

Development and Scale-Up of Copper-Based Chemical Looping with Oxygen Uncoupling

Kevin J. WHITTY^{1*#}, JoAnn S. LIGHTY¹, Andrew FRY¹

¹ Department of Chemical Engineering, University of Utah
50 S. Central Campus Dr., Rm 3290, Salt Lake City, Utah 84112 USA

*Corresponding Author, kevin.whitty@utah.edu, #Presenting Author

Abstract – The University of Utah has been researching chemical looping with oxygen uncoupling of coal since 2007, focusing on copper-based carriers and a system configuration based on two interconnected circulating fluidized bed reactors. R&D has combined fundamental, lab-scale systems with operation of CLOU reactor systems at various scales and computational simulations for performance evaluation and reactor scale-up. Development has progressed from small lab scale through bench scale with a 10 kW dual bed research reactor to semi-pilot scale with a recently-inaugurated 220 kW chemical looping combustion process development unit.

One of the challenges of scaling up copper-based CLOU technology is acquiring enough oxygen carrier material to support operation in larger reactor systems. The UofU CLC PDU, for example, requires 150-200 kg of inventory, so the oxygen carrier must be readily available in large quantities at comparatively low cost. Because no supplier capable of delivering 1+ tons of copper-based oxygen carrier material could be identified, an inexpensive oxygen carrier material was developed in-house and the carrier production process was scaled to produce large quantities of material sufficient for the CLC PDU.

This presentation describes development of the CLOU process at the University of Utah, including evaluation of fundamental processes key to performance of CLOU, modeling and scale-up of the process, large-scale production of copper-based oxygen carrier material and experience to date with the world's largest dedicated CLOU reactor.

1 Introduction

Chemical Looping with Oxygen Uncoupling (CLOU), a variant of chemical looping combustion (CLC) technology, involves use of specific metals and associated oxides to spontaneously release (“uncouple”) oxygen as gaseous O₂ in the fuel reactor. This is possible because the equilibrium behavior or the carrier oxidation/reduction reaction is such that gaseous O₂ is favored in high temperature, low-O₂ condition such as those existing in the fuel reactor of a CLC system. In the air reactor, the high O₂ partial pressure favors the oxidized metal. The advantage of CLOU carriers over conventional CLC carriers is that the released

oxygen can react directly with solid fuel or char, thereby avoiding the need to convert the solid to gas through relatively slow gasification reactions.

Few metal complexes that exhibit CLOU behavior in the range of chemical looping combustion temperatures have been identified. Copper is attractive due its fast reaction rates and it is thermodynamically favored to completely convert gaseous hydrocarbons to CO₂ and H₂O [1]. When used as a CLOU carrier, copper cycles between the Cu⁺² cupric (CuO) and Cu⁺¹ cuprous (Cu₂O) states:



In addition, because of the low heat of reaction, Cu₂O/CuO looping is overall exothermic in both the air reactor and fuel reactor, whereas other materials are exothermic in the air reactor, but would require heat input to the fuel reactor since the heat required to reduce the carrier exceeds that given off by the fuel as it combusts [2].

The equilibrium curve for Reaction 1 is shown in Figure 1. At temperatures above approximately 800°C, in otherwise low-O₂ environments (such as the fuel reactor of a chemical looping system), the reverse of Reaction 1 takes place, generating O₂. If the O₂ continues to be consumed (e.g., by reaction with fuel), the CuO decomposition reaction will continue to progress. It has been shown that conversion of petcoke by CLOU is as much as 50 times faster than conversion by conventional CLC with an iron-based carrier, which requires in-situ conversion of petcoke to syngas by relatively slow gasification reactions [3].

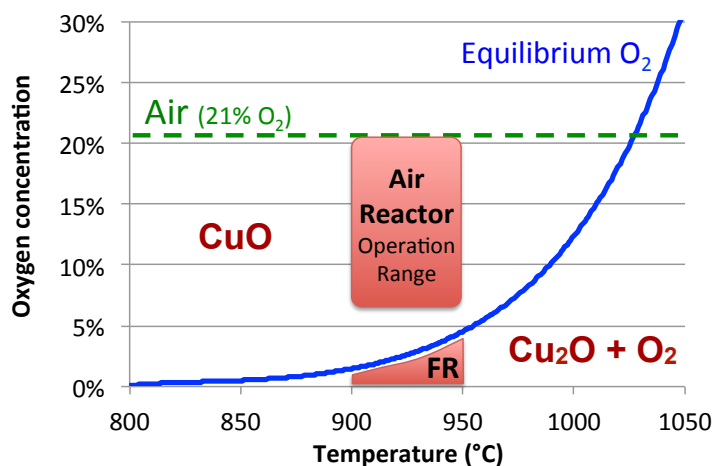


Figure 1: CuO/Cu₂O equilibrium diagram showing the range of operating conditions for CLOU air and fuel reactors.

The University of Utah has been researching copper-based CLOU since 2007. Early studies focused on better understanding the key oxygen carrier reactions and performance of oxygen carriers under simulated environments at lab scale. More recent efforts have involved advanced computational simulation of fluidized bed CLC systems, process modeling and operation of larger scale dual bed systems. This paper provides an update of development activities and progress starting up a 200 kW dual bed CLC system designed specifically for copper-based CLOU.

2 CLOU Oxygen Carrier Development and Production Scale-Up

Since it was first recognized as an efficient CLOU oxygen carrier, many researchers have evaluated performance of $\text{Cu}_2\text{O}/\text{CuO}$ in chemical looping systems, focusing on intrinsic kinetics as well as practical aspects such as agglomeration propensity and carrier durability [1,2,4-14]. Many of these materials display good performance in lab-scale experiments using thermogravimetric analyzers or small fluidized beds. But in order to be truly applicable for large-scale systems, the oxygen carrier must be able to be produced inexpensively at large scale, and it must be especially durable in the comparatively aggressive environment of pilot or commercial-scale systems. Fancy and expensive raw materials or production techniques become untenable when tons of material must be produced.

The University of Utah's new chemical looping combustion PDU requires an inventory of approximately 200 kg of oxygen carrier. To support multiple campaigns and to account for oxygen carrier loss due to attrition or possibly deactivation, it is desirable to produce a minimum of one ton of material at a time. Initially, several companies including catalyst suppliers were contacted to determine whether 1-3 tones of oxygen carrier could be affordably produced by conventional means (e.g. spray drying, extrusion). The responses were either that the equipment available would not support production at that scale, or that the cost would be prohibitively expensive. To make sure that there would be sufficient CLOU oxygen carrier for the PDU, it was decided to reexamine and scale production of a relatively crude oxygen carrier we developed earlier that had shown acceptable reactivity, durability and cost.

The oxygen carrier chosen for production scale-up uses silicon carbide as a support material and has been reported to have good durability and to sustain performance over many cycles [15]. SiC is an unconventional choice of support, but it does have exceptional strength and hardness, approaching that of diamond, and it remains solid to 2730 °C, at which temperature it decomposes. Interestingly, SiC very slowly oxidizes to SiO_2 at high temperatures, so over a long period of time the nature of the oxygen carrier changes. Experience so far indicates no reduction in activity during extended operation.

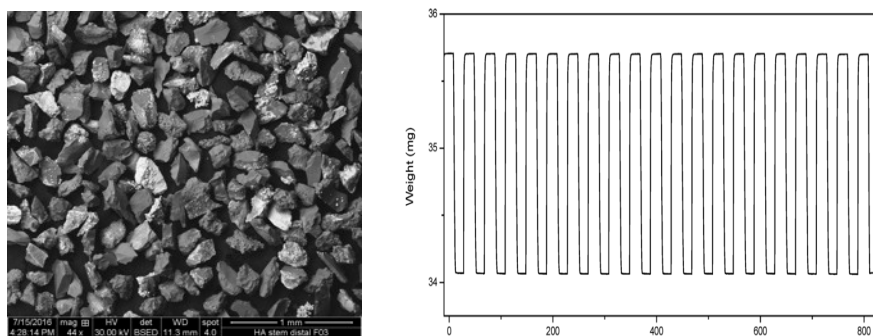


Figure 2: *CuO-on-SiC oxygen carrier particles (left) and TGA curve showing sustained oxidation-reduction (uncoupling) capacity over many cycles (right).*

Highly porous silicon carbide is available as catalyst support (e.g. SICAT spheres) and using this to as support for copper addition through wet impregnation makes a remarkably reactive and well-performing CLOU carrier. However, porous SiC is highly engineered and more expensive by mass than the copper itself, so it is not viable for use as support. Silicon

carbide, however, is available in bulk as blasting grit with particle sizes in the range desired for fluidized bed systems. This form of silicon carbide is more cubic than round and has low porosity, but it is inexpensive.

In order to maintain the structure and robustness of the SiC support, copper is loaded onto the material using the incipient wetness (impregnation) technique. The SiC is thermally pretreated to improve porosity and the particles are bathed in copper nitrate solution using water or another solvent. Multiple additions are used to improve uniformity of copper distribution and the material is heated after each addition to decompose the copper nitrate to CuO and to help bind the copper to the support. Much of the recent research effort has been focused on identifying the best “recipe” for production of the CLOU carrier.

The CLOU oxygen carrier is produced in a rotary kiln, which has several advantages: (1) the entire production process can be carried out in a single reactor without having to transfer solids; (2) the kiln can be controllably heated to temperatures required for copper nitrate decomposition and material calcining; (3) the constant rotation of the kiln keeps the material well mixed and avoids production of clumps; and (4) a sealed kiln with a single gas outlet allows for safe capture of NO₂ produced during nitrate decomposition. The University of Utah has three rotary kilns with production capacities ranging from about 1 kg to 100 kg per batch (Table 1). The largest kiln (RK-100) was commissioned early 2016 and has successfully produced large batches of oxygen carrier with loadings to 20% (the maximum targeted so far).

One challenge of using copper nitrate as the source of copper is that when the nitrate decomposes to form CuO at approximately 180°C, poisonous NO₂ gas is liberated by the reaction $\text{Cu}(\text{NO}_3)_2 \rightarrow \text{CuO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$. The carrier production systems must be designed to safely handle the NO₂ produced. The RK-10 and RK-100 kilns use sodium hydroxide to neutralize the NO₂ in an absorption tower.

Table 1: Oxygen carrier production equipment at the University of Utah

System	Type	Capacity	Heating	Max T	Length	Diam
RV-1	Rotary evap	1 kg	Water bath	95°C	n/a	0.15 m
RK-1	Rotary kiln	1 kg	Elec inductive	800°C	0.15 m	0.10 m
RK-10	Rotary kiln	10 kg	Elec radiative	350°C	0.80 m	0.20 m
RK-100	Rotary kiln	100 kg	Natural gas	600°C	1.4 m	0.40 m



Figure 3: RK-100 rotary kiln for production of CLOU oxygen carrier. The NO₂ absorption tower and caustic circulation system is visible behind the kiln.

The University of Utah is now capable of producing copper-based oxygen carrier at scales commensurate with their semi-pilot scale CLC process development unit. The CuO-on-SiC oxygen carriers currently being produced are not ideal, but are inexpensive for copper-based carriers and are sufficient for process testing and further development of the CLOU process. The University of Utah welcomes collaboration with companies or research groups that feel they have a good CLOU oxygen carrier candidate that is able to be supplied in quantities of one ton or more.

3 CLOU Reactor Design

The advantage of CLOU over conventional chemical looping combustion of solid fuels, which relies on *in situ* gasification and heterogeneous combustion of the resulting syngas by a non-CLOU carrier such as ilmenite, is the much faster char conversion that is achieved by reaction with O₂ versus gasification with H₂O and CO₂. Designing a large-scale CLOU reactor system (larger than what can feasibly be heated electrically) involves specifying details such as those included in Figure 4.

<p>Air reactor</p> <ul style="list-style-type: none"> - Type (bubbling, circulating, etc.) - Target temperature - Size (volume) - Oxygen carrier residence time distribution - Incoming air flow rate - Target outlet oxygen concentration - Air residence time - Air preheat requirements - Cooling duty and cooling system design 	<p>Fuel reactor</p> <ul style="list-style-type: none"> - Type (bubbling, circulating, etc.) - Target temperature - Size (volume) - Oxygen carrier residence time distribution - Fluidization gas (steam, CO₂, mixture) - Fluidization gas preheat requirements - Cooling duty and cooling system design 	<p>Oxygen carrier</p> <ul style="list-style-type: none"> - Metal (CuO) wt% loading - Circulation rate - Particle size <p>Fuel feeding</p> <ul style="list-style-type: none"> - Fuel feed rate - Fuel feed location - Fuel particle size <p>Other</p> <ul style="list-style-type: none"> - Carbon stripper requirements and design - Gas-solid separation system design - Loop seal design and arrangement
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Figure 4: Factors to consider in design of a dual fluidized bed CLOU system.

3.1 Reaction fundamentals

To properly design a CLOU system, it is desirable to have as much information as possible about the underlying processes associated with oxidation and reduction of the oxygen carrier as well as conversion of the coal. Significant research on devolatilization and combustion of coal has been performed and published relationships and predictive models are readily available. Behavior of oxygen uptake and release from copper-based oxygen carrier is less well studied. It is valuable to understand the intrinsic chemical kinetics of both the forward (oxidation) and reverse (reduction) reactions shown in reaction (1). Ideally, it is useful to have rate expressions applicable across a broad range of conditions, for example of the form below for cuprous oxide oxidation:

$$rate = A \exp\left(\frac{-E_a}{RT}\right) [\text{Cu}_2\text{O}]^\alpha [\text{O}_2]^\beta \quad (2)$$

where A is a pre-exponential constant, E_a is the activation energy and α and β are reaction orders.

Interestingly, the thermodynamic behavior shown in Figure 1 affects the rate of the carrier oxidation and decomposition (uncoupling) reactions. It is well understood that rates of reversible reactions such as reaction (1) are affected by the difference between the actual and equilibrium concentrations of reacting species. This has also been observed to occur with copper-based oxygen carriers operating in the CLOU regime [4]. This makes identification of intrinsic kinetics of the respective oxidation and reduction reactions challenging. For example, several groups studying CLOU have reported a decrease in the rate of oxidation by air at higher temperatures [4,5,16], which is due primarily to a decrease in the difference between the equilibrium O_2 partial pressure and air's partial pressure of 0.21 atm. Similarly, in certain types of experiments the rate of cupric oxide reduction to release O_2 is affected by that released O_2 .

To University of Utah has undertaken several studies to investigate and develop rate models for Cu_2O oxidation and CuO uncoupling/ O_2 generation as functions of local environment and oxygen carrier properties. These results have been published [17-20] and other groups have also reported on reaction behavior of copper-based oxygen carriers for CLOU reactors [3-14].

3.2 Reactor modeling

Early reactor models developed at the University of Utah were relatively simple Excel-based mass and energy balance-type models that used published correlations for oxygen carrier circulation rates and gave relatively cursory consideration to reaction kinetics and reactions other than oxygen carrier oxidation and reduction and coal char conversion. A model of this type was used for primary design of a 200 kW dual circulating fluidized bed CLC/CLOU process development unit before its construction began in 2012.

In 2013 the University of Utah established a relationship with CFPD, LLC and acquired a license for CFPD's Barracuda VR[®] software for computational fluid dynamic modeling of dense phase systems. Since that time, several Barracuda VR[®] models have been developed to

simulate performance of various reactor designs. Complexity and representativeness of the models has increased with time as improvements have been made to particle characterization and size distribution, chemical reactions and rates, heat generation and transfer, and submodels for particle-gas interactions. The CLC models are now quite robust and the model of the 200 kW PDU has been valuable for specifying operating conditions and for interpretation of performance during shakedown.

To help understand hydrodynamic behavior of the 200 kW PDU and as a tool for validation of the Barracuda VR[®] models, an acrylic cold flow model of the PDU was constructed. The cold flow model was designed in accordance with Glicksman's scaling relationships for fluidized beds and is approximately 60% the size of the full-scale system. A photo of the cold-flow model and a screen capture of a Barracuda VR[®] simulation are shown in Figure 5.

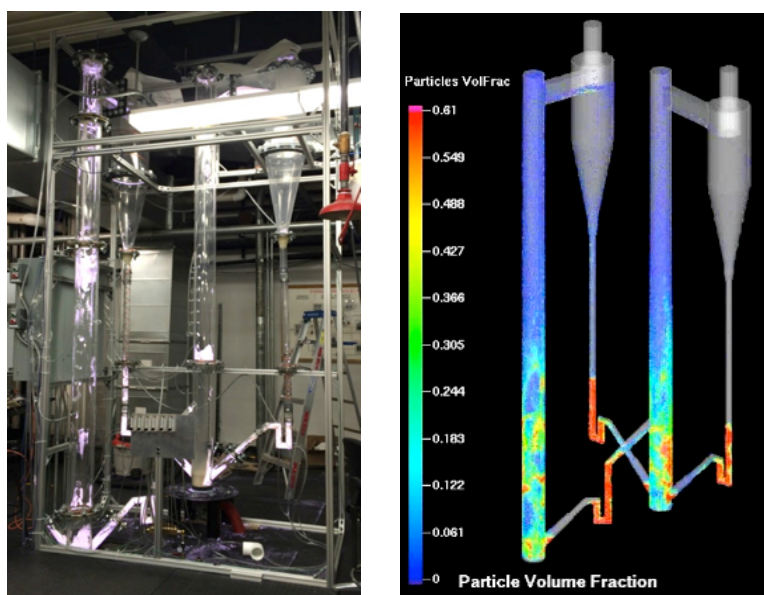


Figure 5: Cold flow model (left) and Barracuda VR[®] simulation of the cold flow model showing particle volume fraction (right).

3.3 Reactor construction

Reactor design at the University of Utah has combined fundamental understanding of oxygen carrier and coal conversion behavior, experience operating fluidized bed reactors at various scales and computational process models and reactor simulations. Two scales and designs of reactor systems have been built. These are described below.

10 kW dual bubbling bed bench-scale reactor. The University of Utah has built a bench-scale dual bubbling fluidized bed chemical looping system that has a capacity of roughly 10 kW or roughly 1.5 kg/h coal feed (Figure 6). The system was constructed by modifying an existing 10 cm diameter electrically heated steam-blown gasifier to serve as the fuel reactor, incorporating an overflow pipe that carries particles through a loop seal into an air reactor. The air reactor is a 15 cm diameter fluidized bed that operates as a bubbling bed with a cone at the top to reduce the diameter to 3.7 cm so that the velocity increases to transport particles through a riser into a cyclone. Particles flow from the cyclone through a

dipleg and loop seal back to the bottom of the fuel reactor. Coal is fed through a twin auger feeder into the bottom of the fuel reactor diametrically opposite the inlet of recycled particles. The 10 kW system is used for scoping studies, to investigate carbon conversion and char properties, and to expose candidate oxygen carrier materials to actual chemical looping conditions for extended lengths of time.

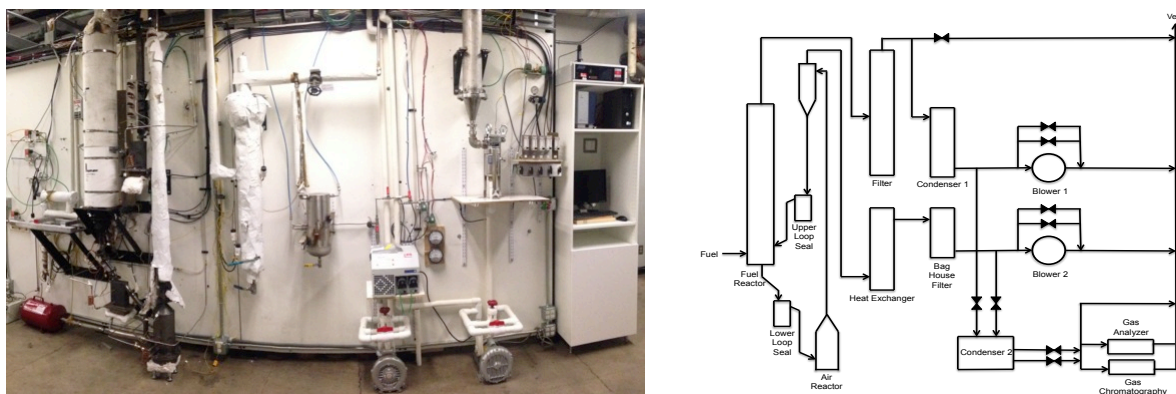


Figure 6: Photograph and schematic of UofU 10 kW bench-scale chemical looping system.

200 kW semi-pilot-scale chemical looping process development unit (PDU). The University of Utah recently completed construction of a relatively large process development unit for CLC and CLOU. The subsystems are sized for a thermal input of roughly 240 kW and based on models of expected performance the unit should be able to comfortably handle operation at 200 kW in CLOU mode. Initial tests will target operation at lower load, closer to 100 kW.

The 200 kW system represents a significant scale-up of CLOU technology for the University of Utah, and several decisions regarding design had to be made. In addition to determining reactor characteristics tabulated earlier, it was necessary to decide whether the reactor should be made of metal and electrically heated or whether it should be refractory lined and preheated. Chalmers University of Technology operates an electrically heated 100 kW chemical looping reactor [21], but that represents an upper limit of what can practically be electrically heated. The University of Utah operates several other pilot-scale systems at its Industrial Combustion and Gasification Research Facility (ICGRF) [22] and all of those systems are refractory-lined. Based on good experience with those pilot systems and concern over durability of materials at combustion temperatures, it was decided to make the CLC PDU a refractory lined system.

Both the air and fuel reactors are circulating fluidized beds. Again, part of the rationale behind that decision was familiarity with operating a similarly-sized circulating fluidized bed combustor, which has been at the ICGRF for over 20 years. Also, CFBs are considered more scalable to industrial scale than bubbling fluidized beds. To help separate control of the two reactors, the fuel reactor recycles material from the cyclone back to the fuel reactor bed, but all material from the air reactor flows through the cyclone into the fuel reactor. A dedicated leg transports particles from the fuel to the air reactor via a loop seal. The resulting configuration of the two beds is shown in Figure 7 and a photograph of the completed system is presented in Figure 8.

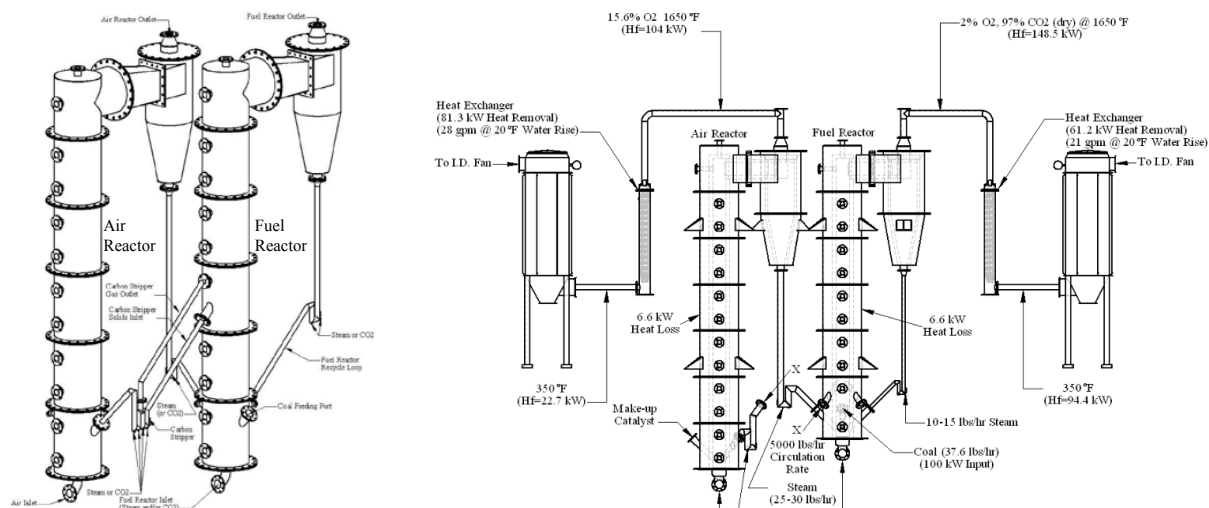


Figure 7: Reactor arrangement and configuration of the 200 kW CLC PDU.



Figure 8: Photograph of the University of Utah chemical looping combustion PDU.

The PDU was built without a carbon stripper to burn out char that is undesirably transferred to the air reactor. CLOU has been demonstrated to achieve much better carbon conversion than conventional CLC of coal with e.g. ilmenite, so the need for a carbon stripper should be less. Nonetheless, incorporation of a carbon stripper will undoubtedly help conversion, even for a CLOU system. It has been decided to operate first without one so that the quantity and nature of char carried to the air reactor can be characterized to help design an appropriate carbon stripper.

4 Current Status of Development

The University of Utah has been working on copper-based chemical looping with oxygen uncoupling for almost ten years. Experimental investigations have during that time progressed from basic lab-scale exploration through systematic characterization of underlying chemistry and processes to operating first single bed and then dual bed lab- and bench-scale fluidized bed chemical looping systems and finally to designing, building and commissioning a semi-pilot scale CLOU process development unit. Modeling has advanced significantly, from simple reactor mass balances to integrated energy and material balances and dense phase multiscale computational fluid dynamic modeling with hydrodynamics, heat transfer and reaction kinetics. Development has gone about as far as it can at lab scale, so the focus is shifting towards operation of the PDU and familiarizing ourselves with performance in that system. An extensive parametric study is planned, under which two U.S. coals, a typical eastern bituminous (Illinois #6) and a Wyoming Powder River Basin (PRB) coal, will be studied. The study will investigate the influence of air and fuel reactor temperatures, fuel feed rate, fuel particle size, oxygen carrier CuO loading and air reactor flow rate on overall performance as well as carbon capture efficiency (U.S. DOE target >90%), carbon dioxide purity (U.S. DOE target >95%) and degree of fuel conversion.

At the time of this writing, the PDU has operated hot while circulating oxygen carrier for more than 200 hours. Testing so far has been conducted using ilmenite as an oxygen carrier and has focused on familiarizing the operators with overall operation of the system including testing response of gas preheating systems, confirming temperature and pressure measurements. The subsystems such as air and steam flow control and preheat, gas coolers and bag houses have been individually tested and found to operate correctly.

A key operational variable is the circulation rate of the carrier material. Extensive testing with ilmenite has been performed to understand how circulation rate is affected by changes in operating conditions, especially the air and fuel reactor flow rates. The flow of oxygen carrier particles from the air reactor to the fuel reactor is measured by turning off fluidizing gas on the loop seal on the transfer line from the air reactor to the fuel reactor, then measuring the rate at which particles fill the vertical dip leg connecting the air reactor cyclone to the loop seal. The dip leg has several pairs of quartz windows at various heights and the rate of particle buildup is determined by measuring the amount of time it takes for particles to block light from one pair of windows to the next. The circulation mass flow is calculated by multiplying the volume of the dip leg between windows by the bulk density of the oxygen carrier material.

Example results of the circulation tests with ilmenite are shown in Figure 9. As expected, circulation rate increases with increasing air flow rate to the air reactor and with increased bed inventory (mass of oxygen carrier in the system). With high inventory, circulation rates in excess of 10 tons/hr can be achieved. Measured circulation rates are higher than expected, partly because very conservative assumptions were made when designing the system. The circulation rates are sufficient to transfer enough oxygen to support operation at the design load of 200 kW and even higher.

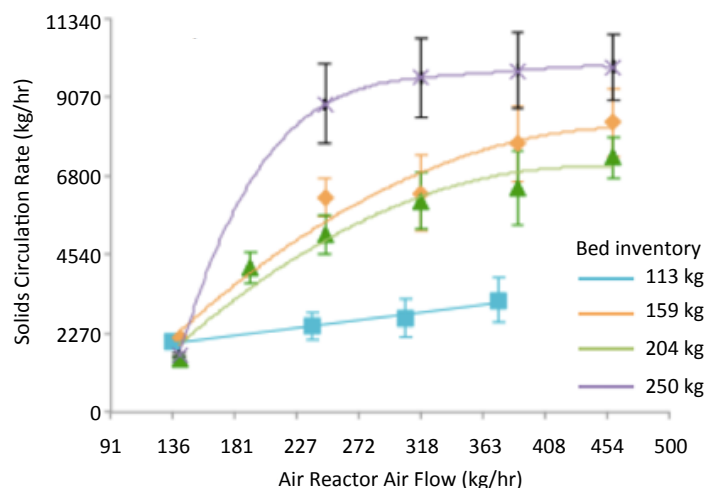


Figure 9: Ilmenite circulation rates in PDU, measured at 600°C.

5 Conclusion

Copper-based chemical looping with oxygen uncoupling is a promising technology and lab-scale and bench-scale studies have demonstrated efficacy of the process. The University of Utah has been working with Cu-based CLOU for almost 10 years and is in the process of starting up the world's largest dedicated CLOU process development unit.

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