CuO: 15.08%					
3 Cu Ores	CuO: 87.28%	N/A (CLOU study)	2–3.7% O ₂ stream produced	Higher Cu content ores agglomerate, stable reactivity	20 cycles	Wen et al., 2012
	CuO: 63.25% CuO: 5.82%					
Refined Chinese copper ore	CuO: 21%	Chinese anthracite	Combustion efficiency: 96%	Slight agglomeration and sintering, stable performance after 1 cycle	5 cycles (10 h)	Zhao et al., 2014
	CuFe ₂ O ₄ : 70%					
Refined Chinese copper ore	CuO: 21%	Syngas	O ₂ transport capacity: 11–14%	Decrease in activity stabilizes after 10 cycles	18 cycles	Yang et al., 2015
	CuFe ₂ O ₄ : 70%					
Refined Chinese copper ore	CuO: 21%	Pine sawdust	Gasification efficiency: 26%	Stable O ₂ transport capacity, slight sintering, good fluidization	21 cycles	Guo et al., 2015
	CuFe ₂ O ₄ : 70%					
Refined Chinese copper ore	CuO: 21%	Chinese anthracite, bituminous, lignite	CLOU process	Some agglomeration at 950C, TOC 4.44%	5 cycles	Wang et al., 2015b
	CuFe ₂ O ₄ : 70%					
Refined Chinese copper ore	CuO: 21%	Syngas (w/H ₂ S)	H ₂ S degrades oxygen transport capacity and reactivity of OC	H ₂ S causes Cu ₂ S and FeS formation	10 cycles	Wang et al., 2016
	CuFe ₂ O ₄ : 70%					
Refined Chinese copper ore	CuO: 21%	Syngas/Coal	CO ₂ yield: 75–90%	Sintering observed, O ₂ transport/CO ₂ yield decrease	20 cycles	Tian et al., 2015
	CuFe ₂ O ₄ : 70%					
			O ₂ transport capacity: 12–14%			

Table 6. A collection of results using gypsum (CaSO_4) as oxygen carriers in CLC.

Ores	CaSO_4 (wt%)	Fuel Used	Conversion/Reformation	Characteristics	Cycles	Source
Granitic limestone	>97.1% CaCO_3	Chilean, Teruel, Alcorisa coals	CO and H_2 conversion >99.5%	No initial SO_2 release, high oxygen transport capacity (-16.7), stable after 8 h reduction time	60 redox cycle for 24 h	Abad et al. 2017
Anhydrite		H_2 and CO	H_2 : 61–97% CO: 18–68%	Increased temperatures improved conversions, improved reactivity for 5 cycles then decreased	15 cycles	Zhang et al. 2013
Natural Anhydrite Ore	CaO: 40.5% SO_3 : 53.9%	$\text{H}_2/\text{CO}/\text{CO}_2$	Initially CO: ~90% H_2 : 100%	Oxygen intensity decreases after reduction, better mechanical strength, reactivity and conversion decreases after 15 cycles. Particles agglomerated or sintered	20 cycles	Song et al. 2008b
Natural Anhydrite Ore	CaO: 94.38%	H_2 and CO	H_2 : 70–97% CO: 15–70% CO_2 yield: 57–85%	Temperature increases conversions and CO_2 yield, low carbon deposition, SO_2 and H_2S formation favored at >950 °C, Slight agglomeration noted		Song et al. 2008a
Natural Anhydrite Ore	CaSO_4 : 94.38%	H_2 and CO	Conversions influenced by temperature	CO conversion and H_2 reduction better at >950 °C Formation of SO_2 and H_2S increase at 950 °C		Shen et al. 2008
Natural Anhydrite Ore	CaSO_4 : 94.38%	CH_4	CH_4 yield: 25–45%	Compact agglomerated state, high OC conversion, yield and reactivity slightly decreased after 4 cycles, carbon deposition occurs, release of SO_2 decreases the reactivity of CaSO_4	6 cycles	Song et al. 2009
Natural Anhydrite Ore	CaSO_4 : 94.4%	CO	Full solids conversion	High temperatures react quicker but formed CaO from CaSO_4 , sintering/agglomeration at higher temperatures, low SO_2 emissions		Xiao and Song 2011
Natural Anhydrite Ore	CaSO_4 : 94.38%	Bituminous Shenhua coal	CO_2 yield: 83.6–89.5%	Higher temperatures promote H_2 combustion, H_2S and SO_2 emissions		Zheng et al. 2014
Natural Anhydrite Ore	CaSO_4 : 95.02%	Shenfu coal char	Low reactivity to CO/ H_2	Steam gasification of coal char, Reactivity increases with temperature, CaSO_4 reactivity decreases with cycles	5 cycles	Ding et al. 2015

Table 7. (a) Results of a literature search for mixes of natural ores used as OC in CLC; (b) Results of a literature search for works using modified ores as OCs in CLC.**(a) Physical Mixes**

Ores	Ratios	Cycles/Testing Time	Fuel	Improvements	Source
Norway Ilmenite:NiO OC	5% NiO	8–14 cycles	CH ₄	Improved CH ₄ conversion	Ryden et al. 2010
Hematite:Cu Ore	0/10, 1/9, 2/8...10/0	18 cycles	Syngas and Anthracite	Improved O ₂ transport capacity with increasing Cu content, CLOU properties observed, better char conversion, higher affinity for gas conversion	Yang et al. 2015
Ilmenite:Mn Ore	8% Mn (max)	18 h	Columbian Coal, Polish Coal, Wood char	Improved gas conversion/CCE, no increase in fines production	Linderholm et al. 2016
Ilmenite:Limestone	20% Limestone	6–18 cycles	Petcoke, Syngas	Improved CO and H ₂ conversion, captures released SO ₂ from coal, improved fuel conversion kinetics	Teyssie et al. 2011
Ilmenite:Limestone	21% Limestone	4 h	Mexican Petcoke	Improved gas conversion, improved char conversion	Cuadrat et al. 2011b
Ilmenite:Olivine	18% olivine		H ₂ /N ₂ , H ₂ /CO, CH ₄	~10% Improved CH ₄ conversion	Proll et al. 2009
Fe Ore:CaO	4:1 Fe:CaO		Shenhua Coal	CaO improved C conversion	Gu et al. 2015
Fe Ore: CaO/Cement	7:2:2 Fe:CaO:Cement			CaO/Cement improved CO ₂ efficiency and prevented sintering	
Ni-Fe mixed natural anhydrite>95% CaSO ₄	92.3% CaSO ₄ with 3.75% NiO, 4.02% Fe ₂ O ₃	9.15 h oxidation, 7.5 h reduction	CH ₄	High oxygen ratio and stability; in-situ desulphurization	Abad et al. 2017
Anhydrite:Fe Ore	Up to 11% Fe ₂ O ₃		Shenhua Coal	Improved CO ₂ yield and concentration, great reduction in sulfur emissions	Zheng et al. 2014
Anhydrite:Hematite	Fe/S ratio from 0.06–0.28	5 cycles	Coal Char	Increased C conversion and CO ₂ yield, reduce in SO ₂ emissions for first cycle, Fe catalyzed CaSO ₄ gasification and reduction	Ding et al. 2015

(b) Modifications

Ore	Addition/Method	Cycles	Fuel	Improvements	Source
Chinese Mn Ore (42% MnO)	Cu (0.5, 2, 10 wt%) wet impregnation	10 cycles	CO/N ₂	Enhanced CO conversion, possible CLOU effect	Xu et al. 2014
Brazilian Mn Ore (72% MnO)	Fe ₂ O ₃ (33%) dry impregnation	20 cycles	CH ₄ , syngas	Decreased attrition, CLOU properties, 20% increase in syngas conversion, improved stability	Haider et al. 2016
Canadian Fe Ore (87% Fe ₂ O ₃)	Mn ₂ O ₃ (33%) dry impregnation	20 cycles	CH ₄ , syngas	Decreased attrition (4.3–2.7%), improved conversion with cycles, 3–10% increased syngas conversion	Haider et al. 2016
Hematite (81.9% Fe ₂ O ₃) conversion (-5%) CO reactivity	Cu (3, 6, 10%) wet impregnation Yang et al. 2014		Up to 33 anthracite	Bituminous coal and improved reduced attrition, stable conversion	Increase in C
Natural Anhydrite	Fe ₂ O ₃ (3, 5, 10, 20, 30%) wet impregnation	15 cycles	Syngas	Improved H ₂ and CO conversion, significant decrease in SO ₂ emission, improved CaSO ₄ stability	Zhang et al. 2013
Gypsum:Bentonite 3:2 mass	Fe(NO ₃) ₃ and K ₂ CO ₃ (1:10) by wet impregnation	10 cycles	Lignite, bitumite, anthracite	Fe addition improves CO ₂ yield and recyclability, K addition improves gasification but causes sintering, reduced attrition (> 1000 h lifespan)	Guo et al. 2014
South Africa Fe Ore (86.72% Fe ₂ O ₃)	K (6, 10, 20%) impregnation	20 cycles	HuaiBei anthracite coal	Enhanced CO conversion, accelerated and improved gasification	Gu et al. 2012
Chinese Ilmenite (51% TiO ₂ , 42% Fe ₂ O ₃)	K (5, 10, 15%), Na(10%), Ca(10%) wet impregnation	40 cycles	CO/N ₂	Increased reactivity for all, increased pore volume	Bao et al. 2013
6 Ores (38–53% Mn)	Ca(OH) ₂ Wet ball milling				
Mn Ore	Ca(OH) ₂ wet ball milling method	20 cycles H ₂ and CH ₄ and CH ₄ conversion 2011	CH ₄ , syngas, wood char	Decreased attrition, improved CH ₄ conversion	Pour et al. 2013
			Similar oxygen capacity, improved kinetics, stability	Fossdal et al.	

Table 8. Decision matrix for natural ore OCs and purified component OCs.

	Fe-based			Mn-based		Cu-based		Ca-based	
	Ilmenite	Fe Ore	Fe ₂ O ₃	Mn Ore	Mn ₃ O ₄	Cu Ore	CuO	Ca Ore	CaSO ₄
Fuel Conversion									
Syngas	+/-	+/-	+	+	+	+	+	+/-	+
CH ₄	+/-	+/-	+/-	+/-	-	+/-	+	+/-	+/-
Coal	+	+	+	+/-	+/-	+	+	+/-	+/-
Physical Properties									
Agglomeration	+	+	+/-	+/-	+	-	+/-	+/-	+/-
Sintering	+	+	+	+	+/-	+/-	-	+/-	+/-
Attrition	+	+/-	+	-	+/-	+/-	+/-	+	+
Miscellaneous									
O ₂ Transport	+/-	+/-	+/-	+/-	+	+	+	+	+
Stability	+	+	+	+/-	+/-	+	+	-	-
Cost	+	+	+/-	+	-	+/-	-	+	+
Processing Ease	+	+	-	+	-	+	-	+	+/-

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References

- Abad, A., Adanez, J., Garcia-Labiano, F., de Diego, L.F., Gayan, P., Celaya, J., 2007. Mapping of the range of operational conditions for Cu-, Fe-, and Ni-based oxygen carriers in chemical-looping combustion. *Chem. Eng. Sci.* 62, 533–549. doi 10.1016/j.ces.2006.09.019
- Abad, A., de las Obras-Loscertales, M., Garcia-Labiano, F., de Diego, L.F., Gayan, P., Adanez, J., 2017. In situ gasification chemical looping combustion of coal using limestone as oxygen carrier precursor and sulphur sorbent. *Chem. Eng. J.* 310, 226–239. doi 10.1016/j.cej.2016.10.113
- Adanez, J., Cuadrat, A., Abad, A., Gayan, P., de Diego, L.F., Garcia-Labiano, F., 2010. Ilmenite activation during consecutive redox cycles in chemical-looping combustion. *Energy Fuels* 24, 1402–1413. doi 10.1021/ef900856d
- Adanez, J., Abad, A., Garcia-Labiano, F., Gayan, P., de Diego, L.F., 2012. Progress in chemical-looping combustion and reforming technologies. A review. *Prog. Energy Combust. Sci.* 38, 215–282. doi 10.1016/j.peccs.2011.09.001
- Arjmand, M., Leion, H., Mattisson, T., Lyngfelt, A., 2014. Investigation of different manganese ores as oxygen carriers in chemical-looping combustion (CLC) for solid fuels. *Appl. Energy* 113, 1883–1894. doi 10.1016/j.apenergy.2013.06.015
- Azis, M.M., Jerndal, E., Leion, H., Mattisson, T., Lyngfelt, A., 2010. On the evaluation of synthetic and natural ilmenite using syngas as fuel in chemical-looping combustion (CLC). *Chem. Eng. Res. Des.* 88, 1505–1514. doi 10.1016/j.cherd.2010.03.006
- Bao, J., Li, Z., Cai, N., 2013. Promoting the reduction reactivity of ilmenite by introducing foreign ions in chemical looping combustion. *Ind. Eng. Chem. Res.* 52, 6119–6128. doi 10.1021/ie400237p

- Bedinger, G.M., 2015. Titanium Mineral Concentrates, U.S. Geological Survey. Berguerand, N., Lyngfelt, A., 2008. The use of petroleum coke as fuel in a 10 kWth chemical-looping combustor. *Int. J. Greenh. Gas Control* 2, 169–179. doi 10.1016/j.ijggc.2007.12.004
- Berguerand, N., Lyngfelt, A., 2009. Chemical-looping combustion of petroleum coke using ilmenite in a 10 kWth unite-high-temperature operation. *Energy Fuels* 23, 5257–5268. doi 10.1021/ef900464j.
- Bidwe, A., Mayer, F., Hawthorne, C., Charitos, A., Schuster, A., Scheffknecht, G., 2011. Use of ilmenite as an oxygen carrier in chemical looping combustion-Batch and continuous dual fluidized bed investigation. *Energy Procedia* 4, 433–440. doi 10.1016/j.egypro.2011.01.072
- Cho, P., Mattisson, T., Lyngfelt, A., 2004. Comparison of iron-, nickel-, copper-, and manganese-based oxygen carriers for chemical-looping combustion. *Fuel* 83, 1215–1225. doi 10.1016/j.fuel.2003.11.013
- Corathers, L.A., 2016. Manganese, U.S. Geological Survey.
- Cormos, C.-C., 2017. Chemical looping with oxygen uncoupling (CLOU) concepts for high energy efficient power generation with near total fuel decarbonisation. *Appl. Therm. Eng.* 112, 924–931. doi 10.1016/j.applthermaleng.2016.10.156
- Cuadrat, A., Abad, A., Garcia-Labiano, F., Gayan, P., de Diego, L., Adanez, J., 2011a. The use of ilmenite as oxygen-carrier in a 500 Wth chemical-looping coal combustion unit. *Int. J. Greenh. Gas Control* 5, 1630–1642. doi 10.1016/j.ijggc.2011.09.010
- Cuadrat, A., Linderholm, C., Abad, A., Lyngfelt, A., Adanez, J., 2011b. Influence of limestone addition in a 10 kWth chemical-looping combustion unit operated with petroleum coke. *Energy Fuels* 25, 4818–4828. doi 10.1021/ef200806q
- Cuadrat, A., Abad, A., Garcia-Labiano, F., Gayan, P., de Diego, L.F., Adanez, J., 2011c. Ilmenite as oxygen carrier in a chemical looping combustion system with coal. *Energy Procedia* 4, 362–369. doi 10.1016/j.egypro.2011.01.063
- Cuadrat, A., Abad, A., de Diego, L., Garcia-Labiano, F., Gayan, P., 2012a. Behavior of ilmenite as oxygen carrier in chemical-looping combustion. *Fuel Process. Technol.* 94, 101–112. doi 10.1016/j.fuproc.2011.10.020.
- Cuadrat, A., Abad, A., Garcia-Labiano, F., Gayan, P., de Diego, L.F., Adanez, J., 2012b. Effect of operating conditions in chemical-looping combustion of coal in a 500 Wth unit. *Int. J. Greenh. Gas Control* 6, 153–163. doi 10.1016/j.ijggc.2011.10.013
- Demirel, Y., Matzen, M., Winters, C., Gao, X., 2015. Capturing and using CO₂ as feedstock with chemical looping and hydrothermal technologies. *Int. J. Energy Res.* 39, 1011–1047. doi 10.1002/er.3277
- Ding, N., Zheng, Y., Luo, C., Wu, Q.-L., Fu, P.-F., Zheng, C.-G., 2011. Investigation into compound CaSO₄ oxygen carrier for chemical-looping combustion. *J. Fuel Chem. Technol.* 39 (3), 161–168. doi 10.1016/s1872-5813(11)60015-7
- Ding, N., Zhang, C., Luo, C., Zheng, Y., Liu, Z., 2015. Effect of hematite addition to CaSO₄ oxygen carrier in chemical looping combustion of coal char. *RSC Adv.* 5, 56362–56376. doi 10.1039/c5ra06887h
- Fossdal, A., Bakken, E., Oye, B.A., Schoning, C., Kaus, I., Mokkelbost, T., Larring, Y., 2011. Study of inexpensive oxygen carriers for chemical looping combustion. *Int. J. Greenh. Gas Control* 5 (3), 483–488. doi 10.1016/j.ijggc.2010.08.001
- Geerts, L., Rijns, E., Witters, H., Weltens, R., Snijkers, F., Health, safety and environmental impact study [Presentations Slides] Le Risque Chimique. [http://www.inrs-
risque-chimique2015.fr/wp-content/uploads/2015/04/17h10-GEERTS-session-1.pdf](http://www.inrs-risque-chimique2015.fr/wp-content/uploads/2015/04/17h10-GEERTS-session-1.pdf)

- Gu, H., Shen, L., Xiao, J., Zhang, S., Song, T., 2011. Chemical looping combustion of biomass/coal with natural iron ore as oxygen carrier in a continuous reactor. *Energy Fuels* 25, 446–455. doi 10.1021/ef101318b
- Gu, H., Shen, L., Xiao, J., Zhang, S., Song, T., Chen, D., 2012. Iron ore as oxygen carrier improved with potassium for chemical looping combustion of anthracite coal. *Combust. Flame* 159, 2480–2490. doi 10.1016/j.combustflame.2012.03.013
- Gu, H., Shen, L., Zhong, Z., Niu, X., Liu, W., Ge, H., Jiang, S., Wang, L., 2015. Cement/CaO-modified iron ore as oxygen carrier for chemical looping combustion of coal. *Appl. Energy* 157, 314–322. doi 10.1016/j.apenergy.2015.06.023
- Guo, Q., Zhang, J., Tian, H., 2012. Recent advances in CaSO₄ oxygen carrier for chemical-looping combustion (CLC) process. *Chem. Eng. Commun.* 199 (11), 1463–1491. doi 10.1080/00986445.2012.668591
- Guo, Q., Liu, Y., Jia, W., Yang, M., Hu, X., Ryu, H.-J., 2014. Performance of Ca-based oxygen carriers decorated by K₂CO₃ or Fe₂O₃ for coal chemical looping combustion. *Energy Fuels* 28, 7053–7060. doi 10.1021/ef5013006
- Guo, L., Zhao, H., Zheng, C., 2015. Synthesis gas generation by chemical-looping reforming of biomass with natural copper ore as oxygen carrier. *Waste Biomass Valor* 6, 81–89. doi 10.1007/s12649-014-9328-1
- Haider, S.K., Azimi, G., Duan, L., Anthony, E.J., Patchigolla, K., Oakey, J.E., Leion, H., Mattisson, T., 2016. Enhancing properties of iron and manganese ores as oxygen carriers for chemical looping processes by dry impregnation. *Appl. Energy* 163, 41–50. doi 10.1016/j.apenergy.2015.10.142
- Hedayati, A., 2011. Evaluation of Novel Ceria-Supported Materials as Oxygen Carriers for Chemical-Looping Combustion. Chalmers University of Technology (Master's Thesis).
- Hu, Y., Wang, W., Hua, X., 2014. Reactivity of iron-based oxygen carriers prepared by wet and dry mixing methods for hydrogen production via biomass derived syngas chemical looping. *Energy Procedia* 61, 1650–1654. doi 10.1016/j.egypro.2014.12.184
- Imtiaz, Q., Hosseini, D., Muller, C.R., 2013. Review of oxygen carriers for chemical looping with oxygen uncoupling (CLOU): thermodynamics, material development, and synthesis. *Energy Technol.* 1 (11), 633–647. doi 10.1002/ente.201300099
- Jerndal, E., Leion, H., Axelsson, L., Ekvall, T., Hedberg, M., Johansson, K., Kallen, M., Svensson, R., Mattisson, T., Lyngfelt, A., 2011. Using low-cost iron based materials as oxygen carriers for chemical looping combustion. *Oil Gas Sci. Technol.* 66 (2), 235–248. doi 10.2516/ogst/2010030
- Karlsson, T., 2014. A Study of Three Iron-Based Oxygen Carriers in a Chemical Looping Combustion Process with a Victorian Brown Coal. Chalmers University of Technology, Goteborg, Sweden (Masters Thesis).
- Larring, Y., Pishahang, M., Sunding, M.F., Tsakalakis, K., 2015. Fe-Mn based minerals with remarkable redox characteristics for chemical looping combustion. *Fuel* 159, 169–178. doi 10.1016/j.fuel.2015.06.083
- Leion, H., Mattisson, T., Lyngfelt, A., 2009a. Use of ores and industrial products as oxygen carriers in chemical-looping combustion. *Energy Fuels* 23 (4), 2307–2315. doi 10.1021/ef8008629
- Leion, H., Jerndal, E., Steenari, B.-M., Hermansson, S., Israelsson, M., Jansson, E., Johansson, M., Thunberg, R., Vadenbo, A., Mattisson, T., Lyngfelt, A., 2009b. Solid fuels in chemical-looping combustion using oxide scale and unprocessed iron ore as oxygen carriers. *Fuel* 88, 1945–1954. doi 10.1016/j.fuel.2009.03.033

- Linderholm, C., Lyngfelt, A., Cuadrat, A., Jerndal, E., 2012. Chemical-looping combustion of solid fuels – operation in a 10 kW unit with two fuels, above-bed and in-bed fuel feed and two oxygen carriers, manganese ore and ilmenite. *Fuel* 102, 808–822. doi 10.1016/j.fuel.2012.05.010
- Linderholm, C., Lyngfelt, A., Dueso, C., 2013. Chemical-looping combustion of solid fuels in a 10 kW reactor system using natural minerals as oxygen carrier. *Energy Procedia* 37, 598–607. doi 10.1016/j.egypro.2013.05.147
- Linderholm, C., Schmitz, M., Knutsson, P., Lyngfelt, A., 2016. Chemical-looping combustion in a 100-kW unit using a mixture of ilmenite and manganese ore as oxygen carrier. *Fuel* 166, 533–542. doi 10.1016/j.egypro.2013.05.147
- Liu, F., Zhang, Y., Chen, L., Qian, D., Nearthery, J.K., Kozo, S., Liu, K., 2013. Investigation of a Canadian ilmenite as an oxygen carrier for chemical looping combustion. *Energy Fuels* 27, 5987–5995. doi 10.1021/ef401513p
- Ma, J., Zhao, H., Tian, X., Wei, Y., Rajendran, S., Zhang, Y., Bhattacharya, S., Zheng, C., 2015a. Chemical looping combustion of coal in a 5 kWth interconnected fluidized bed reactor using hematite as oxygen carrier. *Appl. Energy* 157, 304–313.
- Ma, J., Zhao, H., Tian, X., Wei, Y., Zhang, Y., Zheng, C., 2015b. Continuous operation of interconnected fluidized bed reactor for chemical looping combustion of CH₄ using hematite as oxygen carrier. *Energy Fuels* 29, 3257–3267. doi 10.1016/j.apenergy.2015.03.124
- Markstrom, P., Linderholm, C., Lyngfelt, A., 2014. Operation of a 100 kW chemical-looping combustor with Mexican petroleum coke and Cerrejon coal. *Appl. Energy* 113, 1830–1835. doi 10.1016/j.apenergy.2013.04.066
- Mattisson, T., Adanez, J., Mayer, K., Snijkers, F., Williams, G., Wesker, E., Bertsch, O., Lyngfelt, A., 2014. Innovative oxygen carriers uplifting chemical-looping combustion. *Energy Procedia* 63, 113–130. doi 10.1016/j.egypro.2014.11.012
- Matzen, M., Alhajji, M., Demirel, Y., 2015. Chemical storage of wind energy by renewable methanol production: feasibility analysis using a multi-criteria decision matrix. *Energy* 93, 343–353. doi 10.1016/j.energy.2015.09.043
- Mediara, T., Abad, A., de Diego, L.F., Garcia-Labiano, F., Gayan, P., Adanez, J., 2013. Biomass combustion in a CLC system using an iron ore as an oxygen carrier. *Int. J. Greenh. Gas Control* 19, 322–330. doi 10.1016/j.ijggc.2013.09.012
- Mei, D., Mendiara, T., Abad, A., de Diego, L.F., Garcia-Labiano, F., Gayan, P., Adanez, J., Zhao, H., 2015. Evaluation of manganese minerals for chemical looping combustion. *Energy Fuels* 29, 6605–6615. doi 10.1021/acs.energyfuels.5b01293
- Mei, D., Mendiara, T., Abad, A., de Diego, L.F., Garcia-Labiano, F., Gayan, P., Adanez, J., Zhao, H., 2016. Manganese minerals as oxygen carriers for chemical looping combustion of coal. *Ind. Eng. Chem. Res.* 55, 6539–6546. doi 10.1021/acs.energyfuels.5b01293
- Mendiara, T., de Diego, L.F., Garcia-Labiano, F., Gayan, P., Abad, A., Adanez, J., 2014. On the use of a highly reactive iron ore in chemical looping combustion of different coals. *Fuel* 126, 239–249. doi 10.1016/j.fuel.2014.02.061
- Moghtaderi, B., 2012. Review of the recent chemical looping process developments for novel energy and fuel applications. *Energy Fuels* 26, 15–40. doi 10.1021/ef201303d
- Moldenhauer, P., Ryden, M., Lyngfelt, A., 2012. Testing of minerals and industrial by-products as oxygen carriers for chemical-looping combustion in a circulating fluidized-bed 300 W laboratory reactor. *Fuel* 93, 351–363. doi 10.1016/j.fuel.2011.11.009

- Noorman, S., van Sint Annaland, M., Kuipers, H., 2007. Packed bed reactor technology for chemical-looping combustion. *Ind. Eng. Chem. Res.* 46 (12), 4212–4220. doi 10.1021/ie061178i
- Pans, M., Gayan, P., Abad, A., Garcia-Labiano, F., de Diego, L.F., Adanez, J., 2013. Use of chemically and physically mixed iron and nickel oxides as oxygen carriers for gas combustion in a CLC process. *Fuel Process. Technol.* 115, 152–163. doi 10.1016/j.fuproc.2013.05.013
- Pans, M.A., Gayan, P., de Diego, L.F., Garcia-Labiano, F., Abad, A., Adanez, J., 2015. Performance of a low-cost iron ore as an oxygen carrier for chemical looping combustion of gaseous fuels. *Chem. Eng. Res. Des.* 93, 736–746. doi 10.1016/j.cherd.2014.07.001
- Porrizzo, R., White, G., Ocone, R., 2016. Techno-economic investigation of a chemical looping combustion based power plant. *Faraday Discuss.* 192, 437–457. doi 10.1039/C6FD00033A
- Pour, N.M., Azimi, G., Leion, H., Ryden, M., Lyngfelt, A., 2013. Production and examination of oxygen-carrier materials based on manganese ores and $\text{Ca}(\text{OH})_2$ in chemical looping with oxygen uncoupling. *AIChE J.* 60 (2), 645–656. doi 10.1002/aic.14273
- Proll, T., Mayer, K., Bolhar-Nordenkamp, J., Kolbitsch, P., Mattisson, T., Lyngfelt, A., Hofbauer, H., 2009. Natural minerals as oxygen carriers for chemical looping combustion in a dual circulating fluidized bed system. *Energy Procedia* 1, 27–34. doi 10.1016/j.egypro.2009.01.006
- Ryden, M., Johansson, M., Cleverstam, E., Lyngfelt, A., Tobias, M., 2010. Ilmenite with addition of NiO as oxygen carrier for chemical-looping combustion. *Fuel* 89, 3523–3533. doi 10.1016/j.fuel.2010.06.010
- Schmitz, M., Linderholm, C., Hallberg, P., Sundqvist, S., Lyngfelt, A., 2016. Chemical-looping combustion of solid fuels using manganese ores as oxygen carriers. *Energy Fuels* 30 (2), 1204–1216. doi 10.1021/acs.energyfuels.5b02440
- Schwebel, G.L., Leion, H., Krumm, W., 2012. Comparison of natural ilmenites as oxygen carriers in chemical-looping combustion and influence of water gas shift reaction on gas composition. *Chem. Eng. Res. Des.* 90, 1351–1360. doi 10.1016/j.cherd.2011.11.017
- Shen, L., Zheng, M., Xiao, J., 2008. A mechanistic investigation of a calcium-based oxygen carrier for chemical looping combustion. *Combust. Flame* 1154, 489–506. <http://dx.doi.org/10.1016/j.combustflame.2008.04.017>
- Song, Q., Xiao, R., Deng, Z., Shen, L., Xiao, J., Zhang, M., 2008a. Effect of temperature on reduction of CaSO_4 oxygen carrier in chemical-looping combustion of simulated coal gas in a fluidized bed reactor. *Ind. Eng. Chem. Res.* 47, 8148–8159. <http://dx.doi.org/10.1021/ie8007264>
- Song, Q., Xiao, R., Deng, Z., Zheng, W., Shen, L., Xiao, J., 2008b. Multicycle study on chemical-looping combustion of simulated coal gas with a CaSO_4 oxygen carrier in a fluidized bed reactor. *Energy Fuels* 3611–3672. doi 10.1021/ef800275a
- Song, Q., Xiao, R., Deng, Z., Shen, L., Zhang, M., 2009. Reactivity of a CaSO_4 oxygen carrier in chemical-looping combustion of methane in a fixed bed reactor. *Korean J. Chem. Eng.* 26 (2), 592–602. doi 10.1007/s11814-009-0101-2.
- Song, T., Wu, J., Zhang, H., Shen, L., 2012. Characterization of an Australia hematite oxygen carrier in chemical looping combustion with coal. *Int. J. Greenh. Gas Control* 11, 326–336. doi 10.1016/j.ijggc.2012.08.013
- Song, T., Shen, T., Shen, L., Xiao, J., Gu, H., Zhang, S., 2013. Evaluation of hematite oxygen carrier in chemical-looping combustion of coal. *Fuel* 104, 244–252. <http://dx.doi.org/10.1016/j.fuel.2012.09.030>.

- Strohle, J., Orth, M., Epple, B., 2015. Chemical looping combustion of hard coal in a 1 MWth pilot plant using ilmenite as oxygen carrier. *Appl. Energy* 157, 288–294. doi 10.1016/j.apenergy.2015.06.035
- Sundqvist, S., Arjmand, M., Mattisson, T., Ryden, M., Lyngfelt, A., 2015. Screening of different manganese ores for chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU). *Int. J. Greenh. Gas Control* 43, 179–188. doi 10.1016/j.ijggc.2015.10.027
- Sutton, D., Kelleher, B., Ross, J.R., 2001. Review of literature on catalysts for biomass gasification. *Fuel Process. Technol.* 73, 155–173. doi 10.1016/S0378-3820(01)00208-9
- Teyssie, G., Leion, H., Schwebel, G.L., Lyngfelt, A., Mattisson, T., 2011. Influence of lime addition to ilmenite in chemical-looping combustion (CLC) with solid fuels. *Energy Fuels* 25, 3843–3853. doi 10.1021/ef200623h
- Thon, A., Kramp, M., Hartge, E.-U., Heinrich, S., Werther, J., 2014. Operation experience with a system of coupled fluidized beds for chemical looping combustion of solid fuels using ilmenite as oxygen carrier. *Appl. Energy* 118, 309–317. doi 10.1016/j.apenergy.2013.11.023
- Tian, H., Siriwardane, R., Simonyi, T., Poston, J., 2013. Natural ores as oxygen carriers in chemical looping combustion. *Energy Fuels* 27, 4108–4118. doi 10.1021/ef301486n
- Tian, X., Zhao, H., Wang, K., Ma, J., Zheng, C., 2015. Performance of cement decorated copper ore as oxygen carrier in chemical-looping with oxygen uncoupling. *Int. J. Greenh. Gas Control* 41, 210–218. doi 10.1016/j.ijggc.2015.07.015
- Wang, P., Means, N., Shekhawat, D., Berry, D., Massoudi, M., 2015a. Chemical-looping combustion and gasification of coals and oxygen carrier development: a brief review. *Energies* 8, 10605–10635. doi 10.3390/en81010605
- Wang, K., Zhao, H., Tian, X., Fang, Y., Ma, J., Zheng, C., 2015b. Chemical-looping with oxygen uncoupling of different coals using copper ore as an oxygen carrier. *Energy Fuels* 29, 6625–6635. doi 10.1021/acs.energyfuels.5b01377
- Wang, K., Tian, X., Zhao, H., 2016. Sulfur behavior in chemical-looping combustion using a copper ore oxygen carrier. *Appl. Energy* 166, 84–95. doi 10.1016/j.apenergy.2016.01.011
- Wen, Y.-Y., Li, Z.-S., Xu, L., Cai, N.-S., 2012. Experimental study of natural Cu ore particles as oxygen carriers in chemical looping with oxygen uncoupling (CLOU). *Energy Fuels* 26, 3919–3927. doi 10.1021/ef300076m
- Wilder, F.A., 1918. Gypsum: its occurrence, origin, technology and uses. *Iowa Geol. Surv. Ann. Rep.* 28.
- Xiao, R., Song, Q., 2011. Characterization and kinetics of reduction of CaSO₄ with carbon monoxide for chemical-looping combustion. *Combust. Flame* 158, 2524–2539. doi 10.1016/j.combustflame.2011.05.011
- Xiao, R., Song, Q., Zhang, S., Zheng, W., Yang, Y., 2010a. Pressurized chemical-looping combustion of Chinese bituminous coal: cyclic performance and characterization of iron ore-based oxygen carrier. *Energy Fuels* 24, 1449–1463. doi 10.1021/ef901070c
- Xiao, R., Song, Q.L., Zheng, W.G., Deng, Z.Y., Shen, L.H., Zhang, M.Y., 2010b. Reduction kinetics of a CaSO₄ based oxygen carrier for chemical-looping combustion. *Proceedings of the 20th International Conference on Fluidized Bed Combustion.*
- Xiao, R., Chen, L., Saha, C., Zhang, S., Bhattacharya, S., 2012. Pressurized chemical-looping combustion of coal using an iron ore as oxygen carrier in a pilot-scale unit. *Int. J. Greenh. Gas Control* 10, 363–373. doi 10.1021/ef901070c

- Xu, L., Edland, R., Li, Z., Leion, H., Zhao, D., Cai, N., 2014. Cu-modified manganese ore as an oxygen carrier for chemical looping combustion. *Energy Fuels* 28, 7085–7092. doi 10.1021/ef5017686
- Yang, W., Zhao, H., Ma, J., Mei, D., Zheng, C., 2014. Copper-decorated hematite as an oxygen carrier for in situ gasification chemical looping combustion of coal. *Energy Fuels* 28, 3970–3981. doi 10.1021/ef5001584
- Yang, W., Zhao, H., Wang, K., Zheng, C., 2015. Synergistic effects of mixtures of iron ores and copper ores as oxygen carriers in chemical-looping combustions. *Proc. Combust. Inst.* 35, 2811–2818. doi 10.1016/j.proci.2014.07.010
- Zafar, Q., Abad, A., Mattisson, T., Gevert, B., Strand, M., 2007. Reduction and oxidation kinetics of $Mn_3O_4/Mg-ZrO_2$ oxygen carrier particles for chemical-looping combustion. *Chem. Eng. Sci.* 62, 6556–6567. doi 10.1016/j.ces.2007.07.011
- Zhang, S., Xiao, R., Liu, J., Bhattacharya, S., 2013. Performance of $Fe_2O_3/CaSO_4$ composite oxygen carrier on inhibition of sulfur release in calcium-based chemical looping combustion. *Int. J. Greenh. Gas Control* 17, 1–12. doi 10.1016/j.ijggc.2013.04.010
- Zhao, H., Wang, K., Fang, Y., Ma, J., Mei, D., Zheng, C., 2014. Characterization of natural copper ore as oxygen carrier in chemical-looping with oxygen uncoupling of anthracite. *Int. J. Greenh. Gas Control* 22, 154–164. doi 10.1016/j.ijggc.2013.12.023
- Zhao, H., Guo, L., Zou, X., 2015. Chemical-looping auto-thermal reforming of biomass using Cu-based oxygen carrier. *Appl. Energy* 157, 408–415. doi 10.1016/j.apenergy.2015.04.093.
- Zheng, M., Shen, L., Feng, X., Xiao, J., 2011. Kinetic model for parallel reactions of $CaSO_4$ with CO in chemical-looping combustion. *Ind. Eng. Chem. Res.* 50, 5414–5427. doi 10.1021/ie102252z.
- Zheng, M., Shen, L., Feng, X., 2014. In situ gasification chemical looping combustion of a coal using the binary oxygen carrier natural anhydrite ore and natural iron ore. *Energy Convers. Manage.* 83, 270–283. doi 10.1016/j.enconman.2014.03.079.