Review

Chemical-looping combustion (CLC) for inherent CO2 separations—a review

Mohammad M. Hossain, Hugo I. de Lasa

Chemical Reactor Engineering Center, Department of Chemical and Biochemical Engineering, The University of Western Ontario, London, ON, Canada N6A 5B9

Abstract

This review reports recent advances on chemical-looping combustion (CLC). CLC is a promising technology for fossil fuel combustion preventing CO2 dilution with flue gases, mainly nitrogen. In CLC, the solid oxygen carrier supplies the stoichiometric oxygen needed for CO2 and water formation, and this leads to a free nitrogen mixture. As a result, the requirement of CO2 separation from flue gases, a major cost for CO2 capture, is circumvented. Furthermore, formation of NOx is also reduced. A good oxygen carrier for CLC shall readily react with the fuel gas and shall be reoxidized upon being contacted with oxygen. An oxygen carrier is typically formed by a metal oxide and an inert binder, which provide, respectively, oxygen storage, fluidizability and mechanical strength. Over the last 10 years, several research groups have been researching oxygen carriers which are both active and stable under fluidized bed conditions. While Fe, Ni, Cu, Mn and Co oxides are potential oxygen carrier materials, recent studies show that Ni is best suited for CLC. Few studies have been devoted to the solid-state kinetics of both reduction and oxidation with either a nucleation–nuclei growth or unreacted shrinking core models being considered. In order to implement CLC, two interconnected fluidized bed reactors (the fuel and air reactor) with the oxygen carrier circulated between units have been proposed. While reactor design, modeling and hydrodynamics are matters that have been analyzed by several research groups; these topics still require more attention and investigation. Preliminary economic assessments, have suggested that CLC holds great promise for combustion processes, having the potential for achieving very efficient and low cost CO2 capture. Even with these favorable prospects, commercial scale-up of CLC still depends nowadays on the availability of highly performing and stable oxygen carriers.

© 2008 Elsevier Ltd. All rights reserved.

Keywords:
Greenhouse gas
CLC
CFB-combustion
Oxygen carrier, CO2 capture
Fossil fuel-based power generation

Contents

1. Introduction ............................................................................................................................... 4434
2. Alternative CO2 capture technologies ..................................................................................... 4435
3. CO2 utilization and disposal ................................................................................................. 4435
3.1. CO2 capture costs .................................................................................................................. 4435
4. The novel CLC-combined power generations ......................................................................... 4436
5. CLC reactor system .................................................................................................................. 4437
6. Oxygen carriers ....................................................................................................................... 4439
6.1. Ni-based oxygen carriers ....................................................................................................... 4441
6.2. Fe-based oxygen carriers ....................................................................................................... 4442
6.3. Cu-based oxygen carriers ....................................................................................................... 4442
6.4. Mixed-oxide oxygen carriers ............................................................................................... 4443
7. The chemistry and the thermodynamics of CLC ..................................................................... 4445
8. Coke formation ....................................................................................................................... 4445
9. Effects of sulfur species in fuels ............................................................................................ 4446
10. Reduction and oxidation kinetics .......................................................................................... 4446
11. Conclusions ........................................................................................................................... 4448
Acknowledgements ................................................................................................................... 4449
References .................................................................................................................................... 4449

Corresponding author. Tel.: +1 519 661 2144; fax: +1 519 661 3498.
E-mail address: hdelasa@eng.uwo.ca (H.I. de Lasa).

Available online 29 May 2008

Received in revised form 14 May 2008
Accepted 20 May 2008

Oxygen carrier, CO2 capture

Fossil fuel-based power generation
1. Introduction

In the last decade, significant progress has been made towards a better understanding of the world climate and of the long-term impact of climate change. There is now evidence that the mean annual temperature at the earth’s surface increased over the past 200 years (Halmann and Steinberg, 2000). This temperature increase is commonly known as global warming.

It has been established that emission of greenhouse gases (e.g. CO₂, NOₓ, SOₓ, CH₄) is the main contributor to global warming, and CO₂ is the most prevalent of these gas emissions. Statistics indicate that the CO₂ emissions resulting from human activity have led to an increase in the atmospheric CO₂ concentration, from a pre-industrial level of 280 to 380 ppm (Halmann and Steinberg, 2000).

Combustion of fossil fuels releases a massive amount of carbon as carbon dioxide into the atmosphere. It is estimated that fossil fuel-based power generation contributes today to about one-third of the total carbon dioxide released from fuel combustion (Lyngfelt et al., 2001).

In 1997, the Kyoto Protocol was ratified by most of the developed countries setting the stage for an international effort to reduce CO₂ emissions. One possible approach to minimize CO₂ emissions is to enhance the use of renewable energy resources, such as biomass, solar and wind energies. These alternative energy sources have the intrinsic advantage of not generating CO₂ or contributing with a zero net CO₂ emissions. However, in their current state of development and/or availability, alternative energy technologies cannot fully replace the existing fossil fuels-based power generation. Thus, power generation via fossil fuel combustion with effective CO₂ capture, it appears is going to become a key contributor to the energy supply in the foreseeable future.

In order to capture CO₂, there are currently a number of available processes as follows: (i) pre-combustion, in which the fuel is de-carbonized prior to combustion, (ii) oxy-fuel combustion, which uses pure oxygen obtained from cryogenic nitrogen separation from air and (iii) post-combustion separation, which separate CO₂ form the flue gases using different approaches. These techniques are energy intensive, resulting in a significant decrease of the overall combustion efficiency and as a result in a price increase of the produced electricity. Considering all these factors, chemical-looping combustion (CLC) appears to have the potential for delivering a most efficient and low cost technology. This process was initially proposed to increase thermal efficiency in power generation stations, but later on was identified as having inherent advantages for CO₂ separation with minimum energy losses (Richert and Knoche, 1983; Ishida et al., 1987).

1.1. Chemical-looping combustion

CLC involves the use of a metal oxide as an oxygen carrier. This process is configured with two interconnected fluidized bed reactors: an air reactor and a fuel reactor (Fig. 1). The solid oxygen carrier is circulated between the air and fuel reactors. In CLC, the gaseous fuel is fed into the fuel reactor where it is oxidized by the lattice oxygen of the metal oxide. Complete combustion in the fuel reactor produces CO₂ and water vapor. Therefore, the CO₂ formed can be readily recovered by condensing water vapor, eliminating the need of an additional energy intensive CO₂ separation.

A generalized description of the overall reaction stoichiometry in the fuel reactor can be written as follows:

\[(2n + m)\text{MyO}_x + \text{C}_n\text{H}_{2m} \rightarrow (2n + m)\text{MyO}_{x-1} + m\text{H}_2\text{O} + n\text{CO}_2\quad (1)\]

Once fuel oxidation completed the reduced metal oxide \(\text{MyO}_{x-1}\) (or metal) is transported to the air reactor where it is reoxidized according to the following reaction:

\[\text{MyO}_{x-1} + \frac{1}{2}\text{O}_2(\text{air}) \rightarrow \text{MyO}_x + (\text{air} : \text{N}_2 + \text{unreacted O}_2)\quad (2)\]

The outlet gas stream of the air reactor contains nitrogen and unreacted oxygen. These gases can be released to the atmosphere with minimum negative environmental impact.

While the reduction reaction is often endothermic, the oxidation reaction is exothermic. Heats of the reaction depend on fuel type and on the metal oxide used as oxygen carrier. For a given fuel/oxygen carrier the heats of reaction can be calculated using classical thermodynamics: standard heat of reaction data, the specific heats of species and the reaction temperatures. As a result, the total heat evolved for the combined reduction and oxidation steps remains the same, as the one observed in a conventional combustion where the fuel is burned in direct contact with oxygen from air.

Regarding the oxygen carrier circulation between the two reactors the heat of reaction, the fuel flow rate and the oxygen carrying capacity of the carrier dictate the specific solid circulation rate (Kronberger et al., 2005; Lyngfelt et al., 2001; Garcia-Labiano et al., 2005).

Thus, while CLC does not bring any enthalpy gains, given the overall heat generation is equal to the heat of combustion. Its main advantage, however, resides in the inherent separation of both CO₂ and H₂O from the flue gases. In addition, CLC also minimizes NOₓ formation since the fuel burns in the fuel reactor in an air free environment and the reduced oxygen carrier is re-oxidized in the air reactor in the absence of a fuel, at comparatively lower temperatures. NOₓ formation usually occurs well above 1200 °C a potentially maximum temperature for CLC (Ishida and Jin, 1996).

The large-scale application of CLC is still contingent upon the availability of suitable oxygen carriers. Transition metal oxides such as nickel, copper, cobalt, iron and manganese are good oxygen carrier candidates. These metal oxides are adequate for CLC given their favorable reductive/oxidative thermodynamics. Oxygen carrier particles should also have: (a) high oxidation and reduction activity, (b) stability under repeated oxidation/reduction, (c) mechanical strength in fluidized beds and resilience to agglomeration (Adanez et al., 2004; Cho et al., 2004; Lyngfelt et al., 2001; Mattisson et al., 2004). Other important factors for a successful oxygen carrier are its costs and its environmental impact.
2. Alternative CO₂ capture technologies

The first step of CO₂ sequestration is its separation from the flue gases resulting from a fossil fuel combustion process. Wide ranges of technologies are currently available for CO₂ capture although the majority of them were not specifically developed for CO₂ sequestration. These processes have been practiced for a long time in chemical and petrochemical industries (Halmann and Steinberg, 2000). Existing technologies are based on physical and chemical separation of CO₂ including absorption, adsorption, cryogenics and membranes.

Absorption processes use a suitable solvent to separate CO₂ from the flue gas stream. Alkanolamines such as monoethanolamine (MEA) and diethanolamine (DMEA) are typically used in chemical absorption while methanol, dimethylether polyethylene glycol and sulfolane are employed in physical absorption (Halmann and Steinberg, 2000). Major issues with MEA and other solvents are the equipment corrosion in presence of O₂ and the energy intensive solvent regeneration. In addition, the presence of common flue gas contaminants such as SO₂, NOₓ have a negative impact on solvent-based process performance.

Adsorption processes are based on the selective adsorption of CO₂ on a solid adsorbent such as zeolites, alumina molecular sieve and activated carbon. These processes, which are finding applications in H₂ production from syngas and in natural gas sweetening, require energy intensive adsorbent regeneration.

Porous membranes separate gas molecules of different molecular sizes. Various types of permeable membrane materials are available including polymers, metals and rubber composites (McKee, 2002). Low gas throughputs are the main disadvantages with membrane separation requiring multistage operation or stream recycling.

3. CO₂ utilization and disposal

Once CO₂ is separated from the flue gas stream, it has to be utilized or stored. By far, the most popular use of CO₂ is the enhanced oil recovery (EOR) from depleted reservoirs (Koljonen et al., 2004). CO₂ also has some industrial use in the following areas: food production, chemical industry, fire fighting, fish farms, agricultural greenhouses, rubber/plastic processing and as a supercritical solvent. However, estimations show that the overall use of CO₂ is very small, as compared to the total CO₂ emitted annually (Granite and O’Brien, 2005; Koljonen et al., 2002).

Therefore the captured CO₂ should be stored or disposed permanently in suitable locations (Granite and O’Brien, 2005). In this respect, active and uneconomical oil and gas reservoirs, coal beds and mines, mineral carbonation, saline aquifers and under the ocean disposal are potentially large-scale underground sites for CO₂ storage.

In EOR, CO₂ injection enhances the mobility of the crude helping with its removal from depleted reservoirs (Blok et al., 1997). A similar approach can also be applied in out of commission natural gas fields, where CO₂ injection, might allow enhanced natural gas extraction (McKee, 2002).

Non-minable deep coal beds provide other attractive alternative sites for CO₂ disposal. Sequestration of CO₂ in these sites, have also important related advantages for methane recovery from coal beds. Coal has a larger adsorption affinity for CO₂ than for the displaced methane. As a result about two times more CO₂ (mole basis) can be stored with the following advantages: (i) enhanced methane recovery, (ii) improved mine safety (Koljonen et al., 2002).

The igneous rock composed of magnesium oxide bound to silica, and alumina-forming alumino-silicates can react with CO₂ forming a stable and long-lived solid material. This reaction occurs naturally over long periods of time. Advanced chemical approaches need, however, to be adapted to accelerate this reaction for CO₂ sequestration.

Pressurized CO₂ dissolves in the saline water of deep aquifers. This technique has already been implemented to sequester the CO₂ produced from natural gas sweetening processes. For instance, in a natural gas field, operated by the Statoil Company, one million tonnes of CO₂ were sequestered per year into 3000 ft below the North Sea (Halmann and Steinberg, 2000).

CO₂ can be disposed into the ocean using two primary methods. The first approach involves dissolution of CO₂ by injecting it at approximately 1500 m below sea level. At these conditions, with pressures above 50 bars, it is speculated that liquid CO₂ mixes with seawater. The resulting solution reaches a higher density than that of seawater and the liquid CO₂ sinks. In a second proposed method CO₂ is injected at 3000 m below sea level. The absolute pressure at these conditions is large enough to form a liquid CO₂ phase with a density higher than that of seawater (Halmann and Steinberg, 2000). Thus, at these sea depths CO₂ remains locked by forming “CO₂ lakes” on the ocean floor.

In summary, the capacity offered by various CO₂ disposal sites is very significant. However, there are still considerable uncertainties in determining actual capacities of these sites. According to literature studies, the deep ocean disposal offers the largest CO₂ storage capacity, as compared to other possible storage sites (Halmann and Steinberg, 2000). However, one should well be aware, that in deep ocean CO₂ disposal there are potential risks to the marine life and environment. As a result, additional research is required for comprehensive risk assessments and before large-scale CO₂ deep ocean disposal implementation.

Concerning CO₂ sequestration, a number of environmental, health and safety scenarios may be mentioned with hazardous situations being a function of CO₂ leakage rate, concentration, human exposure duration, site topography and atmospheric conditions. A small leakage can present a serious danger to people. CO₂ can also contaminate potable water by making it more acidic. As well, natural occurrences such as earthquakes and volcanic eruptions can also pose risks to CO₂ storage given they could create large and sudden underground leakages.

3.1. CO₂ capture costs

There are three basic costs involved in CO₂ capture and sequestration: capture/compression, transport and storage. These costs highly depend on the source of CO₂, the capture technology used, the infrastructure required, the transportation distance and the type and availability of disposal sites. On this basis, the CO₂ sequestration cost can be calculated as follows (Rao and Rubin, 2002):

Cost of CO₂ avoided ($/tonne)

\[
\text{Cost of CO}_2 \text{ avoided} (\$/\text{tonne}) = \left( \frac{\text{($/kWh)}_{\text{capture}} - \text{($/kWh)}_{\text{reference}}}{{(\text{tonne CO}_2/\text{kWh})}_{\text{reference}} - (\text{tonne CO}_2/\text{kWh})_{\text{capture}}} \right)
\]

Table 1 summarizes a case study that shows the impacts of MEA-based CO₂ separation unit on performance, emissions and costs. One can observe that the incorporation of the CO₂ capture system in a

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference plant</th>
<th>With CO₂ capture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Net plant capacity (MW)</td>
<td>462</td>
<td>326</td>
</tr>
<tr>
<td>CO₂ emission rate (g CO₂/kWh)</td>
<td>941</td>
<td>133</td>
</tr>
<tr>
<td>SO₂ emission rate (g SO₂/kWh)</td>
<td>2.45</td>
<td>0.0003</td>
</tr>
<tr>
<td>NOₓ emission rate (g NOₓ/kWh)</td>
<td>0.45</td>
<td>0.58</td>
</tr>
<tr>
<td>CO₂ sequestered (tonne/yr)</td>
<td>–</td>
<td>2.58 × 10⁵</td>
</tr>
<tr>
<td>Cost of electricity ($/MWh)</td>
<td>97.0</td>
<td>59.1</td>
</tr>
</tbody>
</table>

Thus, at these sea depths CO₂ remains locked by forming “CO₂ lakes” on the ocean floor.
500 MW plant increases the total capital cost of the facility from 571M (US$) (for the reference plant) to 705M (US$). There is also an additional estimated cost of 59.1 US$ per tonne of CO$_2$ disposed. In this estimation approximately 75% of the cost is associated with the capture and the compression while 8% and 13% costs are assigned to the transportation and the storage, respectively. As per the energy consumption, the CO$_2$ capture unit consumes 27% of the gross plant energy capacity with most of it being utilized for solvent separation and CO$_2$ compression. The presence of nitrogen in the combustion air dilutes the flue gas stream contributing significantly to the energy requirements for CO$_2$ separation. As an example, in the case of a coal-fired power plant using available technologies, almost one fifth of the electricity produced is needed for the CO$_2$ separation (Gielen, 2003). In conclusion, the CO$_2$ capture and sequestration from fossil fuel combustion is a viable option to minimize greenhouse gas emission. The available technologies are technically mature enough to be implemented at large-scale. However, existing technologies are energy intensive and as a result quite costly.

Thus, CLC offers great opportunity to eliminate the energy intensive CO$_2$ removal steps minimizing sequestration cost. However, at its present status this technology is probably not mature enough to be implemented in a commercial scale. Due to these facts, in the last several years, numerous research and development efforts have been addressed towards the establishment of this promising process.

4. The novel CLC-combined power generations

Aside from the need of technological improvement of the CLC system, there are some other important issues that have to be addressed for commercial implementation of an integrated power generation plant, and this includes: (i) the plant configuration, (ii) the possibility of integration with existing power plants, (iii) the operating parameters, (iv) the energy efficiencies, and (v) the economic analysis. In the open literature, there are a number of process simulations available on CLC-based power generation addressing the above issues. Most of these studies consider either methane or syn-gas (CO and H$_2$) as possible fuels with Ni- and Fe-based materials chosen as oxygen carriers due to their favorable cost, reactivity and stability.

A simplified scheme of an integrated CLC-based power plant is shown in Fig. 2 (Brandvoll and Bolland, 2004). In this configuration, the outlet gas stream of the air reactor drives the gas turbine (or air turbine) while the exhaust of the fuel reactor drives the CO$_2$ turbine. The exhaust from the air turbine is circulated through a heat recovery steam generator (HRSG) to produce steam, which is used in the low pressure (bottoming) steam turbine to generate extra power. After circulating through the CO$_2$ turbine, the gas is further cooled to nearly ambient temperature in order to condense the water, leaving almost pure CO$_2$(greater than 90%). Finally, the concentrated CO$_2$ stream is compressed for transportation and sequestration.

As mentioned in the introduction of this review, Richter and Knoche (1983) proposed in the early eighties a CLC process to increase fossil fuel fired power plant thermal efficiency by minimizing the energy degradation (or loss). However, Ishida et al. (1987) were the first authors to report a CLC-based power generation for inherent CO$_2$ separation. According to Ishida et al. (1987), approximately 50–60% electrical efficiency can be obtained by employing a CLC-integrated power generation system. In such process, the calculated CO$_2$ emission rate was 0.33 kg/kWh of produced electricity, which is significantly lower than the one of a conventional fossil fuel power plant.

Anheden and Svedberg (1998) performed a detailed energy analysis for two different CLC gas turbine systems. In the first system, methane was used as a fuel and NiO as oxygen carrier, while in the second system; the fuel employed was gasified coal (CO and H$_2$) and Fe$_2$O$_3$ as oxygen carrier. The power efficiency in both cases was 48%, which is comparable to the one of a conventional power generation station. However, taking into account the gains of inherent CO$_2$ separation, a CLC-based process offers higher overall energy efficiencies.

Brandvoll and Bolland (2004) presented a CLC-based power generation facility considering NiO/yttria-stabilized zirconia (YSZ) as oxygen carrier. The process model was developed using mass and energy balances and involving the six main units of the CLC process including turbine, compressor, pump, reactors, heat exchangers and condensers. Results of this analysis show that approximately a 56% overall efficiency can be achieved with the above mentioned configuration. At similar conditions, a conventional power generation station offers a slightly lower efficiency of 55%.

Naqvi et al. (2004) considered a thermodynamic cycle analysis of a CLC power plant using a steady-state model. In this analysis, the effect of coke formation was included. With this configuration the CLC-based system provides 49.7% efficiency with zero CO$_2$ emissions. A conventional steam cycle operated under similar conditions with solvent CO$_2$ capture yielded 40.1% efficiency.

Wolf et al. (2005) and Wolf and Yan (2005) developed a comparative analysis between a CLC and a MEA process for CO$_2$ capture in a conventional power generation station. According to this study, the energy losses in CLC are smaller than those experienced in conventional combustion, although the electrical efficiency of CLC is slightly lower. However and once the CO$_2$ separation is included in the calculation and given that CLC does not require additional energy for CO$_2$ capture, the CLC process provides a higher efficiency than the one for conventional combustion: 53% electrical efficiency at 1200 °C with almost 100% pure CO$_2$ compressed at 110 bars.

Consonni et al. (2006) studied CLC-combined power generation cycles using two alternatives: (i) an unfired system and (ii) a fired system. In the unfired configuration, natural gas was fed into the CLC system and the maximum calculated temperature was 1050 °C. This temperature is below the maximum temperature allowed in gas turbines. The above configuration offered 48% overall efficiency. To improve this situation, Consonni et al. (2006) incorporated a secondary supplementary combustor between the exit of the oxidation reactor and the gas turbine expander. The supplementary combustor decoupled the maximum temperature of the CLC and the gas turbine and thus increased the plant efficiency approximately to 52%. This configuration has, however, a main disadvantage, there are CO$_2$ emissions from the supplementary fuel combustion unit.

Recently, Naqvi et al. (2007) reported a part-load analysis of a CLC-based power generation process, which is a common practice in power generation and this to comply with power fluctuation demands. This analysis shows that approximately 52.2% net efficiency can be obtained at full load, including CO$_2$ compression up to 200 bars. The net efficiency, however, drops to 49.8% when the load is reduced to 60%, with this efficiency being still higher as compared to the one of conventional power generation.

In conclusion, according to the previous studies CLC offers higher overall efficiencies versus conventional power generation with CO$_2$ solvent separation. One should realize, however, that these CLC-based power efficiency assessments normally assume conditions such as instantaneous reactions in both fuel and air reactors and no oxygen carrier deactivation. These idealized kinetic assumptions still require clarification for proper efficiency calculations. As well, one should notice that there is little or no information available concerning the fuel and air reactors. Successful commercialization of integrated CLC power generation processes certainly depends on the development of both specific process configurations and original reactor designs.
5. CLC reactor system

High performance in CLC requires an intimate contact between the oxygen carrier and the gas phase species. Given phase contacting is strongly related to reactor configuration; the specific selected reactor design is very critical.

Kronberger et al. (2005) reported a comprehensive design procedure for CLC process (Fig. 3). Their procedure considers the fuel and the carrier flow rates, the oxygen capacity of the carrier and the reaction kinetics in both the air and fuel reactors. This design approach also incorporates hydrodynamic considerations, such as particle entrainment, residence time, pressure drop and CO₂ leakage factors.

Wolf (2004) also provided a similar list pointing out the essential features of an efficient CLC system:

(i) Sufficient particle circulation between the fuel and air reactors to achieve complete fuel combustion.
(ii) Adequate contact time between the fuel/air and the solid oxygen carrier to achieve maximum conversion.
(iii) High temperature to maximize the gas turbine efficiency.
(iv) High pressure operation to provide higher overall efficiency of the power generation, with high pressure being also favorable for the down stream CO₂ sequestration.
(v) Limited CO₂ leakage from the fuel to the air reactor.

Concerning CLC reactor design, several designs have been tested using cold-models and hot prototypes. These studies suggest that...
CLC can be carried out in a variety of configurations with the two interconnected fluidized bed arrangements being favored (Lyngfelt et al., 2001; Ryu et al., 2002a,b; Mattisson et al., 2001; Johansson et al., 2002; 2006a,b; Abad et al., 2006).

Fig. 4 reports an interconnected fluidized bed CLC system. For such a process a high-velocity riser and a low velocity bubbling fluidized bed are considered as the air and fuel reactors, respectively. The solid particles leaving the riser are recovered by a cyclone and sent back to the fuel reactor. In the low velocity fluidized bed (fuel reactor), the oxygen is transferred from the carrier to the fuel. In this unit, particles mainly circulate by gravity and as a result the fuel reactor has to be placed at sufficient height in the plant. In the high velocity air riser reactor the volumetric flow rate is approximately 10 times greater than that in the fuel reactor. As a consequence and to maintain a comparable reactor size, a high velocity is adopted for the air reactor. In addition, the high velocity in the riser (air reactor) provides the required driving force to circulate the particles between the two interconnected beds.

Kronberger et al. (2005) studied two different particle separation systems. In the first one, a cyclone was used for solid separation from the air reactor exit stream. Solids leave the fuel reactor by an over flow standpipe and are returned into the air reactor at a height corresponding to the appropriate pressure level. An L-type loop-seal device is used to separate the fuel and air reactors. The second type of solid separation uses a cyclone with a “hat” separator placed at the air reactor exit, with this device reducing exit effects on the solid flows. Due to its conical shape the “hat” allows particles to fall directly on the cyclone minimizing particle back flow. This configuration also reduces particle separator pressure drop.

In order to diminish the installation and operating costs, Kronberger et al. (2004) proposed a two compartment fluidized bed reactor configuration. As shown in Fig. 5, this reactor system has two adjacent fluidized beds, separated by a vertical wall having two orifices. The gas high velocity in the air reactor forces particles to travel upwards with some of the particles falling into the fuel reactor. There is also a slot at the bottom of the vertical wall allowing particles to move back from the fuel reactor to the air reactor.

In the interconnected two fluidized bed configuration, there is always the possibility of gas leakage. A gas (fuel) leakage from the fuel reactor into the air reactor causes carbon dioxide release into the atmosphere, reducing consequently the CLC carbon dioxide capture efficiency. A gas (air) leakage from the air reactor into the fuel reactor dilutes the flue gas stream with N₂, adding extra cost to the CO₂ separation. Therefore, it is essential to minimize gas leakage between air and fuel reactors.

In order to prevent gas leakage between reactors, Lyngfelt et al. (2001) proposed two loop-seal devices, one placed between the air reactor and the cyclone and the other located between the fuel reactor and the air reactor. A loop-seal device with injection steam into the downer (fuel reactor) can also help creating a gas barrier, which minimizes gas leakage.

Recently, Johansson et al. (2003, 2006) have reported an experimental investigation on gas leakage in fluidized bed CLC processes. These authors recommend a number of measures to minimize gas leakage: (a) two loop-seals to prevent gas mixing between the two reactor units, (b) a pot-seal placed between the air and fuel reactors and a pot-seal located at the bottom of the cyclone downcomer. High solid recirculation can also decrease gas leakage given at high solid rates downcomer particles flow more rapidly than the upward gas flow used for aeration. Even more, employing steam instead of air, in the pot-seal aeration, one can further reduce gas leakage.
leakage. It was found that under these operating conditions gas leakage from the fuel reactor to the cyclone can be decreased from 3.5% to 1%, while the gas leakage between the pot-seal and the fuel reactor can be reduced from 12% to 2% (Johansson et al., 2006).

6. Oxygen carriers

The selection of the oxygen carrier is considered as one of the most essential components of the CLC process. Since first proposed by Richter and Knoche (1983), it has been acknowledged that large-scale application of CLC is contingent to the availability of suitable oxygen carriers. In fact the amount of the bed material in each reactor and the solid circulation rates between reactors mainly depends on the oxygen carrying capacity of the carriers. Therefore, a most important characteristic of a successful oxygen carrier is its reactivity in both reduction and oxidation cycles. In addition, its ability to completely combust a fuel is another important criterion for an oxygen carrier selection and this to achieve maximum fuel combustion efficiency. Furthermore, on top of the two cited criteria, oxygen carrier particles should display the following characteristics:

- Be stable under repeated oxidation/reduction cycles at high temperature.
- Be fluidizable.
- Be resistant to agglomeration.
- Be mechanical resistant to the friction stress associated with high circulation of particles.
- Be environmentally benign and
- Be economically feasible.

Most of previous technical literature on CLC has been focused on the development of suitable oxygen carrier materials. Transition metal oxides such as nickel, copper, cobalt, iron and manganese are good candidates given their favorable reductive/oxidative thermodynamic properties.

Table 2 lists the oxygen carrying capacity (moles of oxygen per mole of metal) of above mentioned metal oxides. Among the candidate metal oxides Co3O4 offers the highest amount of oxygen (0.67 moles) per mole of metal. However, NiO, with the potential of transferring 0.5 moles of oxygen per mole of metal, has been considered to be promising given its other favorable properties as discussed in the upcoming sections.

Mattisson and Lyngfelt (2001) and Jerndal et al. (2006) reported a possible choice of oxygen carrier materials based on thermodynamics. Fig. 6 reports the equilibrium constant $K$ (logarithmic scale) versus $1/T$ plots for the reduction of some common materials using methane as the reducing agent (fuel), with a high log $K$ value indicating high metal oxide potential to react with methane. In line with this, possible CLC operating temperatures (600–1200 °C) have been proposed. It is apparent that under these conditions MnO2/Mn2O3, Mn2O3/Mn3O4, Co3O4/CoO and CuO/Cu2O have greater tendency to react with methane as compared to Fe2O3/Fe3O4 and NiO/Ni. However, MnO2, Mn2O3, Co3O4 and CuO decompose into Mn2O3, Mn3O4, CoO and Cu2O, respectively, at low temperatures. Thus, with the only exception of CuO (decomposition temperature of 1030 °C) these materials may not be suitable as oxygen carriers.

As mentioned above, complete conversion of fuel is another important characteristic desirable for an oxygen carrier. In order to verify these characteristics, the degree of methane conversion to carbon dioxide was calculated by using the method of minimization
Operating temperature is close to their melting point. For instance, some metals potentially suitable for use as oxygen carriers (Ryu et al., 2004) as a result unsuitable as CLC materials. Cu has a relatively low melting point (1085 °C) and as a consequence, cannot be used above 900 °C.

Apart from thermodynamics, some physical properties such as density, active surface area, pore volume, particle size and crushing strength are also important parameters for a successful oxygen carrier material (Adané et al., 2004; Cho et al., 2004). The density and particle size not only determine the fluidizability of the oxygen carrier but also may affect the overall reaction rate, given their influence on mass and heat transfer inside the particles. According to the literature, oxygen carriers with particle sizes ranging from 0.8 to 2 mm are suitable for CLC.

### Table 3
Properties of suitable metal/oxygen carriers for CLC (Ryu et al., 2004)

<table>
<thead>
<tr>
<th>Metal/Oxide</th>
<th>M.W.</th>
<th>M.P. (°C)</th>
<th>B.P. (°C)</th>
<th>ΔH‡ 298 (kcal/mol)</th>
<th>ΔS‡ 298 (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (iron)</td>
<td>55.85</td>
<td>1536</td>
<td>2800</td>
<td>0</td>
<td>6.52 ± 0.03</td>
</tr>
<tr>
<td>FeO</td>
<td>71.85</td>
<td>1378</td>
<td>–</td>
<td>–63.2 ± 0.3</td>
<td>14.05 ± 0.2</td>
</tr>
<tr>
<td>Fe3O4</td>
<td>231.55</td>
<td>1597</td>
<td>–</td>
<td>–266.9 ± 1.0</td>
<td>36.2 ± 0.6</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>159.70</td>
<td>1594</td>
<td>–</td>
<td>–196.3 ± 0.8</td>
<td>20.9 ± 0.1</td>
</tr>
<tr>
<td>Ni (nickel)</td>
<td>58.69</td>
<td>1453</td>
<td>2910</td>
<td>0</td>
<td>7.14 ± 0.05</td>
</tr>
<tr>
<td>NiO</td>
<td>74.69</td>
<td>1955</td>
<td>–</td>
<td>–57.5 ± 0.5</td>
<td>9.1 ± 0.1</td>
</tr>
<tr>
<td>Co (cobalt)</td>
<td>58.93</td>
<td>1495</td>
<td>2930</td>
<td>0</td>
<td>7.18 ± 0.1</td>
</tr>
<tr>
<td>CoO</td>
<td>74.93</td>
<td>1905</td>
<td>–</td>
<td>–63.2 ± 0.3</td>
<td>12.65 ± 0.2</td>
</tr>
<tr>
<td>Co3O4</td>
<td>240.79</td>
<td>–</td>
<td>–</td>
<td>–63.2 ± 0.3</td>
<td>24.5 ± 0.05</td>
</tr>
<tr>
<td>Cu (copper)</td>
<td>63.54</td>
<td>1083</td>
<td>2560</td>
<td>0</td>
<td>7.92 ± 0.05</td>
</tr>
<tr>
<td>CuO</td>
<td>143.08</td>
<td>1236</td>
<td>–</td>
<td>–40.9 ± 0.7</td>
<td>22.25 ± 0.1</td>
</tr>
<tr>
<td>CuO</td>
<td>79.54</td>
<td>–</td>
<td>–</td>
<td>–37.1 ± 0.8</td>
<td>10.2 ± 0.05</td>
</tr>
<tr>
<td>Mn (manganese)</td>
<td>54.94</td>
<td>1244</td>
<td>–</td>
<td>0</td>
<td>7.65 ± 0.02</td>
</tr>
<tr>
<td>MnO</td>
<td>70.94</td>
<td>1875</td>
<td>–</td>
<td>–92.0 ± 0.5</td>
<td>14.32 ± 0.2</td>
</tr>
<tr>
<td>Mn2O3</td>
<td>228.82</td>
<td>1505</td>
<td>–</td>
<td>–331.4 ± 1.0</td>
<td>36.8 ± 0.8</td>
</tr>
<tr>
<td>Mn3O4</td>
<td>157.88</td>
<td>–</td>
<td>–</td>
<td>–228.7 ± 1.2</td>
<td>26.4 ± 0.05</td>
</tr>
<tr>
<td>MnO2</td>
<td>86.94</td>
<td>–</td>
<td>–</td>
<td>–124.3 ± 0.5</td>
<td>12.7 ± 0.1</td>
</tr>
<tr>
<td>W (tungsten)</td>
<td>183.85</td>
<td>3410</td>
<td>5555</td>
<td>0</td>
<td>7.8 ± 0.1</td>
</tr>
<tr>
<td>WO2</td>
<td>215.85</td>
<td>1724</td>
<td>–</td>
<td>–140.95 ± 0.2</td>
<td>12.08 ± 0.4</td>
</tr>
<tr>
<td>WO3</td>
<td>231.85</td>
<td>1472</td>
<td>1837</td>
<td>–201.45 ± 0.7</td>
<td>18.14 ± 0.3</td>
</tr>
<tr>
<td>Mo (molybdenum)</td>
<td>95.94</td>
<td>2620</td>
<td>4600</td>
<td>0</td>
<td>6.85 ± 0.05</td>
</tr>
<tr>
<td>MoO2</td>
<td>127.94</td>
<td>–</td>
<td>–</td>
<td>–140.5 ± 0.4</td>
<td>11.95 ± 0.3</td>
</tr>
<tr>
<td>MoO3</td>
<td>143.94</td>
<td>–</td>
<td>–</td>
<td>–178.1 ± 0.2</td>
<td>18.59 ± 0.15</td>
</tr>
<tr>
<td>Cr (chromium)</td>
<td>52.00</td>
<td>1857</td>
<td>2672</td>
<td>0</td>
<td>5.65 ± 0.05</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>152.00</td>
<td>2400</td>
<td>–</td>
<td>–270.0 ± 2.5</td>
<td>19.4 ± 0.2</td>
</tr>
<tr>
<td>CrO2</td>
<td>84.00</td>
<td>–</td>
<td>–</td>
<td>–139.2 ± 2.0</td>
<td>12.2 ± 2.1</td>
</tr>
<tr>
<td>CrO3</td>
<td>100.00</td>
<td>–</td>
<td>–</td>
<td>–138.5 ± 2.5</td>
<td>17.2 ± 2.5</td>
</tr>
<tr>
<td>Nb (niobium)</td>
<td>92.91</td>
<td>2468</td>
<td>4750</td>
<td>0</td>
<td>8.73 ± 0.15</td>
</tr>
<tr>
<td>NbO</td>
<td>108.91</td>
<td>1935</td>
<td>–</td>
<td>–100.3 ± 3.0</td>
<td>11.0 ± 2.0</td>
</tr>
<tr>
<td>Nb2O3</td>
<td>124.91</td>
<td>1902</td>
<td>–</td>
<td>–190.0 ± 2.0</td>
<td>13.03 ± 0.07</td>
</tr>
<tr>
<td>Nb2O4</td>
<td>265.82</td>
<td>1510</td>
<td>–</td>
<td>–454.0 ± 1.2</td>
<td>32.82 ± 0.3</td>
</tr>
<tr>
<td>V (vanadium)</td>
<td>50.94</td>
<td>1904</td>
<td>3350</td>
<td>0</td>
<td>6.92 ± 0.13</td>
</tr>
<tr>
<td>VO</td>
<td>66.94</td>
<td>1790</td>
<td>–</td>
<td>–103.2 ± 1.5</td>
<td>9.32 ± 0.2</td>
</tr>
<tr>
<td>V2O3</td>
<td>149.88</td>
<td>2070</td>
<td>–</td>
<td>–291.3 ± 1.5</td>
<td>23.44 ± 0.3</td>
</tr>
<tr>
<td>VO2</td>
<td>82.94</td>
<td>1545</td>
<td>–</td>
<td>–170.5 ± 0.9</td>
<td>12.37 ± 0.2</td>
</tr>
<tr>
<td>V2O5</td>
<td>181.88</td>
<td>670</td>
<td>1690</td>
<td>–370.6 ± 1.5</td>
<td>31.2 ± 0.4</td>
</tr>
<tr>
<td>Ce (cerium)</td>
<td>140.12</td>
<td>798</td>
<td>3424</td>
<td>0</td>
<td>17.2</td>
</tr>
<tr>
<td>Ce2O3</td>
<td>328.24</td>
<td>–</td>
<td>–</td>
<td>–435.4 ± 0.9</td>
<td>36.0 ± 0.1</td>
</tr>
<tr>
<td>CeO2</td>
<td>172.12</td>
<td>–</td>
<td>–</td>
<td>–260.5 ± 0.4</td>
<td>14.9 ± 0.1</td>
</tr>
<tr>
<td>In (indium)</td>
<td>114.82</td>
<td>157</td>
<td>2073</td>
<td>0</td>
<td>13.82 ± 0.20</td>
</tr>
<tr>
<td>In2O3</td>
<td>277.64</td>
<td>1910</td>
<td>–</td>
<td>–221.3 ± 0.4</td>
<td>25.8 ± 0.8</td>
</tr>
<tr>
<td>Sn (selenium)</td>
<td>118.71</td>
<td>232</td>
<td>2605</td>
<td>0</td>
<td>12.24 ± 0.1</td>
</tr>
<tr>
<td>SnO</td>
<td>134.71</td>
<td>–</td>
<td>–</td>
<td>–68.4 ± 0.3</td>
<td>13.5 ± 0.5</td>
</tr>
<tr>
<td>SnO2</td>
<td>150.71</td>
<td>2000</td>
<td>2500</td>
<td>–138.8 ± 0.5</td>
<td>12.5 ± 0.3</td>
</tr>
</tbody>
</table>


of Gibbs free energy (Mattisson and Lyngfelt, 2001; Jerndal et al., 2006). In this calculation CH4, CO2, CO, H2O2, H2 and O2 are considered as possible gaseous products (between 600 and 1200 °C). Methane to CO2 conversion, however, the overriding chemical transformation property, is described in Fig. 7. This analysis shows that Mn2O3/Mn3O4, CuO/Cu2O, Fe2O3/Fe2O4 and NiO/Ni carriers are able to convert methane to CO2 almost completely.

Another important design consideration in CLC is the melting point of the oxygen carrier. This melting point should be high enough both to withstand the CLC reaction temperature and to avoid agglomeration of circulating particles. Table 3 lists the melting point of some metals potentially suitable for use as oxygen carriers (Ryu et al., 2004). Since the CLC process may be operated between 600 and 1200 °C, there is a concern that some metals soften, if the selected operating temperature is close to their melting point. For instance, Cd, Zn and Ce with melting points below than or close to 600 °C, are as a result unsuitable as CLC materials. Cu has also a relatively low
both iron- and copper-based oxygen carriers attracted significant number of research studies. On the other hand, nickel-based materials received extra attention given its superior reactivity, thermal stability, negligible volatility, with all these being favorable factors for high temperature and high gas turbine performance CLC (Villa et al., 2003).

To increase their reactivity, durability and fluidizability oxygen carrier particles can be prepared by depositing the active metal oxides on an inert support such as SiO₂, TiO₂, ZrO₂, Al₂O₃, YSZ and bentonite.

In the case of a supported metal oxide oxygen carriers, the oxygen carrying capacity is a strong function of the metal loading and of the stability of the carrier over repeated reduction–oxidation cycles. In addition, different oxygen carriers may be reduced to different states depending upon the metal dispersed on the support materials. As a result of this it is quite common to observe a reported mass-based conversion (oxygen ratio) to express the oxygen carrying capacity of a given carrier. Oxygen ratios of different metal supported oxygen carriers are summarized in Table 4.

6.1. Ni-based oxygen carriers

Regarding nickel-based oxygen carriers both bulk and supported NiO/Ni materials have been reported. Bulk NiO has been studied using thermodynamics, reactivity tests and energy analysis. Usually unsupported NiO displays poor reoxidation over repeated reduction and oxidation cycles. This poor performance is the result of nickel agglomeration, which affects reactivity and makes it unsuitable for CLC (Jin and Ishaïda, 2004).

As a result, supported NiO/Ni materials are preferred. Among available support materials, alumina (Al₂O₃) has received the highest attention given its favorable fluidization properties and thermal stability (Ishaïda and Jin, 1997; Ishaïda et al., 1998; Jin et al., 1999, Jin and Ishaïda, 2000, 2001; Mattisson et al., 2003; Adanet et al, 2004; Son and Kim, 2006; Garcia-Labiano et al., 2006; Cho et al., 2004, 2005, 2006; Sedor et al. (2008a,b)). On Al₂O₃ support, nickel is present as a dispersed nickel oxide phase. Dispersed phases are less prone to agglomerate after reduction. Consequently, supported nickel shows more stability, as compared to bulk nickel oxides, and this helps to improve oxygen carrier stability.

Table 4

<table>
<thead>
<tr>
<th>Oxygen carrier</th>
<th>Metal loading (%)</th>
<th>R₀⁰</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO/SiO₂</td>
<td>35</td>
<td>0.074</td>
<td>Zafar et al. (2006)</td>
</tr>
<tr>
<td>NiO/Al₂O₃</td>
<td>20–60</td>
<td>0.043–0.16</td>
<td>Mattisson et al. (2003) and Cho et al. (2005)</td>
</tr>
<tr>
<td>NiO/NiAl₂O₄</td>
<td>40–60</td>
<td>0.09–0.13</td>
<td>Mattisson et al. (2005)</td>
</tr>
<tr>
<td>NiO/MgAl₂O₄</td>
<td>37–60</td>
<td>0.09–0.13</td>
<td>Mattisson et al. (2006)</td>
</tr>
<tr>
<td>NiO/TiO₂</td>
<td>40–60</td>
<td>0.02–0.13</td>
<td>Mattisson et al. (2006)</td>
</tr>
<tr>
<td>CuO/Al₂O₃</td>
<td>41</td>
<td>0.083</td>
<td>Zafar et al. (2006)</td>
</tr>
<tr>
<td>CuO/Al₂O₃</td>
<td>14–35</td>
<td>0.027–0.08</td>
<td>de Diego et al. (2007) and Mattisson et al. (2003)</td>
</tr>
<tr>
<td>CuO/MgAl₂O₄</td>
<td>43</td>
<td>0.087</td>
<td>Zafar et al. (2006)</td>
</tr>
<tr>
<td>FeO/Al₂O₃</td>
<td>39</td>
<td>0.012</td>
<td>Zafar et al. (2006)</td>
</tr>
<tr>
<td>Fe₂O₃/Al₂O₃</td>
<td>60</td>
<td>0.027</td>
<td>de Diego et al. (2007) and Cho et al. (2005, 2006)</td>
</tr>
<tr>
<td>Fe₂O₃/MgAl₂O₄</td>
<td>32</td>
<td>0.0096</td>
<td>Zafar et al. (2006)</td>
</tr>
<tr>
<td>MnO/Al₂O₃</td>
<td>47</td>
<td>0.048</td>
<td>Zafar et al. (2006)</td>
</tr>
<tr>
<td>MnO/MgAl₂O₄</td>
<td>46</td>
<td>0.047</td>
<td>Zafar et al. (2006)</td>
</tr>
<tr>
<td>MnO₂/Al₂O₃</td>
<td>28–60</td>
<td>0.02–0.07</td>
<td>Abad et al. (2007a,b) and Mattisson et al. (2003)</td>
</tr>
<tr>
<td>MnO₂/MgZrO₂</td>
<td>40</td>
<td>0.028</td>
<td>Abad et al. (2006)</td>
</tr>
<tr>
<td>CoO/Al₂O₃</td>
<td>28–35</td>
<td>0.07</td>
<td>Mattisson et al. (2003)</td>
</tr>
</tbody>
</table>

Due to this, NiAl₂O₄ is considered as an undesirable species in a nickel-based oxygen carrier. Furthermore, if the formation of nickel aluminate continues during the reduction/oxidation cycles, the reactivity of the oxygen carrier material decreases with time (Cho et al., 2004).

Formation of NiAl₂O₄ is the result of the interaction between nickel and alumina support. Thus, minimization of metal/support contact is highly desirable. Cho et al. (2005) and Mattisson et al. (2003) recommend using excess nickel in order to compensate for the loss of nickel as nickel aluminate. These authors obtained a stable Ni/Al₂O₃ carrier after few reduction and oxidation cycles. X-ray diffraction (XRD) analysis of the used sample shows that during the initial cycles the excess nickel reacts with Al₂O₃ forming NiAl₂O₄, and this helps to improve oxygen carrier stability.

Taking these factors into consideration, a number of researchers proposed NiAl₂O₄ as a support instead of Al₂O₃ (Jin et al., 1999; Ishaïda et al., 2002; Villa et al., 2003; Ryu et al., 2003; Cho et al., 2004; Mattisson et al., 2006; Readman et al., 2006; Abad et al., 2006; Garcia-Labiano et al., 2006), given the following: (a) the microstructure of NiAl₂O₄ is very stable under the CLC high reduction and oxidation temperatures (up to 1200°C), (b) the Ni/NiAl₂O₄ display excellent reactivity with CH₄, CO and H₂ being completely reoxidized during the regeneration, (c) the agglomeration of nickel crystals after the reduction cycles is prevented, (d) the carbon deposition on Ni/NiAl₂O₄ oxygen carrier is smaller while compared to the one observed on Ni/Al₂O₃, (e) the elemental carbon is the only formed carbonaceous species in the reduced carrier with no evidence of nickel carbide formed. The Ni on Ni/NiAl₂O₄ approach presents, however, the negative feature that it requires more nickel than the one required for Ni/Al₂O₃.

Recently Ni/MgAl₂O₄ has also been investigated as an alternative to Ni/NiAl₂O₄ (Villa et al., 2003; Mattisson et al., 2006; Johansson et al., 2006; Zafar et al., 2006; Ryden et al., 2006; Ryden and Lyngfelt, 2006). The addition of Mg limits the sintering of NiO and stabilizes the Ni²⁺ in cubic (NiO) and spinel (Ni₁₋₀₂Al₂O₄) phases. As a result, the oxygen carrier remains stable over repeated reduction and oxidation cycles even at temperatures above 1300°C.

Apart from the commonly used materials, Ishaïda and his group and Ryu and his collaborators considered YSZ as support for oxygen carriers (Ishaïda et al., 1996, 1998; Ishaïda and Jin, 1996, 1997; Jin and Ishaïda, 2000, 2001, 2004; Ryu et al., 2003). Ni/YSZ displayed excellent reactivity and regenerability given the abundant availability of NiO sites with no metal support complexes detected. It is claimed that NiO loading on YSZ provides high solid diffusivity for the nickel oxide ion and helps improving the composite material reactivity.
Ryu and his coworkers also investigated NiO on bentonite as oxygen carrier, showing its promising activity and stability under repeated redox cycles (Ryu et al., 2001, 2002a,b, 2003; Son and Kim, 2006). However, this material displays inferior performance at higher temperatures due to the limited bentonite thermal stability.

Several researchers also focused on Ni/TiO₂ materials (Ishida et al., 1998; Jin et al., 1999; Johansson et al., 2002; Adanez et al., 2004; Corbella et al., 2005a,b, 2006a,b; Mattisson et al., 2006; Son and Kim, 2006). Cyclic reduction and oxidation of such materials show lower reactivity, as compared to nickel supported on Al₂O₃. In fact, NiO was more prone to interact with TiO₂ forming NiTiO₃ (nickel titanate), which is less reducible as compared to NiO. In some cases, the loaded nickel was completely converted to NiTiO₃, after several reduction and oxidation cycles. A disadvantage of this carrier is its coke formation tendency. Thus, the reduced carrier may contain coke, form CO₂ in the air reactor and decrease the overall CO₂ capture efficiency.

Apart from the above, a few studies have also reported the use of nickel supported on SiO₂ and ZrO₂ (Adanez et al., 2004; Mattisson et al., 2004, 2006; Zafar et al., 2005, 2006). The reactivity of both NiO/SiO₂ and NiO/ZrO₂ materials decreases with reduction–oxidation cycles above 900 °C with the formation of nickel complexes being the main cause of this decaying reactivity.

In summary, it can be concluded that despite some of the described limitations nickel supported on alumina holds significant promise as a potential oxygen carrier material for large scale CLC application.

6.2. Fe-based oxygen carriers

Iron is possibly the most common and one of the cheapest metals available in nature. This makes iron attractive for commercial CLC applications. In addition to this and given the favorable thermodynamics, iron-based materials have received significant attention as oxygen carriers.

A number of attempts have been developed to investigate the reactivity of naturally occurring iron ores such as hematite using multiple reduction and oxidation cycles (Mattisson et al., 2001, 2004). The original hematite is a non-porous smooth textural material of low surface area. Upon being exposed to alternating reduction and oxidation the surface of the particles changes to a coarser texture with cracks and fissures being formed.

Although the reoxidation rates of these natural ores are adequate in CLC, the hematite reaction rates to metallic iron are slow and the transformation of hematite to magnetite is the favored step. This material also has a tendency to agglomerate at high temperatures. To improve reactivity and to overcome agglomeration, alternative approaches consider iron dispersion on a number of supports.

Iron on Al₂O₃ is a CLC support of choice with the reduction rates substantially increased (Abad et al., 2006, 2007a,b; Adanez et al., 2004; Cho et al., 2004, 2005, 2006; Corbella and Palacios, 2007; Garcia-Labiano et al., 2006; Ishida et al., 1998, 2002, 2005; Johansson et al., 2004, 2006; Mattisson et al., 2001, 2003, 2004; Son and Kim, 2006). Reactivity of hematite during the reduction process has been analyzed using in situ XRD. It was confirmed that hematite reduction to magnetite is the fastest step with the subsequent steps, magnetite to ferrous oxide and ferrous oxide to iron, being much slower. From this, it can be concluded that in an iron supported material, the hematite conversion to magnetite is the dominant chemical transformation.

Regarding iron supported materials one can notice the signs of agglomeration. Thus, circumventing agglomeration is a requirement for a stable CLC fluidized bed operation (Cho et al., 2004, 2005).

In addition, the solid-state reaction between iron and Al₂O₃, it is considered the main cause for the loss of particle reactivity. Regarding the metal-support interactions solubility of Fe³⁺ and Al³⁺ cations were detected via XRD spectra (Mattisson et al., 2004). Although Fe₂O₃ is considerably less reactive with Al₂O₃ than other transition metals such as nickel, copper and cobalt, Bolt et al. (1998) demonstrated the existence of Fe₂O₃–Al₂O₃ interactions leading to Fe₃Al₂O₆.

MgAl₂O₄ has also been considered as a support for Fe₂O₃ to avoid aluminate formation (Johansson et al., 2004, 2006; Mattisson et al., 2004, 2006; Zafar et al., 2006). It is believed that the MgAl₂O₄ spinel offers a combination of reactivity and resistance to chemical attack and thermal stability. When loaded with Fe₂O₃, the resultant material displays high reactivity and stability up to 1100 °C. Particle agglomeration was also observed when the material was exposed at elevated temperature to repeated reduction–oxidation cycles.

TiO₂, another potential oxygen carrier support, has the tendency to react with Fe₂O₃ (Ishida et al., 1998; Jin et al., 1999; Johansson et al., 2002; Adanez et al., 2004; Corbella et al., 2005a,b; Mattisson et al., 2004; Son and Kim, 2006). The available oxygen in this support is much smaller than the one theoretically expected given the formation of Fe₃TiO₄. Excess metal loadings do not increase oxygen carrying capacity due to the interactions between metal and support.

Fe₂O₃ supported on SiO₂ was found to provide high reactivity during the first CLC redox cycles. However, SiO₂ was considered unsuitable given its strong affinity to interact with iron leading to a sharply decreased reactivity due to the formation of unreactive iron silicates (Zafar et al., 2005, 2006).

Fe₂O₃ on YSZ was studied by a number of authors (Ishida et al., 1998; Ishida and Jin, 1994, 1997; Jin et al., 1998a,b). These oxygen carriers showed no metal support interaction and stable activity over repeated reductions and oxidations. XRD analysis of the oxidized (used) sample confirmed the sole presence of Fe₂O₃. The reduction rates of Fe₂O₃/YSZ were, however, slower than the ones for iron supported on alumina. It is speculated in this respect, that the complete reduction of Fe₂O₃ to Fe is a primary cause for the slow reduction rates with iron carbide (Fe₃C) contributing to the inferior Fe₂O₃/YSZ reactivity.

6.3. Cu-based oxygen carriers

Copper has several favorable features over other oxygen carrier materials such as Ni and Fe. These features include: (i) Cu-based oxygen carriers are highly reactive in both reduction and oxidation cycles, (ii) CuO reduction is favored thermodynamically to reach complete conversion using gaseous hydrocarbon fuels (e.g. methane), (iii) Cu-based oxygen carriers reduction and oxidation reactions are both exothermic, eliminating the need of energy supply in the reduction reactor, (iv) Cu is considered one of the cheapest metals that can possibly be used in CLC (de Diego et al., 2007; Cao and Pan, 2006; Cao et al., 2006). Despite the above mentioned advantages, CuO has not received significant attention due to its tendency to decompose at comparatively low temperatures (Jenndal et al., 2006; Mattisson et al., 2003). Cu is also prone to agglomerate given its relatively low melting point.

Several contributions address the stability of Cu in CLC. It is shown that at 950 °C CuO/Cu displayed very high reactivity in both reduction and oxidation cycles (de Diego et al., 2004). However, after few cycles the reactivity is drastically reduced, with particle agglomeration being considered as the primary cause of this abrupt reactivity loss.

Cao et al. (2006) considered low temperature operation as a mean of utilizing the benefits of CuO. These authors studied a fluidized bed CLC process at 600 °C using gasified solid fuels along with CuO. No particle agglomeration was observed although Cu₂O was found in the XRD analysis. The formation of Cu₂O was attributed to the
decomposition of CuO. Separate experiments also showed that the decomposition reaction occurred at low oxygen concentrations in the air reactor. Thus, an excess air in the reoxidation cycle is advised as a way of minimizing CuO decomposition (Cho et al., 2004; de Diego et al., 2004).

Similarly at what was observed in the case of nickel and iron, supported Cu-based oxygen carriers are considered a better choice than bulk CuO. Cu/Al2O3 is an oxygen carrier frequently considered in literature (Abad et al., 2006; Adanez et al., 2004, 2006; Cho et al., 2004, Corbella et al., 2005a,b; de Diego et al., 2004, 2005; Garcia-Labiano et al., 2006; Mattisson et al., 2003). Scanning electron microscope (SEM) images of reduced CuAl2O4 material indicate the presence of particle agglomeration with the reactivity being significantly decreased between two consecutive reduction–oxidation cycles. At high temperatures, the agglomeration not only decreases particle reactivity but also quickly defluidize the bed. Alumina formation is another problem found with Cu/Al2O3 particles. For instance, the analysis of a fresh sample calcined above 850 °C showed both CuO and CuAl2O4. However, after a few reduction and oxidation cycles only a CuAl2O4 phase was found (Abad et al., 2006; de Diego et al., 2005). From these observations, it was concluded that the formation of CuAl2O4 is a dominant species following repeated reductions and oxidations, responsible for Cu/Al2O3 deactivation.

Regarding CuAl2O4 as a support of Cu, Cho et al. (2004) unsuccessfully tried to obtain a stable carrier and as a result this alternative is considered as one offering little promise for the implementation of a performing oxygen carrier.

SiO2 was studied as well, by a number of researchers as an oxygen carrier support material for copper (Adanez et al., 2004; Corbella et al., 2006a,b; de Diego et al., 2004; Zafar et al., 2005, 2006). These investigations have shown that SiO2 is quite inert to Cu even at high temperatures and did not form any Cu–SiO2 complex. Particle reactivity was reasonable but inferior to those found with Ni supported on SiO2. Particles showed as well, better stability over repeated reduction and oxidation cycles. However, the prepared sample suffered from CuO decomposition to Cu2O.

Finally, TiO2 as a Cu support display important limitations to be used in CLC due to the tendency of copper to form CuTiO4 (Corbella et al., 2005a,b; de Diego et al., 2004).

6.4. Mixed-oxide oxygen carriers

There are, in the open literature, a limited number of studies focused on using mixed metal oxygen carriers for CLC. It is in this respect, worth mentioning that some supported mixed metallic materials have demonstrated better reactivity in comparison to their monometallic counterparts (Sinfelt, 1983). Recently, Adanez et al. (2006) reported a stable bimetallic Cu–Ni/Al2O3 oxygen carrier. It was claimed that Cu and Ni stabilized each other, providing an improved performance at higher reaction temperatures and higher oxygen carrying capacity. Johansson et al. (2006) also reported a similar result with a mixed iron and nickel oxygen carrier.

Readman et al. (2005) studied the possibilities of a La0.8Sr0.2Co0.2Fe0.8O3–δ with δ representing the oxygen content, function of the O2 partial pressure and the temperature. In situ XRD analysis showed the stable behavior of the sample during the repeated reduction and oxidation. It was found that while the reactivity of this type of composite oxygen carrier was quite high, it displayed a low oxygen carrying capacity.

Jin et al. (1998a,b) reported the synergetic effects of NiO and CoO supported on YSZ. The oxygen carrier was prepared with equal amounts of NiO and CoO, showing excellent regenerability under repeated oxidation and reduction. XRD results confirmed that NiCoO2 is at the origin of the stable behavior of the mixed metal. Despite these encouraging results, YSZ supported bimetallic Co–Ni materials have not received further attention, possibly due to the low thermal stability and high cost of the YSZ zeolite.

Recently, the authors of this review paper demonstrated the excellent reactivity and stability of a Co modified Co–Ni/Al2O3 oxygen carrier (Hossain et al., 2007; Hossain and de Lasa, 2007; Hossain, 2007). The oxygen carrier samples were prepared varying the nickel loading from 2.5 to 20 wt%. The higher limit of nickel loading was selected aiming a possible high oxygen carrying capacity. Even under these Ni loading conditions no metal sintering or agglomeration was observed. Before nickel loading the alumina support was modified with a small amount of cobalt (0.5 to 2.5 wt%). During the metal (Co followed by Ni) loading steps (preparation step) the material went through multiple cycles of impregnation, calcination and reduction. Each of these steps has an impact on the reactivity, stability and fluidizability of the prepared carrier. These effects and the properties of the oxygen carrier prepared were characterized by using different physicochemical techniques such as temperature programmed reduction (TPR), temperature programmed oxidation (TPO), temperature programmed desorption (TPD), pulse chemisorptions, XRD and SEM–EDX (energy dispersive X-ray analysis).

The TPR profile of a Co–Ni/Al2O3 Sample showed two shoulders, one at each side of the maximum TPR peak (Hossain and de Lasa, 2007). The first peak was assigned to the consumption of hydrogen by the dominant metal oxide phases, mainly NiCo2O4 and NiO. In this respect, Hardiman et al. (2004a,b) also found, in a similar catalyst material for steam reforming of methane/ethane, the above mentioned species. While Hardiman et al. (2004a,b) attributed the left-hand side shoulder of the peak to CoO4/2NiCo2O4/NiO and the higher peak to NiAl2O4, it is doubtful that in this study, the Co3O4 phase contributes to the TPR peak at lower temperatures (Hossain and de Lasa, 2007). When comparing between the TPR for Co promoted and an unpromoted Ni/Al2O3 samples, the combined TPR of the right and left shoulders showed for the Co–Ni/Al2O3 approximately 15% larger areas than those for the Ni/Al2O3, with this finding supporting the higher reducibility of the bimetallic oxygen carrier. Another important observation for the bimetallic TPR peak was the 45 °C shift towards lower temperatures, an indication of the higher reactivity of the bimetallic oxides. When exposed to repeated TPR/TPO cycles, an average of 86% conversion was observed for the bimetallic sample instead of the 78% highest nickel conversion for the unpromoted carrier (Hossain, 2007). Therefore and on this basis a significant improvement of oxygen carrying capacity was claimed using the bimetallic carrier.

In CLC the exposure of the oxygen carrier to repeated reduction and oxidation cycles may lead to crystal growth due to agglomeration. This crystal growth can lead to a loss of available metal oxide sites. Therefore, it is important to assess the effect of reduction/oxidation cycling on crystal size/metal dispersion. Pulse chemisorptions provides valuable information on the dispersion and on the crystal size of the supported metals. Metal dispersion can vary depending on several factors such as the type of metal/support, the surface area of the support, the sample preparation methods and the effects of the promoter. In this regard a higher dispersion was observed in the Co promoted sample versus the unpromoted samples (Hossain and de Lasa, 2007). It was also observed that Co helped to increase the dispersion of nickel. The addition of Co altered the metal surface modifying the degree of interaction between Ni and alumina support, maintaining a consistent metal dispersion during the successive oxidations and reductions. It is also apparent that the metal crystal size of this bimetallic sample did not increase over repeated reduction/oxidation cycles, an indication of the absence of metal sintering. As well, the relatively high and stable metallic surface area of the cobalt promoted oxygen carrier further supports the uniform and unchanged metal particle size. According to Bolt et al. (1998), the promotional effects of Co have
been explained by applying the site-preference energy concept. The site preference concept is based on the assumption that metal cations in their oxidized states (Ni^{2+} or Co^{2+}) with lower bonding energies are the favored species to interact with Al_2O_3. Co having a bonding energy of 13 kJ/mol is likely to compete more effectively for the Al_2O_3 sites than Ni, with a 50 kJ/mol bonding energy. Thus, in a bimetallic CoNi/Al_2O_3 sample, the addition of Co enhances the CoAl_2O_4 abundance minimizing the NiAl_2O_4.

The promotional effect of Co was quantitatively established by performing temperature programmed H_2 desorption kinetic analysis (Hossain et al., 2007). It was found that the estimated activation energy of hydrogen desorption for Co−Ni/Al_2O_3 was significantly decreased while compared to the one of an unpromoted Ni/Al_2O_3 sample. This result suggests that doping the fluidizable oxygen carrier with Co diminishes the metal-support interactions and the binding energy between the metals and the H_2 molecules. This effect increases the availability of the reactive species in a Co−Ni/Al_2O_3 sample.

The reactivity and the regenerability of the prepared oxygen carriers was established using the Chemical Reactor Engineering Center (CREC) Riser Simulator under expected conditions (turbulent fluidized bed and temperature between 600 and 900 °C) of an industrial scale fluidized CLC unit. The CREC Riser Simulator is a bench scale mini-fluidized bed reactor, invented at CREC-UWO (de Lasa, 1992). This mini-fluidized reactor (volume of 50 cm^3) was designed for catalyst evaluation and kinetic studies under fluidized bed (riser/downer) reactor conditions. A schematic diagram of the CREC-Riser Simulator, along with the gas injector and anemometer location, is illustrated in Fig. 8. The detail of the CREC Riser Simulator and the experimental procedure can be found elsewhere (de Lasa, 1992; Hossain, 2007). In the CLC cycles methane was used as a fuel in the combustion cycle while air was used in order to regenerate the reduced oxygen carrier. For both cycles the fluidization of the oxygen carrier particles was demonstrated in a plexiglas unit with various dimensions matching the ones of the inconel setup, with this being consistent with the expected behavior of Group A particles of the Geldart powder classification (Hossain, 2007).

The product analysis of the fuel combustion cycle showed both CO_2 and H_2O, as major species of the methane combustion (Hossain and de Lasa, 2007; Hossain, 2007). There were trace amounts of hydrogen; with no CO. The presence of trace amounts of H_2 indicated the occurrence of some methane decomposition and methane reforming. Furthermore, H_2 formation via methane decomposition was confirmed with the product analysis for the oxygen carrier regeneration cycle. Product selectivity during methane combustion with a supported metal oxide is mainly associated with the degree of the reduction of the oxygen carrier (Villa et al., 2003; Adanez et al., 2006). At the beginning of the reaction (or short contact time), the fully oxidized oxygen carrier favors the total oxidation of methane to CO_2 and H_2O. As the reaction proceeds, the partially reduced oxygen carrier catalyzes the reforming reactions producing synthesis gas (CO + H_2). It is equally important to point out that both CO and H_2 are very reactive with the metal oxide being quickly converted to CO_2 and H_2O, respectively. Therefore, it can be assumed that the CO and H_2 species produced via reforming reactions are further oxidized forming CO_2 and H_2O. Consistent with this, no CO was detected as a product of methane combustion with the oxygen carriers. As per the methane and particle conversion, a maximum 80% methane conversion was observed using the bimetallic sample, with the highest methane conversion remaining in the 70% range for the unpromoted carrier. Therefore, a significant improvement of methane conversion was observed using the bimetallic carrier (Hossain and de Lasa, 2007; Hossain, 2007). Following the encouraging reactivity results in the CREC Riser Simulator and to be able to assess oxygen carrier stability, the bimetallic Co−Ni/Al_2O_3 carrier was evaluated over multiple CLC cycles. It was proven with these results that the bimetallic Co−Ni/Al_2O_3 displays a stable conversion during repeated CLC cycles. The addition of Co can also favorably modify metal-support interactions, as assessed via the energies of hydrogen desorption (Hossain et al., 2007).

The XRDs of a fresh sample and a regenerated sample after 10 CLC cycles show that the crystalline phase of the bimetallic oxygen carrier remains unchanged over TPR/TPD cycles. These results are in agreement with the findings of Jin and co-workers (1998) using Co−Ni/YSZ in a CLC process. Thus, XRD helps demonstrate that the bimetallic carrier microstructure, obtained from solid solution of Co and Ni, leads to stable oxygen carrier of high performance. When compared the SEM between a fresh and a used sample after 10 reduction/oxidation cycles in the CREC Riser Simulator, both samples show similar images (Hossain, 2007). The grain sizes of the nickel crystallites remain almost unchanged over the repeated cycles.
Furthermore, the elemental EDX mapping of Al and Ni also show uniform metal crystallite distribution after 10 reduction/oxidation cycles (Hossain, 2007). These results further confirm minimum agglomeration of the nickel particles of the studied bimetallic Co–Ni/Al2O3 oxygen carriers. In this respect, it is likely that cobalt addition changes oxygen carrier surface and reduces the movement of the nickel species, hence minimizing agglomeration.

7. The chemistry and the thermodynamics of CLC

As previously discussed, oxygen carrier materials are composed of an active metal oxide and an inert support/binder. The main function of the inert support is to provide a high dispersion of metal, increase the fluidization characteristics and the mechanical strength of the oxygen carrier. It is believed that only the metal oxide phase is active in the combustion process, participating in both reduction and oxidation reactions.

The following reaction schemes have been proposed for the commonly studied oxygen carriers for CLC application. (Adanez et al., 2004; de Diego et al., 2004; Mattisson et al., 2006; Garcia-Labiano and oxidation reactions.

Shift reaction:
\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad [\Delta H = -41 \text{ kJ/mol}] \]  
(19)

Methanation reaction:
\[ \text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \]  
(20)

Coke formation:
\[ \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \text{(pyrolysis)} \]  
[\Delta G = -38 \text{ kJ/mol}, \Delta H = 88 \text{ kJ/mol}]  
(21)
\[ 2\text{CO} \rightarrow \text{C} + \text{CO}_2 \text{(Boudouard reaction)} \]  
(22)

In the last four reactions (Eqs. (19)–(22)) the metal acts as a catalyst, rather as a reactant. These reactions, mainly catalyzed by the reduced state of the metal, are considered undesirable and can be suppressed by adjusting reaction parameters such as temperature, pressure and oxygen flow in the air reactor.

Although simple metal oxides are considered in the above reaction schemes, complex compounds can be formed due to the metal-support interactions during carrier preparation. In some cases the resultant complexes are difficult to reduce, making the carrier unsuitable for repeated oxidation/reduction cycles.

Corbella et al. (2005a,b) taking into account the metal-support interactions deduced a valuable reaction scheme for CLC. This reaction scheme reveals the contribution of the support material (TiO2 in this case) as an additional oxygen source. Thus, along with the nickel oxide, these authors consider the NiTiO3 species. At 900 °C and atmospheric pressure conditions, they proposed the following reaction scheme:

Reduction reactor:
\[ 4\text{NiTiO}_3 + \frac{3}{2}\text{CH}_4 \rightarrow 4\text{Ni} + 2\text{Ti}_2\text{O}_3 + \frac{3}{2}\text{CO}_2 + 3\text{H}_2\text{O} \]  
[\Delta G = -21 \text{ kJ/mol}, \Delta H = 573 \text{ kJ/mol}]  
(23)
\[ 4\text{NiO} + \text{CH}_4 \rightarrow 4\text{Ni} + \text{CO}_2 + 2\text{H}_2\text{O} \]  
[\Delta G = -259 \text{ kJ/mol}, \Delta H = 134 \text{ kJ/mol}]  
(24)
\[ \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \text{(cok formation)} \]  
[\Delta G = -38 \text{ kJ/mol}, \Delta H = 88 \text{ kJ/mol}]  
(25)

Oxidation reactor:
\[ \text{Ni} + \frac{1}{2}\text{Ti}_2\text{O}_3 + \frac{3}{4}\text{O}_2 \rightarrow \text{NiTiO}_3 \]  
[\Delta G = -293 \text{ kJ/mol}, \Delta H = -444 \text{ kJ/mol}]  
(26)
\[ \text{Ni} + \frac{1}{4}\text{O}_2 \rightarrow \text{NiO} \]  
[\Delta G = -134 \text{ kJ/mol}, \Delta H = -234 \text{ kJ/mol}]  
(27)
\[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \text{(cok removal)} \]  
[\Delta G = -394 \text{ kJ/mol}, \Delta H = -394 \text{ kJ/mol}]  
(28)

Their study also shows that the first reaction of the proposed scheme should include NiTiO3 as a prominent species in the reduction reactor. Although the second reaction (Eq. (24)) is favored, its contribution is not as significant, given this nickel oxide is a phase of minor importance in this supported carrier (Corbella et al., 2005a).

8. Coke formation

Carbon formation is a possible side reaction in CLC. The pyrolysis (Eq. (21)) and Boudouard reactions (Eq. (22)) are amongst the most probable reactions leading to coke formation (Mattisson et al., 2006).

Pyrolysis is an endothermic reaction, thermodynamically favored at high temperatures. The exothermic Boudouard reaction is more likely to take place at lower temperatures. Kinetically, both pyrolysis and Boudouard reactions are known to have a limited importance in
the absence of a catalyst. Transition metals, such as Ni and Fe, can catalyze; however, carbon formation. Coke formation also depends on reaction conditions, such as the availability of oxygen, fuel conversion, reaction temperature and pressure (Cho et al., 2005; Ryu et al., 2003; Corbella et al., 2005a,b).

In CLC, the carbon deposition on the solid carrier may limit the efficiency of the total CO₂ capture (Corbella et al., 2005a,b). Therefore, it is important not only to understand the possible carbon formation mechanisms but also to investigate the operating strategies that need to be implemented to minimize/avoid carbon formation.

Regarding carbon deposition, the majority of the reported data have been obtained in TGA units at high concentration of fuel gas. Ishida and co-workers (1998) reported carbon deposition on Ni and Fe supported YSZ oxygen carriers. Their study shows that carbon formation is mainly caused by the Boudouard reaction, with the amount of carbon deposited on the nickel-based oxygen carriers being greater than that found on iron-based materials under the same conditions. In addition, it is shown that an increase in temperature decreases the amount of carbon deposited on a NiO/YSZ particle with carbon deposition being almost completely phased out at 900 °C.

Ryu et al. (2003) reported using a nickel-based oxygen carrier material, exactly the opposite temperature trends suggesting that carbon formation decreased while temperature was augmented.

Recently, Cho and co-researchers (2005) reported a comprehensive investigation on carbon formation on CLC oxygen carriers using a laboratory scale fluidized bed. Their study reveals that carbon formation on a nickel-based carrier is strongly dependent on the oxygen availability. At the early stage, when there is sufficient oxygen, no carbon formation is observed. Rapid carbon formation starts, however, when more than 80% of the available oxygen is consumed.

It has been suggested that pyrolysis is the main reaction by which carbon deposition occurs on nickel supported on YSZ or NiAl₂O₃ carriers. Carbon deposition by pyrolysis can be controlled by the addition of steam (Jin et al., 1998; Jin and Ishida, 2004; Villa et al., 2003; Ryu et al., 2003). One should however notice that no excess steam is needed and process produced steam from the reduction reaction should be accounted in the required steam calculations (Jin et al., 1998a).

Ishida et al. (1998) proposed a correlation between the carbon deposition boundary and the input ratio between water vapor and fuel gas as follows:

\[
\frac{x_{\text{H}_2\text{O}}}{x_{\text{CO}}} = \frac{(x_{\text{CO}_2\text{in}} + 1/\delta d_{\text{CO}})(x_{\text{H}_2\text{O}_{\text{in}}} + 1/y d_{\text{CO}})}{x_{\text{CO}_2\text{in}} x_{\text{CO}_{\text{in}}} - 1/d_{\text{CO}}} + \frac{1}{x_{\text{CO}_{\text{in}}} y_{\text{CO}}} \tag{29}
\]

where

\[
d_{\text{CO}} = \frac{2P_{\text{total}} K_1^2}{2P_{\text{total}} K_1^2 x_{\text{CO}} + 1/\delta - 4P_{\text{total}} K_2^2 (x_{\text{CO}_{\text{in}}} x_{\text{CO}_2\text{in}}) + 1/\delta^2}^{1/2} \tag{30}
\]

For the variables of the above equations refer to the manuscript nomenclature.

To validate the model data was collected in a TGA reactor using H₂ and CO as fuel.

As indicated above, temperature is an important variable that can be adjusted to suppress coke deposition (Ryu et al., 2003). Usually, an increased temperature is favorable for both increasing methane conversion and decreasing coke formation. However care should be taken when selecting the maximum operating temperatures, since higher temperatures also cause metal sintering and phase transformation.

The introduction of a second metal can also reduce the carbon deposition on the catalyst materials. For example, trace amounts of noble metal are beneficial in a naphtha reforming catalyst to reduce carbon deposition.

Regarding bimetallic oxygen carriers, Jin et al. (1998b) were the only authors to consider a bimetallic CoO–NiO/YSZ system for a CLC study. Their study suggest that carbon deposition can be completely eliminated by employing cobalt as a promoter along with NiO being the main active species on the YSZ support. It is speculated that formation of a solid solution between nickel and cobalt might change the free energy of the carbon formation reactions, giving rise to reduced coke deposition.

9. Effects of sulfur species in fuels

Natural gas, refinery gas and syngas, are considered as potential fuels for CLC. Commonly, these fuel gases contain a small amount of sulfur containing species like H₂S, COS, mercaptans and thiophen and thiophen aromatics. These sulfur compounds may react with both the oxygen and supported metal in the fuel reactor. These reactions can contribute not only SOₓ formation but also have unfavorable effects deactivating the oxygen carrier via the formation of metal sulfides.

Jernald et al. (2006) and Mattisson et al. (2006) recently discussed the effects of sulfur components in CLC processes. These authors studied the thermodynamics of the reactions between model solid oxygen carriers with some of the above mentioned sulfur bearing components. It is shown that CuO, FeO, MnO-based oxygen carriers can convert H₂S completely to SO₂ between 600 and 1200 °C. At similar reaction conditions, it is predicted that the H₂S conversion is somewhat lower with NiO oxygen carriers. This reaction is significantly influenced by temperature and pressure, with the oxidation of H₂S being increased at higher temperatures and lower pressures (Hepola and Simell, 1997).

Regarding metal sulfides, their formation mainly depends on the type of metal used in the oxygen carrier as well as on the concentration of sulfur species in the fuel reactor (Jernald et al., 2006; Mattisson et al., 2006). Among the metals considered for CLC, Fe sulfides or sulfates are not thermodynamically allowed while Ni is more prone to react with H₂S or SO₂ forming nickel sulfide. Therefore, in those cases and before entering the CLC unit the fuel has to be desulfurized to prevent oxygen carrier deactivation. Thus, further expenses are expected for the processing of flue gases containing SOₓ species.

10. Reduction and oxidation kinetics

The reaction mechanism and the kinetics parameters for a given reaction system play an important role in the design and performance of a reactor. For example, the temperature profile in a particle depends on the heat generation rate, which is directly related to the overall reaction rate. Further, the overall reaction rate depends on the specific rate constant (k) that can be estimated through kinetic modeling (Garcia-Labiano et al., 2005). Given the above mentioned facts, kinetic studies are considered as a pre-requisite for fundamentally based reactor designs.

Reviewing the technical literature one can notice that mainly two general types of models have been considered to represent the kinetics of reduction and oxidation of metal-supported oxygen carriers: (i) nucleation and nuclei growth model (Koga and Harrison, 1984; Richardson et al., 1996, 2004) and (ii) unreacted shrinking core model (Richardson et al., 2004; Utgard et al., 2005; Sohn and Szekely, 1972; Szekely et al., 1973).

The unreacted shrinking core model incorporates the dependence of particle size and pore structure of the solid reactant particles on the rate of reaction. According to this model, as the reaction progresses the metal–metal oxide interface moves towards the center of the grain, leaving behind a porous metallic/metal oxide product layer through which gaseous reactants and products diffuse (Szekely et al., 1973; Levenspiel, 1999).
The nucleation model considers the chemical mechanism and kinetics of the gas–solid reactions only. This model does not include morphological factors, which may be equally important in determining the kinetics. It has been shown that the reaction rate of the gas–solid reactions can be influenced by the grain size for a particle diameter greater than 10 μm (Richardson et al., 2003). Specifically for the porous particles, the effect of particle size and its state during the course of the reaction is very important in determining reaction rates.

To take into account the various aspects discussed above, literature studies investigated both the nucleation and nuclei growth model and unreacted shrinking core model, in order to describe the gas–solid reaction kinetics during both the reduction and oxidation cycles of the CLC processes.

According to the unreacted shrinking core models, the surface (front) separating the solid reactant core from the outer ash (product) layer. Initially the external surface of the solid participates in the reaction. The thickness of the ash layer increases with time leading to the shrinking core of unreacted solid. Therefore, the heterogeneous reaction proceeds via three steps:

(i) external mass transfer,
(ii) internal mass transfer,
(iii) chemical reaction.

Assuming a hypothetical gas–solid reaction (Levenspiel, 1999):

\[ A(g) + bB(s) → cC(g) + dD(s) \]  

According to the unreacted-core shrinking model the change of the core radius \( r_c \) can be expressed as

\[ \frac{dr_c}{dt} = \frac{bC_A}{r_c^2/R_p^2 k_g + (R_p - r_c)C/R_p D_e + 1/k_s} \]  

and the solid conversion can be determined by the following relationship:

\[ 1 - X = \left( \frac{r_c}{R_p} \right)^3 \]  

The three terms in the denominator of Eq. (32) represent the external gas film diffusion, the ash-layer diffusion and the chemical reaction, respectively.

Ishida and co-workers (1996) were the first group to test this model on NiO/YSZ particles considering all three phenomenological steps. It was shown that in the reduction cycle, the external mass transfer (gas film) coefficient was much larger than \( k_g \) and \( D_e \) suggesting that the rate of reaction was mainly controlled by the strongly temperature dependent intrinsic reaction step. The gas film diffusion was also reported as influencing the rate of the reduction reaction, especially at higher conversion levels.

Regarding the oxidation reaction, it was proven to be controlled by both chemical reaction and ash-layer diffusion, as both rate parameters show a significant influence on the reaction rate. However, it was agreed that using smaller size particles helps minimizing the gas layer diffusion resistance.

Similar results were reported by Ryu et al. (2001) using a NiO/bentonite oxygen carrier, a gas phase reactant first order reaction, spherical shaped particles and negligible external mass transfer. These authors reported the following integral form of the heterogeneous reaction model:

\[ t = \frac{C_{NiO}R_p}{bkC} \left[ 1 - (1 - X)^{1/3} \right] + \frac{C_{NiO}R_p}{6bD_e C_{NiO}} \left[ 1 - 3(1 - X)^2/3 + 2(1 - X) \right] \]  

where the first term represents the chemical reaction contribution and the second term describes the diffusion layer contribution.

Comparison of the experimental data with the proposed model showed that the reduction rate is controlled by chemical reaction while the oxidation of the reduced particles is controlled by diffusion (Ryu et al., 2001). Since NiO has a higher density than Ni, in the early reduction stages, the gas species (CH4) reacts with oxygen forming a loose layer of Ni (ash) and thereafter CH4 can easily diffuse through the loose Ni layer. On the other hand, during the oxidation, the thickness of the compact NiO layer increases with reaction time and oxygen diffusion may control the oxidation.

Garcia-Labiano et al. (2005, 2006) studied the CLC kinetics taking into consideration of the structural variations of the oxygen carrier. Plate and spherical geometries were studied using the changing grain size model. These shapes were selected based on the oxygen carrier preparation method and subsequent characterization results. In the case of Ni-based material, prepared by freeze-granulation, the spherical shape was considered. For Cu-based materials, prepared by impregnation, the plate shape approximation was applied. In both cases small particles (30–70 μm) were selected to minimize mass transfer limitations. Under these conditions the following equations were adopted:

For spherical grains:

\[ t = \frac{\rho_m X}{bC(1 - 1/X^{1/3})} \]  

For plate like particles:

\[ t = \frac{\rho_m X}{bC} \]  

One should note that for both oxidation and reduction the experimental data fitted well and the proposed model pointing towards an intrinsic reaction control regime. In addition, this study shows: (a) the determined reaction order between 0.25 and 1 are dependent on the studied oxygen carriers, (b) the chemical reaction occurring with product gases, namely CO2 and H2O, have no effect on the reaction rate.

Ryu et al. (2003) reported a power law model assuming a first order reaction with respect to both the gas phase reactant and the solid oxygen carrier.

\[ \frac{dC_{NiO}}{dt} = k'C_{CH4}C_{NiO} \]  

Keeping a constant concentration of methane in the gas phase, the integral form of the model simplifies as follows:

\[ -\ln(1 - X) = k't \]  

Despite the simplicity of the model, the predicted conversion agreed well with the experimental values.

Most recently, Hossain and de Lasa (2007, Hossain, 2007), and Sedor et al. (2008a,b) developed phenomenological kinetic models involved in a CLC process. Both the nucleation and nuclei growth model and unreacted shrinking core models were formulated based on the physicochemical characteristics of the prepared oxygen carriers and the observed reaction rates under various experimental conditions.

Fig. 9 shows the possible steps during a gas–solid reaction following the nucleation and nuclei growth model (Hossain, 2007). According to this model the gas–solid reactions proceed by nucleation (nuclei formation) and subsequent nuclei growth. Before nucleation there is an induction period for the activation of the solid phase to form nuclei. The length of the induction period primarily depends on the gas–solid system and reaction temperature. Nucleation is a dynamic process, which pragmatically initiates the reaction. The progress of the reaction then continues with nucleation and growth of the already formed nuclei. The nuclei growth occurs due to the overlap of the nuclei and/or ingestion of a nuclei site.
The overall conversion of the reaction is determined by the relative rate of nucleation, nuclei growth and the concentration of the potential nuclei-forming sites (also called germ nuclei). For a particular gas–solid reaction, the nuclei growth rate is constant at a given temperature and composition of the gas phase. Either nucleation and nuclei growth or their combination can be the rate-determining step of the overall reaction and the energetics of the reaction process is primarily dependent upon the rate-determining step.

Generally, the experimental x-t (conversion-time) profiles of a gas–solid reaction show a sigmoid shape. This function can be modeled by a nucleation and nuclei growth mechanism (Richardson et al., 1994, 2004; Hossain and de Lasa, 2007). This type of conversion function \( f(x) \) may be described in terms of the reaction rate controlling Avrami–Erofeev (A–E) model (Avrami, 1939, 1940, 1941; Hardiman et al., 2005; Malecka et al., 2002, 2004). A clarified derivation of Avrami–Erofeev model can be found in Hossain and de Lasa (2007). This model was originally applied to describe the kinetics of phase transformations of steel. Later on, it found numerous applications in kinetics of crystallization, precipitation, decomposition of various solids, thin film growth and polymerization. More recently, this model has been successfully implemented to analyze reduction and oxidation data of both bulk and supported metal oxides (Richardson et al., 2004; Hardiman et al., 2005; Kanervo and Krause, 2001, 2002).

According to the A–E model, the reduction and oxidation of the supported metal oxide proceeds through nucleation and possible crystal growth; this leads to the following equation (Hossain and de Lasa, 2007):

\[
f(x) = n(1-z)\ln(1-z)^{(n-1)/n}
\]

where, \( n \) is the Avrami exponent indicative of the reaction mechanism and crystal growth dimension. Different values of the \( n \) parameter lead, as reported in Table 5, to various random nucleation, two-dimensional nuclei growth and three-dimensional nuclei growth.

Along with the Arrenhius expression and A–E equation the following mathematical form was obtained

\[
\frac{dx(t)}{dt} = nk_0 \exp\left[-\frac{E_{\text{app}}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \left(1 - z\right) \left(-\ln(1-z)\right)^{(n-1)/n} \tag{40}
\]

The unreduced shrinking core model was developed considering that during the reduction and oxidation cycles of the oxygen carrier particle, the stoichiometric ratio between the molar volume of NiO and Ni were changed according to the followings:

Reduction cycle: \( \text{NiO} + \text{H}_2 = \text{H}_2\text{O} + \text{Ni} \) \tag{41}

\[
Z = \frac{\text{v}_{\text{NiO}}}{\text{v}_{\text{Ni}}} = \frac{6.59}{10.97} \approx 0.6 < 1
\]

Oxidation cycle: \( 2\text{Ni} + \text{O}_2 = 2\text{NiO} \) \tag{43}

\[
Z = \frac{2\text{v}_{\text{NiO}}}{2\text{v}_{\text{Ni}}} = \frac{2 \times 10.97}{2 \times 6.59} = 1.7 > 1
\]

Thus, after reduction of the oxygen carrier particle, the porosity of the carrier material increases due to the shrinkage of the particle volume inside the pores. However the opposite occurs with, after reoxidation with the pore volume decreasing.

Fig. 10 illustrates the schematics of the cyclic reduction and oxidation process described by spherical shrinking core model (Hossain, 2007). According to the shrinking core spherical grain model, the particle conversion is obtained from the changing volume of the particle as follows:

\[
x = 1 - \frac{\text{volume of unreduced core}}{\text{volume of total particle}} = 1 - \left(\frac{R_0}{R_p}\right)^3
\]

Thus, considering the surface reaction using first order reaction kinetics with respect to the gas phase reactant concentration the following expression was obtained:

\[
\frac{dx}{dt} = k_0 \exp\left[-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \left(1 - z\right)^{2/3(1 - az)} \tag{46}
\]

The developed nucleation and nuclei growth model (Eq. (40) and unreacted shrinking core model (Eq. (46)) were discriminated on the basis of correlation coefficients \( R^2 \), lowest sum of square (SSQ) residuals and smallest individual parameter confidence intervals. Given the \( R^2 \) values and parameter spans (±5%) obtained, it was concluded that best fitting with the nucleation and crystal growth model, was achieved with an "n" value of one, as shown in Fig. 11 (Hossain and de Lasa, 2007). The random nucleation model ("n" value of 1) was selected consistent with the close to constant crystallite size observed during the repeated reduction and oxidation cycles
developed in a multiple cycle CLC process (Hossain and de Lasa, 2007; Hossain et al., 2007).

11. Conclusions

CO₂ capture and sequestration from flue gases from fossil fuel combustion may become a viable alternative to minimize emissions of greenhouse gases. Chemical-looping combustion (CLC) offers in particular, great opportunity to eliminate the energy intensive CO₂ separation, reducing as a result CO₂ sequestration costs. However, at the present time CLC is not a fully established technology and valuable research is currently being developed to address the outstanding issues for large-scale implementation.

Recent literature considers suitable oxygen carriers for CLC-based power generation. From the reported research, it can be concluded that the synthesis of a reactive and stable oxygen carrier is one of the main challenges still facing CLC. Among the studied oxygen carriers, Ni-based materials shows promising reactivity and stability over repeated reduction/oxidation cycles. However, Ni-based oxygen carriers need further improvement for extended operation. The reactive metal oxide on the unpromoted sample deactivates gradually given the high metal-support interaction, with this leading to the hard to reduce nickel aluminate. A small amount of Co doping decreases, however, the metal-support interaction yielding easily to reduce oxides and providing stability to the oxygen carrier. The resulting material can also be readily re-oxidized to its original state. In this regard, bimetallic Co–Ni/Al₂O₃ shows high activity and stability over multiple reduction/oxidation cycles.

Regarding solid-state reaction kinetics, it has been studied using the nucleation/ nuclei and the unreacted shrinking core models. It has been found that the nucleation/nuclei model with random nucleation provides a better description of both the reduction and the oxidation.

Finally and concerning large-scale CLC fluidized bed reactor design the configuration of two interconnected fluidized bed reactors (air and fuel reactors) appears as a preferred best option. Even if one can acknowledge that there still are important issues that require further research, this reactor arrangement provides high solid circulation and valuable operational process flexibility with minimum air and fuel reactor effluent cross-contamination.

Notation

- \( b \) is the stoichiometric coefficient of the solid phase reactant
- \( \alpha \) conversion
- \( C_{(\cdot)} \) concentration of the gaseous reactant
- \( C_{(\cdot)0} \) initial concentration of the gaseous reactant
- \( X \) mole fraction of the solid
- \( \theta \) time
- \( \epsilon \) reaction rate per unit mass of the oxygen carrier
- \( p \) particle density
- \( K \) equilibrium constant
- \( k \) specific rate of the overall reaction
- \( K_i \) specific rate constant for surface reaction
- \( P_{\text{total}} \) total pressure
- \( R_p \) particle radius
- \( x_{(\cdot)} \) mole fraction of the gas

Greek symbols

- \( \alpha \) degree of conversion of oxygen carrier
- \( \beta \) rate of temperature increase
- \( \gamma \) diffusivity ratio of H₂O to CO
- \( \delta \) diffusivity ratio of CO₂ to CO
- \( \rho_p \) particle density
- \( V_i \) molar volume

Acknowledgements

M.M.H. gratefully acknowledges the National Sciences and Engineering Research Council of Canada (NSERC) for a Canada Ph.D. Graduate Scholarship (CCS-D) and The University of Western Ontario for President’s Scholarship for Graduate Studies (PSGS). The Authors also wish to thank the NSERC Strategic Grant program for their financial support to this project.

References


inherent CO2 separation; application of chemical-looping combustion. Chemical
Engineering Science 56, 3101–3113.
Malecka, B., Crozdz-Ciesla, E., Malecki, A., 2002. Non-isothermal studies on
mechanism and kinetics of thermal decomposition of cobalt (II) oxalate
In: Proceedings of First Bienniel Meeting of the Scandinavian-Nordic Section of
the Combustion Institute, April 18–20, Coteborg, Sweden.
in chemical-looping combustion of methane with inherent separation of CO2.
supported on alumina with alternating and oxygen—Application of chemical-
of different types of iron oxide particles—Application to chemical-looping combustion.
fossil fuels, Technology Status Report, IEA Coal Research, The clean coal center
(http://www.earthspace.org/r/1ES17005/STRMay2002.pdf), (accessed April 25,
2007).
Naqvi R., Bolland O., Brandvoll O, Helle K., 2004, Chemical looping combustion-
based oxygen carrier particles for chemical-looping combustor. Korean Chemical
Engineering 20, 960–966.
based oxygen carrier particles for chemical-looping combustor. Korean Chemical
Sedor, K.E., Hossain, M.M., de Lasa, H.I., 2008a. Reactivity and stability of Ni/Al2O3
oxide reduction by hydrogen. Applied Catalysis A: General 246, 137–150.
Sedor, K.E., Hossain, M.M., de Lasa, H.I., 2008b. Reduction kinetics of a fluidizable
nickel-alumina oxygen carrier for chemical-looping combustion. Canadian
Sinfelt, J.H., 1983. Bimetallic catalysts: discoveries concepts and applications, an
boundary—III: a general dimensionless representation of the irreversible reaction
between a porous solid and a reactant gas. Chemical Engineering Science 27, 763–778.
Son, S.R., Kim, S.D., 2006. Chemical-looping combustion with NiO and Fe2O3 in
a thermobalance and circulating fluidized bed reactor with double loops. Industrial
& Engineering Chemistry Research 45, 2689–2696.
moving boundary—V an experimental study of the reduction porous nickel-oxide
Ni based mixed oxide materials for CH4 oxidation under redox cycle conditions.
Journal of Molecular Catalysis A: Chemical 204–205, 637–646.
Wolf, J., 2004. CO2 mitigation in advanced power cycles—Chemical looping
combustion and steam-based gasification. Doctoral Thesis, Department of
Chemical Engineering and Technology Energy Processes, KTH-Royal Institute of
Technology, SE-100 44 Stockholm, Sweden.
Wolf, J., Yan, J., 2005. Parametric study of chemical looping combustion for tri-
generation of hydrogen heat and electrical power with CO2 capture. International
carriers in chemical looping combustion for CO2 capture in power generation.
Fuel 84, 993–1006.
Zafar, Q., Mattisson, T., Gevert, B., 2005. Integrated hydrogen and power production
with CO2 capture using chemical-looping reforming-redox reactivity of particles of
CoO, MnO2, NiO, and Fe2O3 using SiO2 as support. Industrial & Engineering
Chemistry Research 44, 3485–3496.
Zafar, Q., Mattisson, T., Gevert, B., 2006. Redox investigation of some oxides of
transition-state metals Ni, Cu, Fe, and Mn supported on SiO2 and MgAl2O4.
Energy & Fuels 20, 34–44.