



Enhancing properties of iron and manganese ores as oxygen carriers for chemical looping processes by dry impregnation



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HIGHLIGHTS

- Oxygen carriers were produced by impregnation of metal ores with iron and manganese oxides.
- The oxygen carriers were examined in a bench scale fluidised-bed reactor for CLOU and gaseous fuel conversion.
- Impregnation of these ores positively influences their mechanical properties.
- Above 850 °C, iron ore based oxygen carriers exhibited full syngas conversion.
- Iron ore impregnated with Mn₂O₃ showed significant CLOU behaviour.

ARTICLE INFO

Article history:

Received 10 May 2015

Received in revised form 20 October 2015

Accepted 22 October 2015

Available online 18 November 2015

Keywords:

CO₂ capture

Chemical looping

Oxygen carriers

Natural ore

Chemical-looping with oxygen uncoupling

ABSTRACT

The use of naturally occurring ores as oxygen carriers in CLC processes is attractive because of their relative abundance and low cost. Unfortunately, they typically exhibit lower reactivity and lack the mechanical robustness required, when compared to synthetically produced carriers. Impregnation is a suitable method for enhancing both the reactivity and durability of natural ores when used as oxygen carriers for CLC systems. This investigation uses impregnation to improve the chemical and mechanical properties of a Brazilian manganese ore and a Canadian iron ore. The manganese ore was impregnated with Fe₂O₃ and the iron ore was impregnated with Mn₂O₃ with the goal of forming a combined Fe/Mn oxygen carrier. The impregnated ore's physical characteristics were assessed by SEM, BET and XRD analysis. Measurements of the attrition resistance and crushing strength were used to investigate the mechanical robustness of the oxygen carriers. The impregnated ore's mechanical and physical properties were clearly enhanced by the impregnation method, with boosts in crushing strength of 11–26% and attrition resistance of 37–31% for the impregnated iron and manganese ores, respectively. Both the unmodified and impregnated ore's reactivity, for the conversion of gaseous fuel (CH₄ and syngas) and gaseous oxygen release (CLOU potential) were investigated using a bench-scale quartz fluidised-bed reactor. The impregnated iron ore exhibited a greater degree of syngas conversion compared to the other samples examined. Iron ore based oxygen carrier's syngas conversion increases with the number of oxidation and reduction cycles performed. The impregnated iron ore exhibited gaseous oxygen release over extended periods in an inert atmosphere and remained at a constant 0.2% O₂ concentration by volume at the end of this inert period. This oxygen release would help ensure the efficient use of solid fuels. The impregnated iron ore's reactivity for CH₄ conversion was similar to the reactivity of its unmodified counterpart. The unmodified manganese ore converted CH₄ to the greatest extent of all the samples tested here, while the impregnated manganese ore exhibited a decrease in reactivity with respect to syngas and CH₄ conversion.

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1. Introduction

Chemical looping combustion (CLC) is an emerging technology for high-efficiency fossil fuel conversion with inherent carbon capture. The technology's major advantage centres on its ability to

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separate oxygen from air and carry out fuel conversion directly with a hydrocarbon fuel. This avoids post-combustion flue gas treatment and its associated energy penalties [1]. CLC systems are based on already established fluidised-bed technology. While systems have been proposed using fixed and moving bed, and pneumatic transport variants, commonly proposed CLC systems generally comprise two interconnected circulating fluidised-bed reactors. A solid oxygen carrier (typically containing a transition metal oxide) is transferred from one reactor to the other, which provides the oxygen required for combustion. The two fluidised-beds are represented as the air reactor (AR) and fuel reactor (FR). The simplified process is shown in Fig. 1. In the FR, the oxygen carrier (OC) provides oxygen, for combustion of fuel in the absence of air. Following the combustion reaction, the reduced form of oxygen carrier is then transferred to the AR, where it is re-oxidised in air, and the looping process continues [2].

The progress required for industrial applications of CLC centres on the development of suitable oxygen carriers. Research into this field has been prolific, with many possible candidate materials tested [3]. A suitable oxygen carrier material for CLC should be relatively inexpensive, mechanically robust and reactive. The reactivity of oxygen carriers depends on several aspects of the chemistry of materials used, including the reducibility to a lower oxidation state, which facilitates the necessary conversion of fuel to combustion products; and the oxidation potential and behaviour of such materials. Oxygen carriers are required to undergo these reactions continuously over many cycles. It is therefore necessary they possess the required chemistry so that these reactions take place at temperatures appropriate for power generation (800–1100 °C). Research on CLC systems using gaseous fuels has received the bulk of attention so far, but current trends in research are increasingly directed to the use of solid fuels such as coal and biomass. Solid fuel conversion in the CLC process requires the presence of steam and/or CO₂ to gasify the solid fuels and produce the intermediate gaseous products CO and H₂, which can then react directly with the solid oxygen carrier [2]. However, this gasification step is relatively slow, limiting the overall fuel conversion rate [4]. In order to overcome this obstacle, the use of oxygen carrier materials that can decompose at high temperatures and under low oxygen partial pressures thereby releasing gaseous oxygen, can be employed [5]. This CLC process is known as chemical looping with oxygen uncoupling, (CLOU) as it does not depend solely on the in-situ gasification step [6]. Determination of the extent of oxygen release under low oxygen partial pressures is an important test to conduct when screening oxygen carriers for their suitability for the conversion of solid fuels in CLOU processes. Considering these prerequisites for a suitable oxygen carrier, the selection narrows towards a number of key transition metals such as Cu, Ni, Mn, Fe and Co and their corresponding oxide systems. Substantial reviews on these systems as well as naturally occurring materials such as ores and some waste or by-product materials have been investigated, elsewhere for both CLC and CLOU systems [3,7,8].

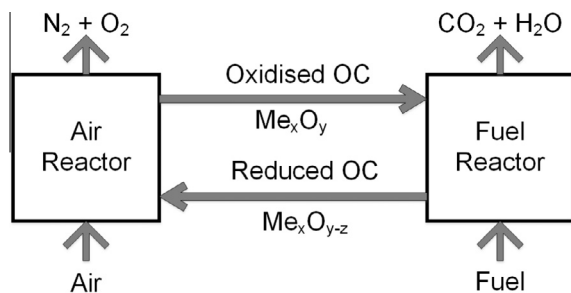


Fig. 1. Simplified schematic of a CLC process.

The earliest example of a CLOU system was the 'Brin process', which was one of the first widely used chemical methods of producing gaseous oxygen. The process utilised the reversible decomposition of barium peroxide to liberate gaseous oxygen and produce barium oxide. It was found that over several cycles the barium oxide systems lost activation, and required catalytic regeneration. The manufacture of gaseous oxygen using this production method ceased in 1906 in favour of the more economically attractive fractionation of liquid air [9]. Though the barium oxide system is not considered today for modern day CLOU processes, due to its toxicity, research continues into prolonging the process life of oxygen carriers. The use of combined materials offers a potential for increasing the process life of oxygen carriers. This is achieved by mixing an active phase material with another or with an inert material as a support. The most well investigated CLOU carrier is currently the Cu/CuO/Cu₂O system due to its favourable reaction kinetics but unfortunately it suffers from agglomeration issues due to the low melting point of Cu (1085 °C), which is close to the practical temperature required for oxygen release [10]. The loss of active oxygen carrier material through processes of attrition, agglomeration and deactivation has also caused research to look towards cheaper materials such as naturally occurring metal ores. Metal ores tend to show inferior chemical reactivity, and their stability and mechanical strength are generally less than synthetically produced ones, although iron ores, comprised mainly of hematite (Fe₂O₃), seem to possess suitable mechanical properties. It has been reported by Mattisson et al. [11] that hematite's methane conversion increases with numbers of oxidation and reduction cycles, though reactivity with methane yields low conversion rates. Nonetheless, the hematite/magnetite (Fe₂O₃/Fe₃O₄) system does not release gaseous oxygen, which is required for rapid and complete solid fuel conversion. Manganese ores have been looked at extensively by Arjmand et al. [12] and they have reported that in general fuel conversion increases with temperatures and that ready liberation of gaseous oxygen at low-oxygen partial pressures is limited to specific manganese ores. Manganese ores are also kinetically hindered during oxidation phases with maximum oxygen partial pressures of 5%. Therefore manganese ores require oxidation to occur at temperatures below 900 °C. Rydén et al. [13] extensively reviewed and investigated the combinations of manganese with other materials, and concluded that manganese in perovskite structures, coupled with calcium-manganates could operate at favourable temperatures and release substantial amounts of gaseous oxygen for CLOU. More notably the combination with iron as another cheap material is evidently interesting for manufacturing low-cost CLOU oxygen carrier. Iron ore's low reactivity and manganese ore's temperature limitations can be improved by combining the metal oxide active phases with other materials. Azimi et al. [14] conducted investigations concerning the Fe–Mn oxide systems looking at the experimental assessment of fuel conversion and oxygen release of varying molar ratios and calcination temperatures of the combined oxide system produced by spray drying. Their study concluded the combined Fe–Mn oxide system is a promising oxide combination, in which the oxidised forms of hematite and bixbyite ((Fe,Mn)₂O₃) can be reduced to magnetite and hausmannite ((Fe,Mn)₃O₄), which yields oxygen release corresponding to 3.3–3.4% change of mass.

Impregnation methods can successfully combine an active phase of a metal oxide onto an inert support material. The technique involves introducing a metal salt solution onto a porous inert support material. The salt solution is first dehydrated to remove the aqueous component and then thermally treated to decompose the salt component, and yield the required loading of active metal oxide. The support material is used to increase the mechanical strength of the oxygen carrier particle, in turn increasing the longevity of carrier particles. Several research groups have used the

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