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Review

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

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A B S T R A C T

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.

## 1. Introduction

Chemical looping combustion (CLC) is one method of electricity generation being developed to address the concerns of growing levels of atmospheric $CO_2$. CLC is a unique form of fuel combustion that can use most fuels (renewable or fossil based) and exhibits inherent $CO_2$ 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 (Porrazzo 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

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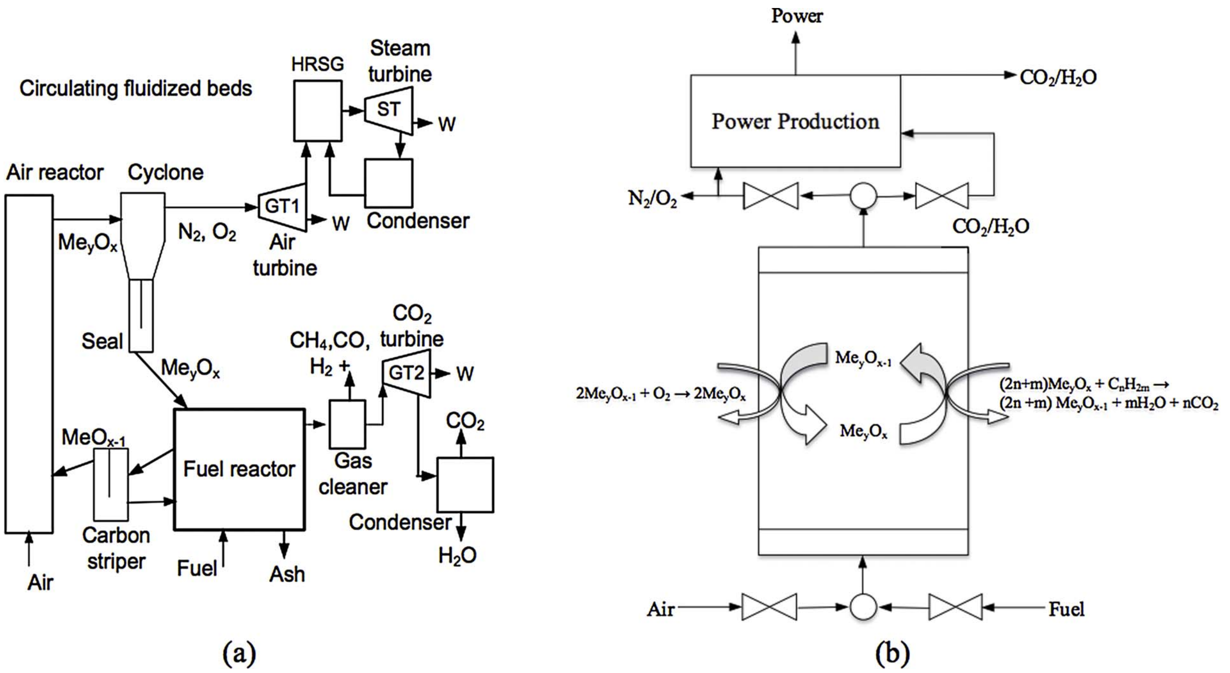

**Fig. 1.** Chemical looping technology: (a) Circulating fluidized bed (pressurized), (b) Fixed bed reactor with periodically changing input streams.

cycles shown in Reactions (1) and (2), respectively.

$$(2n+m)Me_yO_x + C_nH_{2m} \rightarrow (2n+m)Me_yO_{x-1} + mH_2\,O + nCO_2 \tag{1}$$

$$(2n+m)Me_yO_{x-1} + \left(n + \frac{1}{2}m\right)O_2 \rightarrow (2n+m)Me_yO_x \tag{2}$$

$$C_nH_{2m} + \left(n + \frac{1}{2}m\right)O_2 \rightarrow mH_2\,O + nCO_2 \tag{3}$$

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 ($\Delta H_2 < < 0$). 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). eG-CLC 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 (Porrazzo 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