

Applications of Chemical Looping Combustion of Solid Fuels

E.A Goldstein^{*1}, R. E. Mitchell
 Department of Mechanical Engineering
 Stanford University
 Palo Alto, CA 94305-3032

Abstract

The potential for applying chemical looping combustion (CLC) technology to coal-fired energy conversion systems has been examined through thermodynamic modeling. The thermodynamic models were developed to investigate the energetics of a practical CLC system utilizing coal. Iron-, nickel- and copper-based metal oxides were selected for the study. With each metal oxide, the equilibrium calculations indicate comparable efficiencies with respect to conventional power plants. The Ni- and Fe-based metal oxides require a large charge of metal oxide to fully convert CO in the synthesis gas to CO₂, whereas the Cu-based metal oxides did not. The Ni system, in particular, required 10 to 20 times the stoichiometric amount of NiO to completely oxidize the coal in the temperature range 900 to 1200 °C. Sulfur species produced during coal conversion were also tracked for each metal oxide investigated. At near stoichiometric CuO-to-coal ratios, about 10% (by mass) of the copper leaving the fuel reactor was in the form of Cu₂S. There were no undesirable species produced in the Fe system; small amounts of Ni₃S₂ and NiS were formed in the Ni-based system.

Introduction

The Energy Information Administration estimates that nearly half of the world's coal resources are distributed between China and the United States. Additionally, the World Coal Institute reports that nearly half of the electricity generated in the United States and nearly eighty percent of the electricity generated in China comes from coal combustion. As a matter of national security, neither nation can afford to reduce coal consumption within the time frame that will prevent further global warming from occurring. As long as coal is readily available and can be used to produce inexpensive electricity, it will be used for power generation. Options for coal use that do not adversely impact the environment need to be developed. One option for coal utilization for power generation without the uncontrolled release of CO₂ is Chemical Looping Combustion (CLC).

Background

CLC is an oxyfuel combustion approach that can lead to coal power plants with potentially, one hundred percent CO₂ capture. Unlike most other oxyfuel combustion approaches, CLC uses a solid oxygen carrier, a metal oxide, to separate oxygen from air. As a result, oxyfuel combustion can be realized without the energy penalty of an air separation unit. Conventionally, CLC systems have been applied to gaseous fuels (CO, H₂, CH₄, and natural gas) in a two-fluidized bed reactor arrangement as shown in Figure 1 [1, 2]. Some of the oxygen carriers that have been investigated are listed in Table 1.

The CLC system shown in Figure 1 consists of two fluidized bed reactors: the fuel [metal oxide reduction] reactor and the metal oxide regeneration reactor. The fuel

reactor is where the metal oxide is reduced and the fuel is oxidized to CO₂ and H₂O. Globally,

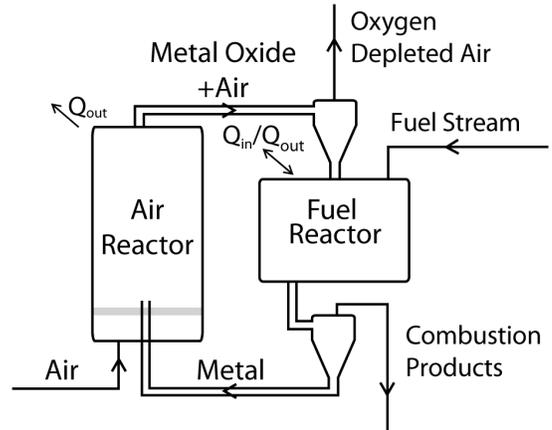
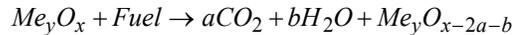


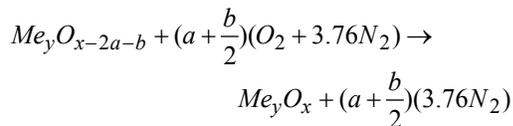
Figure 1: Conventional System Schematic

Table 1: Metal oxides investigated

Oxidized Metal	Reduced Metal
Fe ₂ O ₃	Fe ₃ O ₄
CuO	Cu ₂ O
NiO	Ni
Mn ₃ O ₄	MnO
SrO ₂	SrO
BaO ₂	BaO

¹ Corresponding author: eagoldst@stanford.edu

This reactor can either be endothermic or exothermic depending on the fuel and the oxygen carrier being considered. The gaseous exhaust from this reactor can be expanded in a turbine to produce power. The reduced metal oxide is then transported to the regeneration reactor, where the oxygen-depleted metal is oxidized with the oxygen in air. Globally,



This reaction is exothermic and provides a hot stream of oxygen-depleted air that can also be expanded to produce power.

One common challenge with metal oxide selection from a practical sense is that fluidization conditions can fail if the metal oxides begin to agglomerate [3]. To deal with this, many research groups prepare metal oxides with a variety of different inert support materials. These inert support materials have been reported to not only prevent agglomeration but also found to enhance the reactivity of the metal oxide [3-5]. Table 2 lists common inert support materials along with the metal oxides they have been studied with.

Table 2: Common metal oxide supports

Inert Support Material	Metal Oxides	Reference
YSZ	Fe, Ni	[6, 7]
SiO ₂	Fe, Ni, Mn, and Cu	[4, 8]
Al ₂ O ₃	Fe, Ni, Mn, and Cu	[4, 8, 9]
ZnO	Fe, Ni, Mn, and Cu	[8, 10, 11]
TiO ₂	Fe, Ni, Mn, and Cu	[7, 8, 10, 11]
MgAl ₂ O ₄	Fe, Ni	[10, 11]

Coal based CLC has emerged as a focus of study only in the past five years. There are two approaches when applying CLC to solid fuels, direct and indirect CLC. In indirect coal CLC, coal is gasified to produce a synthesis gas prior to CLC so that only gaseous fuels are present in the fuel reactor where they are reduced by metal oxides. In direct coal CLC, coal and metal oxide are directly mixed in the fuel reactor and metal oxides are separated from the flue gas before being transferred to the air reactor.

Both approaches face unique challenges. In the implementation of indirect coal CLC, coal gasification complicates the system design by requiring a separate gasifier, which inevitably lowers the overall efficiency due to the irreversible heat transfer processes among additional reactors. In direct coal CLC, solids separation between metal oxide, coal and ash is not only difficult but can also result in a number of issues such as metal oxide

deactivation (for example, by ash or tar deposition). In addition, the potential exists for unburned solid fuel to be carried to the metal oxide regeneration reactor, resulting in CO₂ emissions.

Direct coal CLC, if practically possible, will have a higher thermal efficiency than indirect CLC. In this study, since indirect coal CLC systems are believed to have fewer practical challenges, an indirect coal CLC system has been modeled.

Regardless of the approach to coal CLC, metal oxide interactions with the impurities present in coals also need to be addressed. For example, most coals contain sulfur, which can react with the metal oxide forming such undesirable compounds as sulfates and sulfides. In cyclic operation, these species will build up in the system if not removed. Metal oxides that do not form metal sulfates or sulfides to any appreciable extent at the selected operating temperatures need to be identified.

For the proposed study, Fe-, Ni- and Cu-based metal oxide systems were compared in a thermodynamic analysis in order to determine system energetics as functions of operating conditions. Considered were the metal oxide type, the reaction temperature, and the metal oxide-to-coal flow rate. Of interest were the power output, the thermal efficiency and the degree of formation of undesirable compounds.

Model Description

A thermodynamic model of the CLC system diagrammed in Figure 2 was developed. The model consists of three reactors that are assumed to have product streams in equilibrium: a fuel reactor, a metal oxide regeneration reactor and a gasifier. Included in the model are two reversible turbines (one for expansion of the oxygen-depleted air from the regeneration reactor and the other for expansion of the combustion products from the fuel reactor) and three reversible compressors (one for compression of the gasifying agent, another for compression of the air for the metal oxide regeneration reactor, and a third for compression of CO₂ to a liquid phase for transportation). The equilibrium calculations were carried out using HSC Chemistry[®] 6.1, which assumes ideal gas behavior, unity activities for solids and ideal mixtures.

The fuel properties used in the model were assumed to be those of Wyodak coal, a sub-bituminous coal from the Powder River Basin. An ultimate analysis is presented Table 3. In all of the models, the gasifier was run with a coal-to-CO₂ ratio 1:1 and a coal-to-steam ratio of 1:1 at 900 °C and 21 bar. At these ratios, there was essentially no solid carbon leaving the gasifier. Also shown in Table 3 are the calculated composition of the synthesis gas and its heating value. The ratio of the syngas heating value to that of the coal is presented as well. Note that at the coal-to-steam ratio used in the calculations, the syngas heating value is only about 10%

of the heating value of the coal. Energy requirements for gasification come from the heat released from both the regeneration reactor and the fuel reactor, as the chemical reactions occurring are exothermic when the gaseous fuel is primarily CO and H₂.

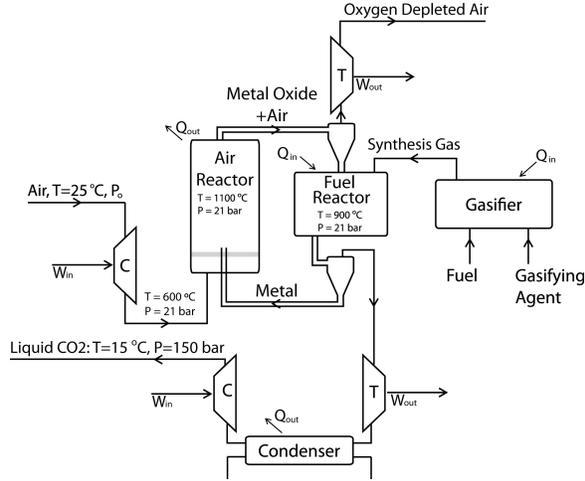


Figure 2: System schematic

Table 3: Wyodak coal ultimate analysis and synthesis gas composition

Wyodak Coal Ultimate Analysis, % mass [12]		Synthesis gas composition	
C	75.48 %	CO	39.9 %
H	6.11 %	CO ₂	10.0 %
O (bal)	16.92 %	H ₂	34.1 %
N	1.02 %	H ₂ O	11.1 %
S	0.47 %	CH ₄	4.6 %
Syngas Heating Value		Minor Species	
3.1 MJ/kg		COS	32.7 ppm
Heating value efficiency		H ₂ S	896.6 ppm
10 %		NH ₃	45.3 ppm
		HCN	1.4 ppm

For the three metal oxide systems considered, the potential species allowed to exist can be found in Appendix A. The stoichiometric amounts of metal oxide required to oxidize one kilogram (1 kg) of Wyodak coal are shown in Table 4. Note the large quantities of metal oxide required with the iron system. This will be discussed later in the paper.

For each calculation, a specified amount of metal oxide (Fe₂O₃ for the iron system, NiO for the nickel system and CuO for the copper system) was charged to the fuel reactor for each kilogram of coal. The equilibrium composition was calculated based on the temperature, pressure, and atoms present.

Table 4: Stoichiometric amount of metal oxide to combust 1 kg of Wyodak coal

	<i>Stoichiometric metal oxide for Wyodak Coal [kg]</i>
$3Fe_2O_3 \rightarrow 2Fe_3O_4 + \frac{1}{2}O_2$	72.4
$NiO \rightarrow Ni + \frac{1}{2}O_2$	9.2
$CuO \rightarrow Cu_2O + \frac{1}{2}O_2$	12.0

In order to make a meaningful comparison of the coal CLC system with the three metal oxides, the CO mole fraction at the outlet of the fuel reactor was constrained to be less than 500 ppm. The iron and nickel systems were run from 900 to 1200 °C and the copper system was run at 900 °C. This temperature limit on the copper system was imposed because Cu has a lower melting point (1035 °C) than the metal oxides in the iron and nickel systems (1368 °C and 1455 °C). Temperatures less than 900 °C were not considered as the energy requirements for gasification at 900 °C could not be met. All runs were conducted at a pressure of 21 bar. The power, process heat and efficiency curves calculated take into account work requirements to compress the exhaust CO₂ to 150 bar, a pipeline pressure for CO₂ transport. In the calculations, process heat is defined as

$$Q_{ProcessHeat} = Q_{AirReactor} + Q_{FuelReactor} - Q_{Gasifier}$$

and net work is defined as

$$W_{net} = W_{AirTurb} + W_{FuelTurb} - W_{AirComp} - W_{CO_2CompSeq} - W_{CO_2CompGasification}$$

Here, comp [=] compression and turb [=] turbine and seq [=] sequestration. A basis of 1 kg of coal per hour was used for all calculations.

Under all of the conditions that the model was implemented, there was no appreciable carbon deposition. Also, the metal oxide loading had an insignificant effect on net work and on the process heat from the cycle. As such, power, efficiency and process heat were varied by altering the air flow rate into the regeneration reactor.

In all of the cases considered, the nitrogen-containing species formed in the gasifier from the nitrogen in the coal (NO, NO₂, NH₃, and HCN) were converted primarily to N₂ in the fuel reactor, with little (≤ 10 ppb) NO_x. Also in all of the cases considered, all of the sulfur species formed in the gasifier from the sulfur in the coal (COS, H₂S, SO₃) were converted to SO₂ in the fuel reactor.

The Iron System

Calculated values for power, efficiency and process heat for the proposed iron-coal CLC system at temperatures of 900 and 1200 °C as a function of air flow rate are shown in Figure 3. The calculations were made for initial Fe₂O₃ loadings of 85 kg/hr and 110 kg/hr respectively, at 900 and 1200 °C. These flow rates were selected to meet the 500 ppm upper bound of CO in the exhaust of the system. From Figure 3, it can be seen that as the air flow rate increases, more power is produced and a more efficient system is realized. This is because at higher air flow rates, more mass can be expanded through the air reactor turbine. The maximum air flow rate occurs when the process heat is zero. At flow rates higher than this critical air flow rate, there would be insufficient energy for the endothermic gasification reactions and thus, the system would be unable to operate at the specified conditions. Comparison of the power plots at 900 and 1200 °C indicates that at this maximum air flow rate, both systems have commensurate efficiencies.

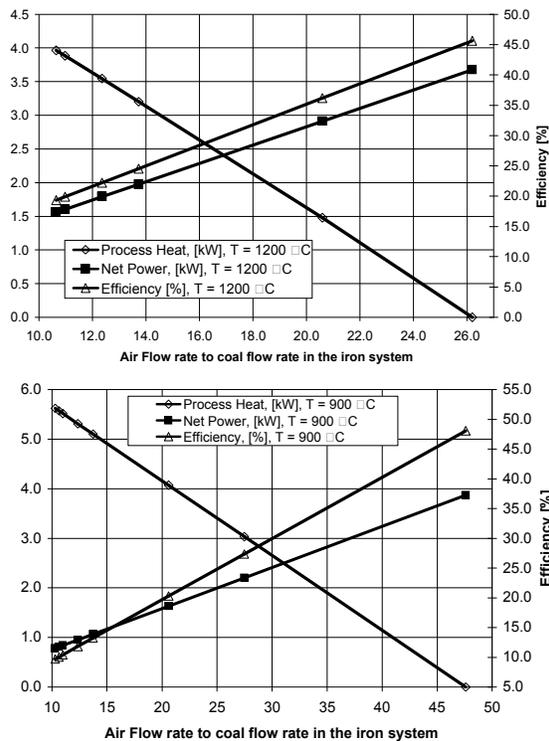


Figure 3: Power output, process heat and system efficiency for the iron-coal CLC system at 900 and 1200 °C

Shown in Figure 4 are the equilibrium pollutant concentrations for the iron-coal CLC system as a function of the metal oxide-to-coal ratio. The plots indicate that the minimum Fe₂O₃-to-coal flow rate ratio required to meet the 500 ppm exhaust criteria is 82 at 900 °C and 92 at 1200 °C. The results shown in Figure 4 also indicate

that the metal oxide mass flow rate (and to a lesser degree the reactor temperature) affect the CO and SO₂ concentration in the exhaust. This implies that if the system is operated at a higher temperature, larger Fe₂O₃ to coal flow rate ratios will be required to oxidize the fuel such that the plant emissions standards are met.

The iron system does not have any undesirable species formation at the temperature and pressure conditions considered. Similar results have been observed by others modeling CLC with CH₄, CO and H₂ [13].

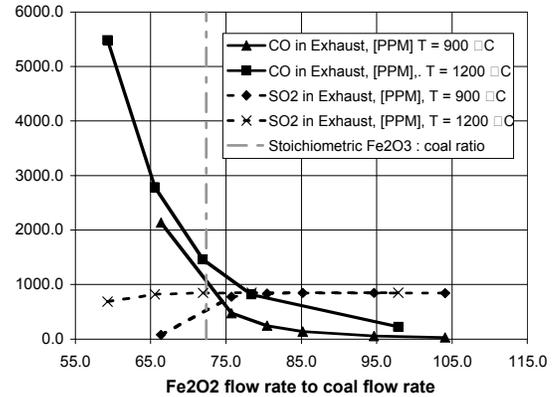


Figure 4: Gas phase species concentration in the exhaust of the iron-coal CLC system at 900 and 1200 °C

The Nickel System

The efficiency, power and process heat calculations for the nickel-coal CLC system are illustrated in Figure 5. Trends similar to those of the iron system are exhibited. The 900 and 1200 °C plots were made for initial NiO loading of 140 kg/hr and 250 kg/hr, respectively. One deviation from the iron-coal CLC system plots is that at the critical airflow rate, lower temperature operation yields higher efficiencies than higher temperature operation. Shown in Figure 7 are calculated equilibrium pollutant concentrations as a function of the NiO flow rate and shown in Figure 6 is the NiO utilization, where utilization is defined as:

$$Utilization \equiv \frac{m_{NiO,in} - m_{NiO,out}}{m_{NiO,in}} * 100$$

The first observation from Figure 6 and Figure 7 is that a large charge of NiO is required to meet the CO emissions upper bound. A second observation is that a significant amount of NiO circulates around the bed without contributing much to the oxidation of the synthesis fuel stream.

Similar to the iron system, only a small amount of undesirable sulfur species were formed in the fuel reactor at the temperatures and pressure considered. The primary

sulfur species formed were NiS and Ni₃S₂. The formation of both species was less than 0.1 % of the total NiO flow rate. Similar results have been observed previously modeling Ni in a sulfur environment [13].

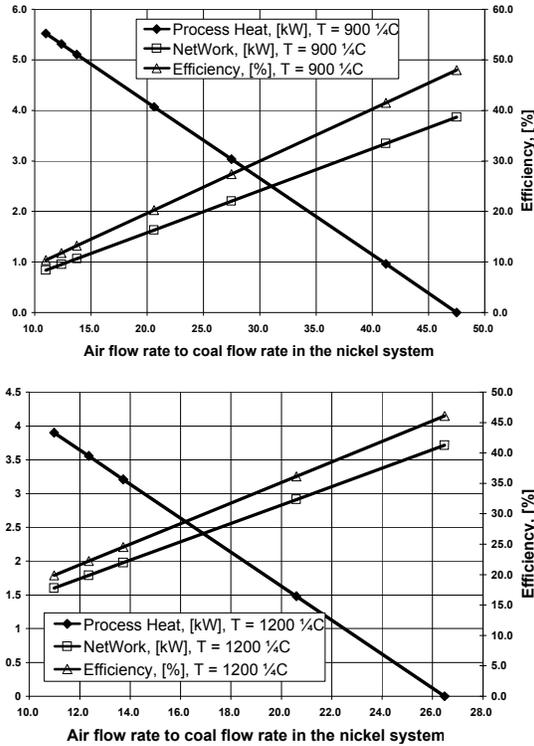


Figure 5: Power output, process heat and system efficiency for the nickel-coal CLC system at 900 and 1200 °C

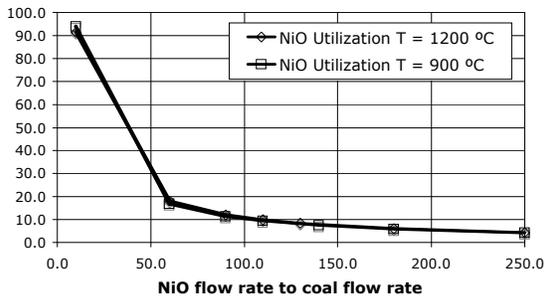


Figure 6: NiO utilization for the nickel coal CLC system at 900 and 1200 °C

The Copper System

Since the melting point of copper is on the order of 1000 °C, the fuel reactor cannot be operated at or above 1000 °C. Results for the copper system are shown only at one temperature, 900 °C. The power, process heat and efficiency calculations are shown in Figure 8. The trends exhibited are the same trends observed with the iron and nickel systems. The calculations were made using an initial CuO loading of 13 kg/hr. Equilibrium pollutant

concentrations as a function of CuO loading are shown in Figure 9; the flow rates of undesirable species, shown in Figure 10, indicate that Cu₂S is formed in significant quantities at larger flow rates of CuO. These results are in agreement with those obtained by Jerndal *et al.*, [13] when modeling CLC with CuO in sulfur-containing systems.

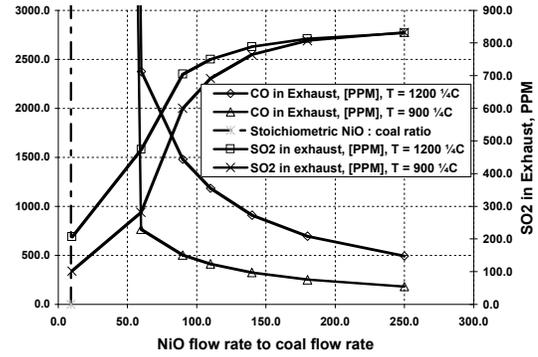


Figure 7: Gas phase species concentrations in the exhaust of the nickel-coal CLC system at 900 and 1200 °C

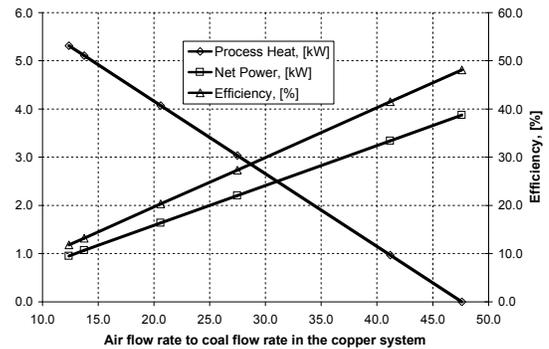


Figure 8: Power output, process heat and system efficiency for the copper-coal CLC system at 900 °C

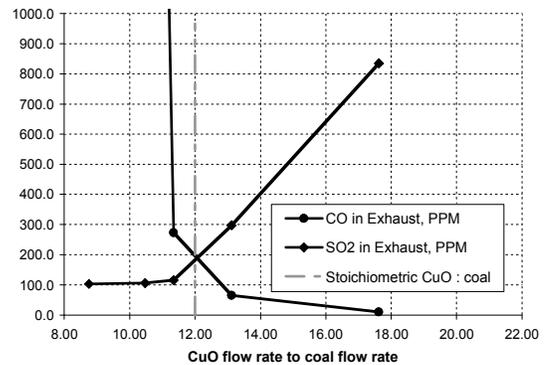


Figure 9: Gas phase species concentrations in the exhaust of the copper-coal CLC system at 900 °C

Comparisons

Each of the three systems has been described based on power, efficiency, process heat, potential pollutants, metal oxide flow rates and production of undesirable species. All three systems can be designed to have efficiencies commensurate to conventional coal-fired power plants. Also, with each system there is the flexibility to provide process heat and electricity under variable loads.

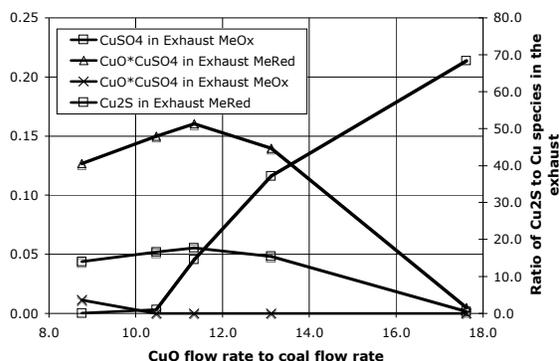


Figure 10: Undesirable metal oxide species in the copper-coal CLC system at 900 °C

Considering the CO and SO₂ emissions as a function of the respective metal oxide flow rate, it is noted that the nickel system requires at a minimum 10 to 25 times more than the stoichiometric amount of metal oxide to fully oxidize CO while the copper and iron systems require metal oxide charges comparable to their stoichiometric amounts. In any practical system, the metal oxide charge should be as small as possible to minimize plant size and material costs. To address the high CO emissions for the nickel system, another system architecture with the catalytic conversion of the CO might yield a system with smaller NiO flow rates.

Of the three systems considered, the copper system is the only one to have an appreciable accumulation of undesirable species. The calculations suggests that to meet the 500 ppm CO exhaust criteria, 10 % of the copper in CuO could be converted to Cu₂S. Since the results presented here are the steady state solutions, this amount of Cu₂S is also destroyed in the air reactor such that no net accumulation of Cu₂S occurs. Kinetic studies investigating the rate at which Cu₂S is produced and destroyed need to be determined in order to assess whether accumulation will be an issue.

Conclusions

A thermodynamic analysis of a coal-CLC system was undertaken in order to assess the power output, system efficiency, thermal management, and the impact of the fuel-to-metal oxide feed ratio. The iron-based system produced no undesirable compounds and required about a stoichiometric amount of Fe₂O₃ for oxidation of the fuel.

Under the reactor conditions examined for the nickel-based system, no sulfur species were produced, however a large NiO charge was required to completely oxidize the synthesis gas produced from coal gasification. The CuO-based CLC system was capable of oxidizing the synthesis gas at the specified conditions, however an appreciable amount of Cu₂S was produced. This renders CuO a less desirable metal oxide to use in a coal-CLC scheme.

Acknowledgements

This work would not have been possible without the support from California Energy Commission Grant 55181A/07-05 and Clean EnGen Group L.L.C.

References:

- [1] Johansson, M., Mattisson, T. and Lyngfelt, A., *Ind. Eng. Chem. Res.*, 2006, vol. 45, (17). pp. 5911-5919,
- [2] Abad, A., Mattisson, T., Lyngfelt, A. and Rydén, M., *Fuel*, 2006, vol. 85, (9). pp. 1174-1185,
- [3] Cho, P., Mattisson, T. and Lyngfelt, A., *Ind. Eng. Chem. Res.*, 2006, vol. 45, (3). pp. 968-977,
- [4] Hossain, M. M. and de Lasa, H. I., *Chemical Engineering Science*, 2008, vol. 63, (18). pp. 4433-4451,
- [5] Johansson, M. 2007. "Screening of oxygen-carrier particles based on iron-, manganese-, copper- and nickel oxides for use in chemical-looping technologies". Degree of Doctor of Philosophy, Chalmers University of Technology, Goteborg.
- [6] Jin, H. and Ishida, M., *Ind. Eng. Chem. Res.*, 2002, vol. 41, (16). pp. 4004-4007,
- [7] Lyngfelt, A., Leckner, B. and Mattisson, T., *Chemical Engineering Science*, 2001, vol. 56, (10). pp. 3101-3113,
- [8] Adanez, J., de Diego, L. F., Garcia-Labiano, F., Gayan, P., Abad, A. and Palacios, J. M., *Energy & Fuels*, 2004, vol. 18, (2). pp. 371-377,
- [9] Zhao, H., Liu, L., Wang, B., Xu, D., Jiang, L. and Zheng, C., *Energy Fuels*, 2008, vol. 22, (2). pp. 898-905,
- [10] Mattisson, T., Johansson, M. and Lyngfelt, A., *Energy & Fuels*, 2004, vol. 18, (3). pp. 628-637,
- [11] Mattisson, T., Johansson, M. and Lyngfelt, A., *Fuel*, 2006, vol. 85, (5-6). pp. 736-747,
- [12] Database, T. P. S. C. S. B. a., "Wyodak Seam (Wyodak -Anderson) Campbell County, WY," Institution, City, Type Report DECS-26, 1994.
- [13] Jerndal, E., Mattisson, T. and Lyngfelt, A., *Chemical Engineering Research and Design*, 2006, vol. 84, (9). pp. 795-806,

Appendix A: Species considered in the equilibrium calculations

	Fe	Ni	Cu
<i>Common Gas phase Species</i>	O ₂ , N ₂ , CO, CO ₂ , H ₂ , H ₂ O, CH ₄ , C ₂ H ₄ C ₂ H ₆ , NH ₃ , NO, NO ₂ , HCN, H ₂ S, COS, SO ₂ , H ₂ SO ₄ , SO ₃		
<i>Solid Species</i>	Fe	Cu	Ni
	Fe(OH) ₂	Cu ₂ O	Ni ₃ C
	Fe ₂ N	Cu ₂ S	NiO
	Fe ₂ O ₃	CuO	NiO*OH
	Fe ₂ S	CuO*CuSO ₄	NiS
	Fe ₃ C	CuSO ₄	NiSO ₄
	Fe ₃ O ₄	C	Ni
	FeCO ₃	S	Ni ₃ S ₂
	FeO		C
	FeS		S
	FeS ₂		
	FeSO ₄		
	C		
	S		