

## Article

# Coal Chemical-Looping with Oxygen Uncoupling (CLOU) Using a Cu-Based Oxygen Carrier Derived from Natural Minerals

Ping Wang <sup>1,\*</sup> , Bret Howard <sup>1</sup>, Nicholas Means <sup>1,2</sup>, Dushyant Shekhawat <sup>3</sup> and David Berry <sup>3</sup>

<sup>1</sup> Department of Energy (DOE), National Energy Technology Laboratory (NETL), 626 Cochran's Mill Road, Pittsburgh, PA 15236, USA; bret.howard@netl.doe.gov (B.H.); nicholas.means@netl.doe.gov (N.M.)

<sup>2</sup> Leidos Research Support Team, 626 Cochran's Mill Road, P.O. Box 10940, Pittsburgh, PA 15236-0940, USA

<sup>3</sup> DOE, NETL, 3610 Collins Ferry Road, Morgantown, WV 26507, USA; Dushyant.Shekhawat@netl.doe.gov (D.S.); David.Berry@netl.doe.gov (D.B.)

\* Correspondence: ping.wang@netl.doe.gov; Tel.: +1-412-386-7539

Received: 18 December 2018; Accepted: 9 April 2019; Published: 17 April 2019



**Abstract:** Chemical-looping with oxygen uncoupling (CLOU) is considered a promising technology to burn solid fuels with improved CO<sub>2</sub> capture and has the potential to improve fuel conversion and reaction rates. Cu-based oxygen carriers (Cu-OC) are often used in solid fuel CLOU. This study focused on investigating Cu-OC derived from a natural mineral for solid fuel CLOU because of their potentially lower cost compared to synthetic OCs. Reactivity and recyclability of a natural ore-derived Cu-OC on coal char (Powder River Basin sub-bituminous coal) were studied at 900 °C in Ar and air using TGA-QMS and fixed-bed reactor-QMS for five cycles. Cu-OC was prepared by simply heating chalcopyrite in air. Chalcopyrite is one of the principle copper sulfide ores and one of the primary ores for copper. The prepared Cu-OC had primarily CuO and CuFe<sub>2</sub>O<sub>4</sub> (CuOFe<sub>2</sub>O<sub>3</sub>) as active compounds based on XRD analysis and an oxygen capacity 3.3% from oxygen uncoupling. The carbon conversion efficiency  $X_c$  was 0.94 for reduction at a ratio of Cu-OC to char  $\phi = 75$  and the product gas was primarily CO<sub>2</sub> with trace O<sub>2</sub>. The reactivities and the rates were similar for five redox cycles. These results indicate that the natural ore-derived material with low cost has potential as a competitive oxygen carrier in solid fuel CLOU based on its reactivity in this study.

**Keywords:** chemical-looping with oxygen uncoupling (CLOU); coal; Cu-based oxygen carrier; reactivity; recyclability; natural minerals; chemical-looping combustion

## 1. Introduction

Chemical-looping with oxygen uncoupling (CLOU) is a promising solid fuel chemical-looping combustion (CLC) process for CO<sub>2</sub> emission control [1,2]. CLOU uses a solid oxygen carrier (OC) that releases gaseous O<sub>2</sub> to combust the solid fuels [3]. It results in a higher fuel conversion and reaction rate than in-situ gasification CLC (iG-CLC), which uses an OC (typically Fe-based OC) to convert syngas generated from fuel gasification [1,4]. Some metal oxides with oxygen uncoupling properties are CuO/Cu<sub>2</sub>O, Mn<sub>2</sub>O<sub>3</sub>/Mn<sub>3</sub>O<sub>4</sub>, and Co<sub>3</sub>O<sub>4</sub>/CoO [3]. Cu-based OCs are often used in solid fuel CLOU and have demonstrated complete fuel conversion with near 100% CO<sub>2</sub> capture [5,6]. Cu-based OCs are also the focus of this study. Synthetic Cu-based oxygen carriers (60 wt.% CuO on a MgAl<sub>2</sub>O<sub>4</sub> support) have successfully been tested in a 1.5 KWth continuously-operating CLOU reactor using bituminous coal [7] and pine wood [8]. Recently, efforts towards development of OCs for CLOU have focused on combined metal oxides consisting of Cu-based and Mn-based materials mixed with Ca, Mg, Cu, Fe, or Si [9–11]. For reactivity and kinetic studies of the Cu-based OCs in CLOU, Thermogravimetric analysis (TGA) is typically used along with fixed bed and fluidized bed reactors [12–15]. The majority

of studies focus on the oxygen uncoupling and oxidation of the Cu-based OCs or reduction of the Cu-based OC with gas fuels.

To fully convert solid fuels in CLOU, OCs with high O<sub>2</sub> uncoupling capacity and/or low cost are required to generate excess oxygen [2,5]. Moreover, low cost OCs for reaction with solid fuels are preferred due to losses of OC in the challenging ash separation process, especially for coals with high ash content. Natural minerals are attractive for solid fuel CLC because of their potentially lower cost compared to synthetic OCs [4,16]. Natural copper ores have been investigated for CLOU and have demonstrated gaseous oxygen-releasing properties [17–21]. Three natural copper ores with low (5.82 wt.%) and high (63.52 and 87.28 wt.%) CuO content (primary mineral phase of CuO) were studied in cycle tests of oxygen uptake in air and release in CO<sub>2</sub> in a fluidized-bed reactor. The low Cu content ore did not have agglomeration for 20 cycles at a high temperature (980 °C) but both of the high Cu content ores showed agglomeration [21]. A medium Cu content OC (CuO 21 wt.% and CuFe<sub>2</sub>O<sub>4</sub> 70 wt.%), prepared from natural copper ore, was evaluated for oxygen release/uptake rates and cyclic redox reactivity of anthracite coal CLOU at 900 °C and 950 °C in a batch fluidized-bed reactor [19]. The CLOU tests reached high combustion efficiency, above 96% and CO<sub>2</sub> yields above 0.95. Slight agglomeration and sintering were observed during the 10 h of testing. The same copper ore OC was modified by mechanical mixing with cement (calcium aluminate cement 10–30 wt.%) [20]. The modified OC with 20 wt.% cement was tested with both synthesis gas and lignite coal at 950 °C and showed better reactivity and improved agglomeration resistance than the unmodified copper ore OC. The same medium Cu content OC was also evaluated for CLOU with different coals (anthracite, bituminous, and lignite) over a range of temperatures 850–950 °C [18]. Carbon conversion rates decreased with the coal rank. No serious agglomeration was observed except for the high volatile lignite at 950 °C due to radical temperature increase. Until recently, there has been little research on copper ore for coal CLOU and limited types of ores have been studied. Further investigation of copper ore for coal CLOU is needed [16].

Copper ores are abundant and consist of two primary types: copper sulfides and copper oxides [22]. Chalcopyrite (CuFeS<sub>2</sub>) is one of the principle copper sulfide ores and the most important ore for copper production [23]. Therefore, chalcopyrite was selected for this study. Since the chalcopyrite ore is a naturally occurring mineral and is mined at a large scale, it often contains a large portion of gangue mineral including quartz, clay, and other non-copper-bearing minerals. During copper production, a copper concentrate is first generated from the chalcopyrite ore and typically consists of 24–28% copper, 23–25% iron, and 25–30% sulphur [24]. These copper concentrates could be a resource for OCs because they naturally contain both copper and iron and are readily available in large quantities in the ore markets. However, it has proven difficult to obtain small samples from copper mining companies for use in lab studies because of safety and security concerns when shipping these materials. Therefore, the ore used in this study was a chalcopyrite mineral sample but not the copper concentrate from mining companies. Coal is an abundant and inexpensive energy resource. Coal power plants generate large-scale, stable electricity output as part of the regional and global energy mix. The objective of this study is to investigate the reactivity and recyclability of natural copper ore for coal CLOU. Information resulting from this research could help to further develop low cost oxygen carriers for solid fuel CLOU technology.

## 2. Experimental

### 2.1. Coal Char Preparation and Characterization

Coal char was prepared by pyrolyzing a Powder River Basin (PRB) sub-bituminous coal obtained from the U.S. Department of Energy's National Carbon Capture Center (NCCC). Ground coal, with a particle size of 106–180 µm, was pyrolyzed at 1000 °C for one hour in a fixed bed reactor under flowing nitrogen. Table 1 lists the proximate and ultimate analysis results for the coal and the coal char on a dry basis. The moisture content of the coal and char were 1.20 wt.% and 12.29 wt.%, respectively.

The pyrolysis temperature was selected to be higher than the CLOU test temperature (900 °C) for the purpose of removing all volatile content from the char sample.

**Table 1.** Proximate and ultimate analysis of the Powder River basin (PRB) sub-bituminous coal and char.

Sample	Proximate Analysis (% Dry Basis)			Ultimate Analysis (% Dry Basis)				
	Fixed Carbon	Volatile Matter	Ash	C	H	N	S	O (Diff.)
PRB Coal	47.66	45.08	7.26	65.44	4.39	0.72	0.48	21.71
PRB Char	85.60	1.98	12.42	85.60	0.23	1.12	0.53	0.10

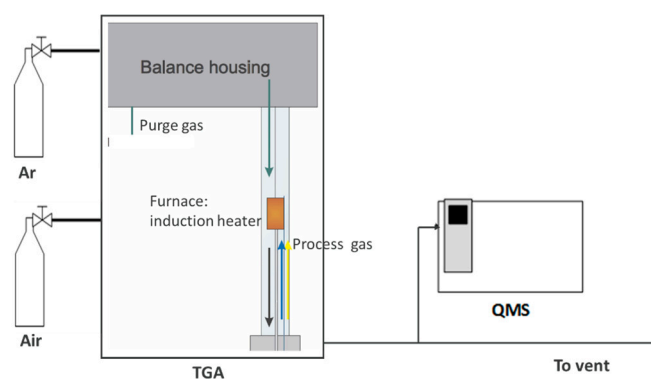
## 2.2. Cu-Based OC (Cu-OC) Preparation and Characterization

The Cu-OC was prepared from a chalcopyrite sample mined in Mexico. The chalcopyrite was analyzed to determine its mineral composition using X-ray diffraction (XRD) (PANalytical X'Pert PRO). The fresh chalcopyrite sample consisted of chalcopyrite ( $\text{CuFeS}_2$ , 75 wt.%) with minor quartz ( $\text{SiO}_2$ , 20 wt.%), trace kaolinite (a clay mineral,  $\text{Al}_2\text{Si}_2\text{O}_3(\text{OH})_4$ , 3 wt.%), and trace siderite ( $\text{FeCO}_3$ , 2 wt.%). The chalcopyrite ore composition by weight percentage was estimated by the reference intensity ratio (RIR) method from the XRD data. Table 2 summarizes the XRD analysis results for the various OC samples generated in this study.

**Table 2.** XRD analysis of main phase compounds in chalcopyrite, fresh Cu-based oxygen carriers (Cu-OC), uncoupled Cu-OC, reduced, and reoxidized Cu-OC with char in Ar at 900 °C.

Chalcopyrite		Fresh Cu-OC	Uncoupled Cu-OC	Reduced Cu-OC	Reoxidized
Chemical	wt%			with Char	Cu-OC with Char
$\text{CuFeS}_2$	75	$\text{CuO}$ $\text{CuFe}_2\text{O}_4$ ( $\text{CuOFe}_2\text{O}_3$ ) (tetragonal)	$\text{Cu}_2\text{O}$	$\text{Cu}_2\text{O}$	$\text{CuO}$ $\text{CuFe}_2\text{O}_4$ (tetragonal)
		$\text{Fe}_2\text{O}_3$	$\text{CuFe}_2\text{O}_4$ (cubic) $\text{CuFeO}_2$ ( $\text{Cu}_2\text{OFe}_2\text{O}_3$ ) $\text{Fe}_2\text{O}_3$	$\text{CuFe}_2\text{O}_4$ (cubic) $\text{CuFeO}_2$ $\text{Fe}_2\text{O}_3$	$\text{CuFe}_2\text{O}_4$ (cubic) $\text{Fe}_2\text{O}_3$
$\text{SiO}_2$	20	$\text{SiO}_2$	$\text{SiO}_2$	$\text{SiO}_2$	$\text{SiO}_2$
$\text{FeCO}_3$	2				
kaolinite	3				

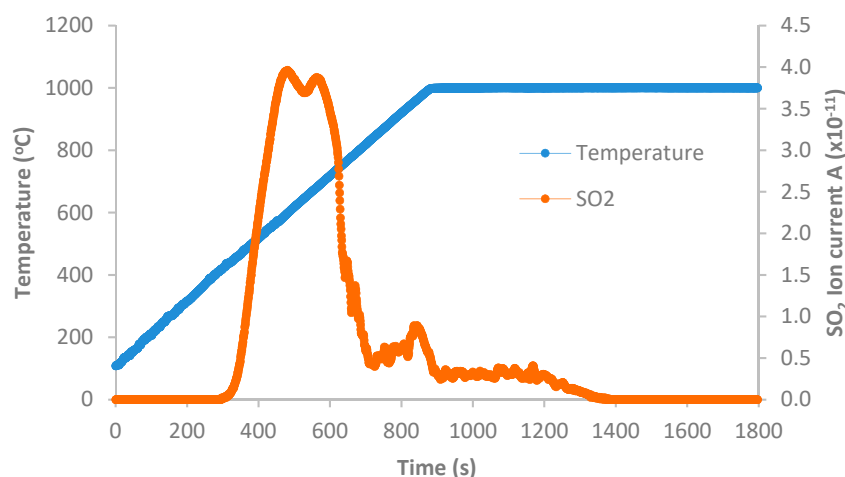
To prepare the Cu-OC, the chalcopyrite was crushed, ground, and sieved to a particle size range of 106–180  $\mu\text{m}$ . The particles were then heated at 900 °C for two hours in a fixed bed reactor under flowing air to convert the sulfide ore to the oxide form releasing S as sulfur dioxide ( $\text{SO}_2$ ). The selected heating temperature of 900 °C to prepare the Cu-OC was based on an ore oxidation behavior test using a TGA (Linsens HS-TGA) and a quadrupole mass spectrometer (QMS) (Pfeiffer Ominstar GSD 301) (Figure 1).



**Figure 1.** Schematic diagram of a thermogravimetric analyzer-quadrupole mass spectrometer (TGA-QMS) system used in this study.

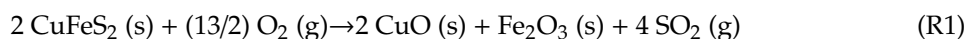
In the ore oxidation test, the ground chalcopryrite (approximately 175 mg) was tested under “simulated air” (22.4 vol.% O<sub>2</sub>/Ar) at 1000 °C using a non-isothermal method. The sample was heated from room temperature to 100 °C at 5 °C/min and held at 100 °C for 1 min to remove moisture. Then, the temperature was increased to 1000 °C at 60 °C/min and held for about 30 min. The product gases were analyzed on-line by the QMS every second during the reaction. The resulting Cu-OC was analyzed to determine the crystalline phase composition by XRD.

During the TGA-QMS test of Cu-ore oxidation, the TGA detected the sample weight loss with a maximum rate at approximately 500 °C. The final weight loss was approximately 16% and was primarily due to decomposition of CuFeS<sub>2</sub> releasing SO<sub>2</sub> with contributions from FeCO<sub>3</sub> releasing CO<sub>2</sub> and Al<sub>2</sub>Si<sub>2</sub>O<sub>3</sub>(OH)<sub>4</sub> releasing H<sub>2</sub>O. All of the expected gases (SO<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O) were detected by QMS during the chalcopryrite oxidation test. Figure 2 shows the SO<sub>2</sub> ion current from the QMS and the sample temperature versus time for the ground chalcopryrite oxidation. Most of SO<sub>2</sub> was released in the temperature range of 436–845 °C with the maximum at about 600 °C. Thus, the temperature of 900 °C was selected to prepare Cu-OC from the chalcopryrite based on this result.



**Figure 2.** SO<sub>2</sub> ion current from QMS and temperature versus time for the ground chalcopryrite oxidation in simulate air (22.4 vol.% O<sub>2</sub>/Ar) at 1000 °C in a TGA-QMS.

The fresh Cu-OC consisted primarily of CuO (major component) and CuFe<sub>2</sub>O<sub>4</sub> (CuOFe<sub>2</sub>O<sub>3</sub>, intermediate component) with minor amounts of hematite (Fe<sub>2</sub>O<sub>3</sub>) and SiO<sub>2</sub> from the XRD analysis (Table 2). The oxidation is a complex process and may involve several stages of reaction [23]. The overall oxidation of chalcopryrite may be viewed as follows:



In the oxidation process, CuFe<sub>2</sub>O<sub>4</sub> may be formed from CuO and Fe<sub>2</sub>O<sub>3</sub>. Conversion of the chalcopryrite to an oxygen carrier is a relatively simple process compared to synthetic Cu-Fe OC preparation which could require multiple steps and many chemicals, another benefit of using chalcopryrite as a resource for a Cu-based OC with low cost.

### 2.3. Analysis of the Cu-OC

#### 2.3.1. Cu-OC Oxygen Uncoupling

Cu-OC oxygen uncoupling was tested using a TGA-QMS under Ar at 60 mL/min. A sample of the Cu-OC (approximately 30 mg) was heated from room temperature to 100 °C at 30 °C/min and held at 100 °C for 5 min to remove moisture from the OC. Then the temperature was increased to 900 °C at 60 °C/min and held for about 60 min. The QMS quantified the oxygen gas (O<sub>2</sub>) on-line every second

during the reaction. The resulting reduced Cu-OC was analyzed to determine the crystalline phase composition by XRD.

The non-isothermal method used in this study was done to quantify the gaseous oxygen released from the OC. For the isothermal method used for CLOU, a sample was heated to the test temperature in an air atmosphere then tested by switching to inert gas [25]. In the isothermal method, it is difficult to determine the released oxygen from the OC because the gas from the TGA is a mixture of residual oxygen from the air and the released O<sub>2</sub> from the OC with a relatively low concentration (<1% O<sub>2</sub> in this study).

### 2.3.2. Recyclability of the Cu-OC with Coal Char in a TGA-QMS

The recyclability of the Cu-OC with coal char CLOU was evaluated at 900 °C for five cycles in the TGA-QMS. For one CLOU cycle, Cu-OC reduction with the coal char was first tested under Ar using the same experimental procedure described in Section 2.3.1. A test sample of the Cu-OC and the char was physically mixed with a ratio of Cu-OC to char ( $\phi$ ) by weight of 75. This ratio was calculated based on oxygen. The available gaseous oxygen in the Cu-OC from oxygen uncoupling is the stoichiometric amount of oxygen required to fully combust the char to CO<sub>2</sub> (Reaction R2). After the reduction of the sample, the reduced Cu-OC was immediately reoxidized at 900 °C for about 15 min under an oxygen gas environment. The oxygen gas was 22.4 vol.% O<sub>2</sub>/Ar at 60 mL/min. The QMS quantified the primary reaction gases (O<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>). The reduced and reoxidized Cu-OC were analyzed to determine the crystalline phase composition by XRD.



After one CLOU cycle, the system was cooled to room temperature. The gas was switched to Ar for 2nd cycle testing. The same amount of coal char was again added to the sample crucible with the oxidized Cu-OC and coal ash from the previous cycle. The 2nd cycle and subsequent cycles were conducted following the same procedure.

### 2.3.3. Recyclability of the Cu-OC with Coal Char in a Fixed Bed Reactor-QMS System

The same multicycle tests were repeated using a fixed bed reactor-QMS system to generate samples for BET surface area analysis. The purpose of this test was to obtain more sample for the BET measurements because Cu-OCs, like other OCs, have low surface areas. The BET surface areas of the fresh and used Cu-OC were evaluated by N<sub>2</sub> adsorption isotherms performed at 77 K in a Quantachrome Autosorb 1-C.

## 2.4. Data Analysis

For TGA data, the reactivities of the Cu-OC are evaluated based on mass changes in solids. The Cu-OC oxygen uncoupling, reduction, and re-oxidation reactivity with coal char, and recyclability were evaluated by calculating sample weight change and rates of change.  $m_o$  for oxygen uncoupling,  $m_{red}$  for reduction, and  $m_{ox}$  for oxidation are defined as follows:

$$m_o = \frac{m_{oc} - m}{m_{oc}} \times 100 \quad (1)$$

$$m_{red} \text{ or } m_{ox} = \frac{m - (m_{oc} + m_c)}{m_{oc} + m_c} \times 100 \quad (2)$$

where  $m$ ,  $m_{oc}$  and  $m_c$  are the mass of the test sample at the reaction time, the initial mass of the Cu-OC and the initial mass of the coal char, respectively. The maximum oxygen uncoupling  $m_o$  is the oxygen transport capacity  $R_{oc}$  ( $R_{oc} = (m_{ox} - m_{red})/m_{ox} \times 100$ ,  $m_{ox}$ : mass of the fully oxidized oxygen carrier;  $m_{red}$ : mass of the reduced oxygen carrier [4]).

For QMS data, the reactivities of the Cu-OC are evaluated based on changes in the number of moles of the gases produced. The oxygen uncoupling ( $X_o$ ) was determined by calculating the moles of oxygen generated by uncoupling and rate of the change is ( $dX_o/dt$ ).  $X_o$  is defined as follow:

$$X_o = \frac{n}{n_{max}} \quad (3)$$

where  $n$  is the moles of oxygen generated over the reaction time ( $t$ ) and  $n_{max}$  is the maximum moles of the oxygen generated.

In the coal char CLOU, the char reacted with gaseous oxygen released by heating Cu-OC and generated primarily  $CO_2$  and CO. The reactivity of the coal char was evaluated by calculating the carbon conversion efficiency ( $X_c$ ) and its rate ( $dX_c/dt$ ) based on the QMS data [5].  $X_c$  is defined as follows:

$$X_c = \frac{n_c}{n_0} = \frac{\sum_{t=0}^t F(y_{CO_2} + y_{CO})}{n_0} \quad (4)$$

where  $n_c$  is the moles of carbon in product gases such as  $CO_2$  and CO over the reaction time  $n_0$  is the moles of the carbon in the initial coal char sample;  $F$  is the gas flow rate; and  $y_i$  is volumetric concentrations of the carbon containing gas ( $i$ ).

A major purpose for developing coal CLOU is for  $CO_2$  emission control, so a primary goal of coal CLOU is to convert carbon to  $CO_2$ . In this study, the coal CLOU process performance was evaluated by calculating the  $CO_2$  conversion efficiency ( $Sc_{O_2}$ ) based on the QMS data [5].  $Sc_{O_2}$  is defined as follows:

$$Sc_{O_2} = \frac{n_{CO_2}}{n_t} \quad (5)$$

where  $n_{CO_2}$  and  $n_t$  are the total moles of accumulated carbon in  $CO_2$  and in the total carbon containing product gases over the reaction time ( $t$ ), respectively.

### 3. Results and Discussion

#### 3.1. Cu-OC Oxygen Uncoupling

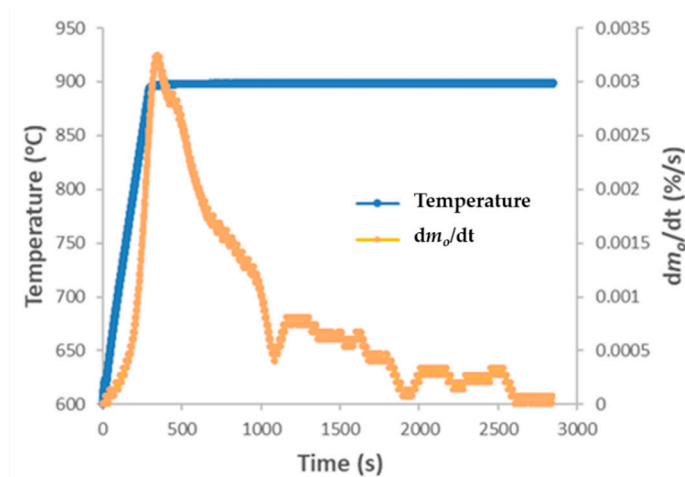
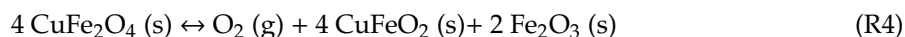
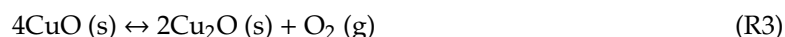
When the Cu-OC was heated over 600 °C, gaseous  $O_2$  was initially generated and detected by the QMS in the product gas and simultaneously a sample weight loss was detected by the TGA (Figures 3 and 4). When the temperature was increased over 820 °C, the gaseous  $O_2$  concentration and the oxygen uncoupling rate quickly increased with a maximum at 900 °C (Figures 3 and 4). These oxygen uncoupling behaviors of the Cu-OC were similar to those of pure CuO [5]. Based on the TGA data, the maximum oxygen uncoupling ( $R_{oc}$ ) and oxygen uncoupling rate were 3.3% and 0.0032%/s, respectively (Table 3). Table 3 summarizes the reactivities results of OC uncoupling and carbon conversion in reduction for the Cu-OC in this study and pure CuO from reference [5]. The oxygen uncoupling ( $R_{oc}$ ) was similar to the 4% oxygen uncoupling of 40 wt.% CuO with  $ZrO_2$  support OC synthesized by mechanical mixing followed by pelletizing by pressure [25].

**Table 3.** Oxygen capacity, carbon conversion efficiency, maximum conversion, and conversion rates and temperatures for Cu ore OC in Ar at 900 °C and pure CuO from reference [5].

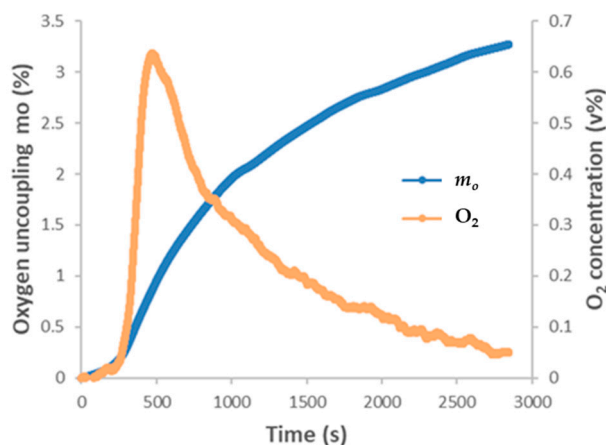
Sample	T (°C)	Oxygen Uncoupling			Carbon Conversion in Reduction				Test System
		$m_{o,max}$ $R_{oc}$ (%)	Tmax (°C)	$dX_o/dt_{max}$ (1/s)	$X_c$	$Sc_{O_2}$	Tmax (°C)	$dX_c/dt_{max}$ (1/s)	
Cu ore OC	900	3.3	900	0.0012					TGA-QMS
Pure CuO	850	10	850	0.0015					fixed bed-QMS
	950	10	922	0.0077					fixed bed-QMS
Cu ore OC/char	900				0.94	1	838	0.005	TGA-QMS
$\phi = 75$	900				0.95	1	835	0.006	fixed bed-QMS
Pure CuO/char	850				0.98	1	801	0.006	fixed bed-QMS
$\phi = 26$	950				0.99	1	833	0.011	fixed bed-QMS



The fresh Cu-OC consisted primarily of major amounts of CuO and intermediate amounts of  $\text{CuFe}_2\text{O}_4$  ( $\text{CuOFe}_2\text{O}_3$ ). CuO released gaseous  $\text{O}_2$  and was reduced to  $\text{Cu}_2\text{O}$  at temperatures above 600 °C (Reaction R3 [3]). XRD indicated that  $\text{Cu}_2\text{O}$  was generated and no CuO was detected in the residue of the Cu-OC oxygen uncoupling test.  $\text{CuFe}_2\text{O}_4$  decomposes to generate gaseous  $\text{O}_2$ , delafossite ( $\text{CuFeO}_2$ ), and  $\text{Fe}_2\text{O}_3$  (Reaction R4) [26]. The XRD analysis of this residue also showed that a Cu-Fe-O compound of  $\text{CuFeO}_2$  ( $\text{Cu}_2\text{OFe}_2\text{O}_3$ ) formed. The  $\text{Fe}_2\text{O}_3$  decreased and the  $\text{CuFe}_2\text{O}_4$  ( $\text{CuOFe}_2\text{O}_3$ ) phase changed (tetragonal to cubic) compared to the fresh Cu-OC (Table 2). So, some  $\text{CuFe}_2\text{O}_4$  in the Cu-OC decomposed and released  $\text{O}_2$  because  $\text{CuFe}_2\text{O}_4$  was detected by the XRD. Both CuO and  $\text{CuFe}_2\text{O}_4$  are active compounds in the Cu-OC. Zhao et al. studied a Cu-ore oxygen carrier with 21% CuO and reported both the CuO and  $\text{CuFe}_2\text{O}_4$  released gaseous  $\text{O}_2$  but the CuO released oxygen faster than the  $\text{CuFe}_2\text{O}_4$  [19].



**Figure 3.** The Cu-OC oxygen uncoupling rate ( $dm_o/dt$ ) and reaction temperature versus time at 900 °C in Ar in a TGA-QMS.



**Figure 4.** The Cu-OC oxygen uncoupling (TGA) and gaseous  $\text{O}_2$  concentrations (QMS) versus time at 900 °C in Ar in a TGA-QMS.

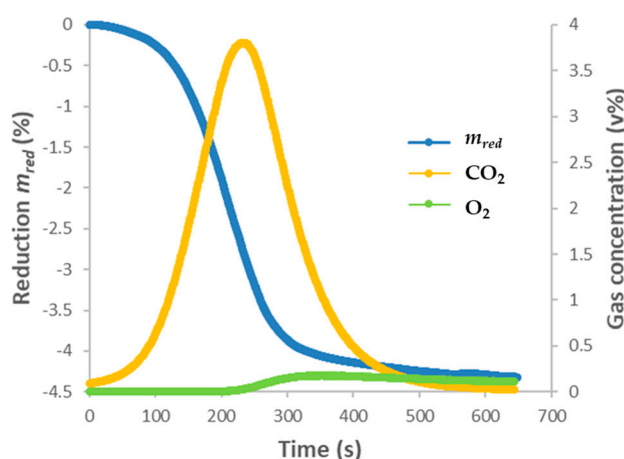
Based on simple stoichiometric calculations, the maximum oxygen uncoupling or oxygen transport capacity of pure CuO from oxygen uncoupling is 10 wt.% [2]. The equilibrium oxygen concentration at 900 °C is about 1.7 vol.% [3]. Comparing of the oxygen transport capacities of the Cu-OC with pure CuO, the Cu-OC was estimated to contain approximately 33% active CuO (releasing of gaseous  $\text{O}_2$ ) by

weight. The active CuO content in the Cu-OC was lower than the ideal CuO content from the material prepared from chalcopyrite. Based on reaction R1, the ideal CuO content should be ~40 wt.% CuO since 20% of the chalcopyrite consists of  $\text{SiO}_2$ . The reason for the lower active CuO is due to  $\text{CuFe}_2\text{O}_4$  formation from the CuO and  $\text{Fe}_2\text{O}_3$  reaction.  $\text{CuFe}_2\text{O}_4$  in the tetragonal phase was detected by XRD in the fresh Cu-OC.  $\text{CuFe}_2\text{O}_4$  in the cubic phase was detected in the Cu-OC after the uncoupling based on XRD. Some  $\text{CuFe}_2\text{O}_4$  decomposed and released  $\text{O}_2$ , which also was from the CuO in  $\text{CuFe}_2\text{O}_4$  (Reaction R4) [26].

Based on the QMS data, the maximum oxygen concentration and the oxygen uncoupling rate ( $dX_o/dt$ ) were 0.68 vol.% (Figure 4) and  $0.0012 \text{ s}^{-1}$  at  $T_{\text{max}}$  of  $900^\circ\text{C}$ , respectively (Table 3). The pure CuO oxygen uncoupling rates tested in a fixed bed reactor were  $0.0015 \text{ s}^{-1}$  at  $T_{\text{max}}$  of  $850^\circ\text{C}$  and  $0.0077 \text{ s}^{-1}$  at  $T_{\text{max}}$  of  $922^\circ\text{C}$  for the tests at test temperatures of  $850^\circ\text{C}$  and  $950^\circ\text{C}$ , respectively (Table 3) [5]. The Cu-OC oxygen uncoupling rate at  $950^\circ\text{C}$  was close to the value for pure CuO at  $850^\circ\text{C}$  and lower than pure CuO at  $950^\circ\text{C}$ . Both CuO concentration and temperature affected the oxygen uncoupling rate.

### 3.2. Reduction and Reoxidization of Cu-OC with Coal Char

The mixture of Cu-OC and char with  $\phi = 75$  was evaluated through a redox cycle test of reduction in Ar then reoxidation in air at  $900^\circ\text{C}$ . When the Cu-OC and char were heated above  $600^\circ\text{C}$ ,  $\text{CO}_2$  was generated and detected by the QMS in the product gas and, simultaneously, a sample weight loss was detected by the TGA (Figure 5). Char combustion took place because the Cu-OC began releasing  $\text{O}_2$  at  $\sim 600^\circ\text{C}$  from the Cu-OC oxygen uncoupling (Figures 3 and 4) (Reaction R3 and R4), which combusted the char (Reaction R2). The combustion had a peak at  $\sim 838^\circ\text{C}$ , which was close to the peak temperature ( $\sim 833^\circ\text{C}$ ) for the reaction of pure CuO and coal in a TGA under  $\text{N}_2$  [27]. The maximum combustion rate was  $0.028\%/s$  (Figure 6) and was eight times faster than the Cu-OC oxygen uncoupling rate (without char) because the combustion reaction (Reaction R2) consumed the oxygen from the Cu-OC uncoupling (Reaction R3 and R4) and increased the Cu-OC oxygen uncoupling rate. The final reduction  $m_{\text{red}}$  was 4.3% which was the same as the theoretical  $m_{\text{red}}$  4.3% based on the char being fully combusted to  $\text{CO}_2$  (Reaction R2) and gaseous oxygen being released from the Cu-OC. This means that the char was converted to  $\text{CO}_2$  in the reduction of Cu-OC with the char. The product gas was mainly  $\text{CO}_2$  with a trace amount of  $\text{O}_2$  detected by the QMS (Figure 5). The  $\text{CO}_2$  conversion efficiency  $S_{\text{CO}_2}$  was 1. The final carbon conversion efficiency  $X_c$  was 0.94 (theoretical  $X_c = 1$ ) and the maximum rate  $dX_c/dt$  was  $0.005 \text{ s}^{-1}$  based on the QMS data (Table 3).

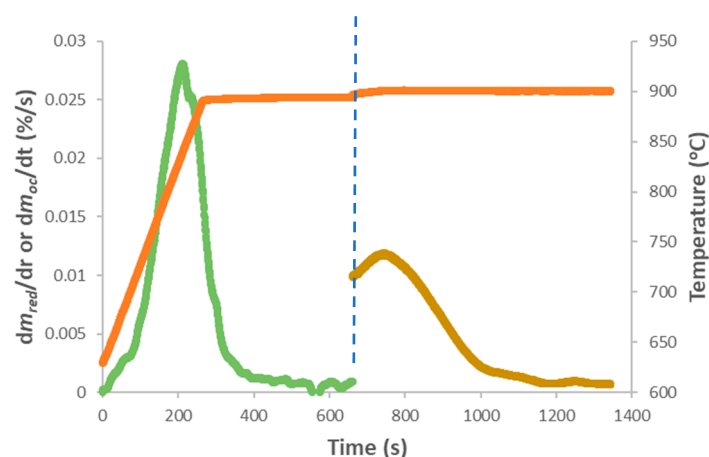


**Figure 5.** The reduction  $m_{\text{red}}$  of Cu-OC with coal char,  $\text{CO}_2$  and  $\text{O}_2$  concentrations (QMS) versus time in Ar at  $900^\circ\text{C}$  in a TGA-QMS.

The reduced Cu-OC was fully oxidized at  $900^\circ\text{C}$  in air. The final oxidation  $m_{\text{ox}}$  was 3.2% lower than the final  $m_{\text{red}}$  because of the  $m_{\text{ox}}$  and  $m_{\text{red}}$  calculations (Equations (1) and (2)). In the  $m_{\text{red}}$  calculation,  $m$  included both char and the Cu-OC. But for  $m_{\text{ox}}$ , only Cu-OC was counted in the reoxidation



calculation. The final  $m_{ox}$  was close to the theoretical  $m_{ox}$  3.0% based on the oxygen used to combust the char (Reaction R3) and the  $m_{ox}$  calculation (Equation (2)) including char in the sample weight. The slightly higher  $m_{ox}$  was due to extra  $O_2$  released during the reduction and this was also reoxidized. This additional oxidation was not included in the theoretical  $m_{ox}$ . The maximum oxidation rate was 0.012%/s, less than half the reduction rate of the OC with char (0.028%/s) (Figure 6). The temperatures during the reoxidation were slightly higher than during the reduction due to exothermal reoxidation (Reaction R3) (Figure 6).

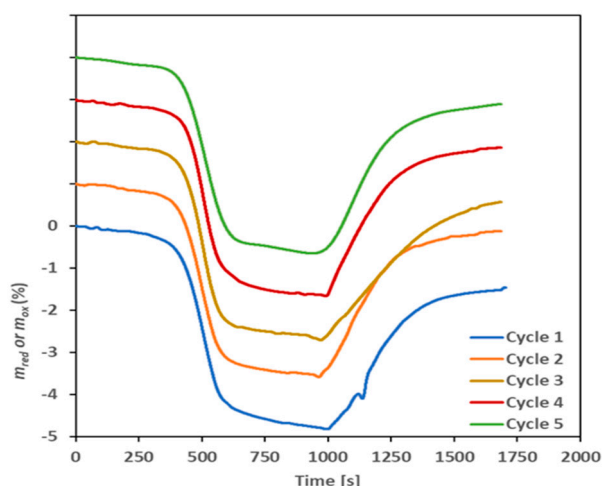


**Figure 6.** The reduction rate of Cu-OC with coal char in Ar ( $dm_{red}/dt$ ), reoxidation rate of reduced Cu-OC in air ( $dm_{ox}/dt$ ), and the reaction temperatures versus time at 900 °C in a TGA-QMS.

The Cu-OC reduced with the char primarily consisted of  $Cu_2O$  and  $CuFeO_2$  which were reoxidized to  $CuO$  and  $CuFe_2O_4$  (tetragonal and cubic phases) based on XRD analysis (Table 2). The experimental results were very close to the theoretical calculations based on active  $CuO$  uncoupling. For the Cu-OC,  $\phi = 75$  was used to fully combust the char to  $CO_2$ . For pure  $CuO$   $\phi = 26$  was selected [5]. Based on a comparison of the  $\phi$  of the Cu-OC with that of pure  $CuO$ , the Cu-OC was estimated to contain ~35% of active  $CuO$  by weight.

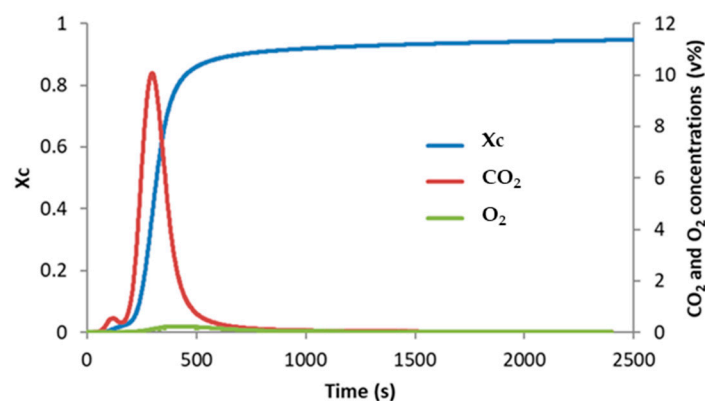
### 3.3. Recyclability of Cu-OC in Coal Char CLOU Tested in a TGA-QMS and Fixed-Bed Reactor-QMS

Figure 7 shows the reactivities of five cycles of a mixture of Cu-OC and coal char in Ar at 900 °C then oxidized in air at 900 °C. Fresh coal char was added to the oxidized OC, which also contained any residual coal ash, after each cycle. The reactivities and the rates for the reduction of Cu-OC with char were similar for all five cycles. For the reoxidation of the Cu-OC with char, the oxidation  $m_{ox}$  and the rates for cycles 2, 4, and 5 were similar but were slight lower for cycle 1 and 3 (Figure 7). This is due to slightly lower oxygen concentrations in the oxidation gas ( $O_2/Ar$ ) at beginning of the oxidation. Overall, the result indicates that the Cu-OC was stable during the five cycle tests.



**Figure 7.** The reactivities of the Cu-OC with coal char  $m_{red}$  in Ar and  $m_{oc}$  in air of five cycles versus time at 900 °C in a TGA-QMS.

The recyclability of the Cu-OC in coal char CLOU also was tested for five cycles in the fixed bed reactor using the same procedure that was used for the TGA tests. Figure 8 shows the carbon conversion efficiency  $X_c$  and generated  $CO_2$  concentration for the reduction of Cu-OC with coal char in one cycle of the five-cycle test. The  $CO_2$  conversion efficiency  $S_{CO_2}$  was 1 because the generated gas was mainly  $CO_2$  with little  $O_2$  and  $H_2O$ . There were two  $CO_2$  peaks, a very small peak around 600 °C and a large sharp peak around 835 °C. This was similar to the reduction test using pure CuO with PRB coal char at 950 °C, which had a small peak at ~670 °C and a large peak at 833 °C [5]. The small peak may be due to the small particle size fraction of the CuO that released oxygen at a lower temperature because a small peak at a lower temperature of 675 °C along with a large sharp were also observed in pure CuO oxygen uncoupling test in Ar. The carbon conversion efficiency  $X_c$  was 0.95, close to the theoretical  $X_c = 1$ , which means that the carbon in the coal char was close to complete conversion (Table 3). The carbon conversion rate  $dX_c/dt$  was  $0.006\text{ s}^{-1}$  (Table 3). The reaction rates of pure CuO with PRB coal char were  $0.006\text{ s}^{-1}$  and  $0.011\text{ s}^{-1}$  at test temperatures of 850 °C and 950 °C using the same fixed bed reactor-QMS (Table 3) [5]. For 40 wt.% CuO with  $Fe_2O_3$  and  $SiO_2$  OC synthesized by mechanical mixing followed by pelletizing by pressure at  $\phi = 67$ , the carbon conversion efficiency rate at 1000 °C was  $0.0077\text{ s}^{-1}$  [28] and close to the rate of the Cu-OC from the Cu-ore in this study



**Figure 8.** The carbon conversion efficiency  $X_c$  and generated  $CO_2$  concentration (v%) in the reduction of Cu-OC with coal char versus time in one cycle of the five-cycle test in a fixed bed reactor-QMS.

For the five-cycle test, the carbon conversion efficiency and carbon conversion rates were similar for all five cycles. The results from the fixed bed reactor were similar to the TGA results since both are the same type of reactor the carbon conversion  $X_c$  and rate  $dX_c/dt$  measured in TGA-QMS were

slight lower than in the fixed-bed reactor (Table 3) because sample in the fixed-bed reactor was heated faster than in the TGA. In the fixed-bed reactor, The fixed-bed reactor was preheated to 400 °C and had heating rate ~65 °C/min [5].

The BET surface areas of the fresh Cu-OC and the used Cu-OC after five cycles in the fixed bed reactor were 0.36 and 0.2 m<sup>2</sup>/g, respectively. Both the fresh and used Cu-OC had low surface areas. The fresh Cu-OC surface area in this study was close to the reported by Zhao et al. for a fresh OC prepared from natural copper ore (21 wt.% CuO) for CLOU, 0.217 m<sup>2</sup>/g [19]. Their used OC, after 10 h reduction/oxidation CLOU cycles with anthracite coal in a batch fluidized bed reactor, had a BET surface area of 0.115 m<sup>2</sup>/g. They explained the slight decrease in BET surface area of the used OC as being due to slight sintering of the OC particles or blockage of the pores and available surface area by the ash generated from coal CLOU, but the impact was very limited [19]. In this study, there was no significant agglomeration observed at 900 °C. After a redox cycle, the OC particles were very weakly bound together but easily loosened to powder again by light pressure. Tian et al. studied Cu ore OC with lignite coal in a batch-scale fluidized bed reactor at 950 °C for 10 cycles and observed a sintering problem in the later cycles [20]. In the future, higher temperatures will be tested to evaluate the sintering, agglomeration, or partial melting of the particles.

Natural ore has potential as a competitive oxygen carrier in solid fuel CLOU based on its reactivity as observed in this study. Based on extensive research on Fe-based OC for iG-CLC, the reactivity of mineral OC is typically lower than synthetic OC [4]. Research on the mineral Fe-OC is continuing because the mineral OC is inexpensive compared to the synthetic OC. For CLOU, a low-cost OC is even more important than iG-CLC because CLOU requires more OC to fully convert the fuels to CO<sub>2</sub> due to its low oxygen capacity. Moreover, low cost is preferred for solid fuel CLOU due to ash from fuel combustion that causes loss of OC reactivity and loss of OC with separation of the ash. Mineral Cu-based OC is much lower in cost than synthetic Cu-OC based on Cu material prices. Cu ore (copper concentrate with 20–30% Cu) costs approximately \$0.0695/lb [29], much cheaper than Cu metal at about \$2.8875/lb [30]. Cu powder is used to produce CuO by roasting it in air among other different CuO processes. Moreover, Cu-ores are abundant. Converting Cu-ore to an OC is a simple process as compared to production of a synthetic Cu-Fe OC which can require multiple steps and use many chemicals. Future investigation to increase the CuO content of mineral Cu-based OC and operating at higher temperatures could increase the reactivity and make it a more attractive OC. For commercial applications, further study of the long-term cyclic stability of the Cu-OCs with coal is required. Increasing the CuO content in the Cu-OC derived from natural copper ore is needed to increase oxygen transfer capacity and lower the ratio of Cu-OC to fuel to lower the operational cost of a future plant.

#### 4. Conclusions

This study investigated Cu-based OCs derived from natural minerals for solid fuel CLOU to potentially lower the OC cost. Chalcopyrite, which contains primarily CuFeS<sub>2</sub>, has potential as a Cu-OC resource. It is one of the primary ores of copper, so is readily available. The Cu-OC used in this study was prepared by simply heating ground chalcopyrite in air 900 °C to remove the sulfur. The prepared Cu-OC consisted primarily of CuO and CuFe<sub>2</sub>O<sub>4</sub> (CuOFe<sub>2</sub>O<sub>3</sub>) from the XRD analysis and had oxygen uncoupling properties based on TGA-QMS testing. The oxygen transport capacity of Cu-OC was 3.3% from both CuO and CuFe<sub>2</sub>O<sub>4</sub> oxygen uncoupling. For the reduction of the Cu-OC with coal during CLOU at 900 °C in Ar, the coal char conversion efficiency  $X_c$  was 0.95 and the product gas was primarily CO<sub>2</sub> with trace O<sub>2</sub>. The Cu-OC showed high reactivity and cyclic stability in a five-cycle test. Therefore, the natural ore has potential as a competitive oxygen carrier in solid fuel CLOU based on its reactivity in this study. For commercial applications, further study of the long-term cyclic stability of the Cu-OC with coal is certainly required. Increasing the CuO content in the Cu-OC made from natural copper ore and increasing the reaction temperature are needed to improve the

oxygen transfer capacity and lower the ratio of Cu-OC to fuel to reduce the operational cost of a CLOU system.

**Author Contributions:** P.W. is the primary author of this article; B.H., N.M., D.S. and D.B. participated in materials preparation and characterizations, test system setup, discussions, and to the writing and editing of the manuscript.

**Funding:** This research was supported by the Department of Energy, National Energy Technology Laboratory.

**Acknowledgments:** Special thanks to Sittichar Natesakhawat for conducting sample BET surface analysis. Disclaimer: This report was prepared as an account of work sponsored by the Department of Energy, National Energy Technology Laboratory, an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

- Adanez, J.; Abad, A.; Mendiara, T.; Gayan, P.; de Diego, L.F.; Garcia-Labiano, F. Chemical looping combustion of solid fuels. *Prog. Energy Combust. Sci.* **2018**, *65*, 6–66. [\[CrossRef\]](#)
- Wang, P.; Means, N.; Shekhawat, D.; Berry, D.; Massoudi, M. Chemical-looping combustion and gasification of coals and oxygen carrier development: A brief review. *Energies* **2015**, *8*, 10605–10635. [\[CrossRef\]](#)
- Mattisson, T.; Lyngfelt, A.; Leion, H. Chemical-looping with oxygen uncoupling for combustion of solid fuels. *Int. J. Greenh. Gas Control* **2009**, *3*, 11–19. [\[CrossRef\]](#)
- Adanez, J.; Abad, A.; Garcia-Labiano, F.; Gayan, P.; de Diego, L.F. Progress in chemical-looping combustion and reforming technologies. *Prog. Energy Combust. Sci.* **2012**, *38*, 215–282. [\[CrossRef\]](#)
- Wang, P.; Means, N.; Howard, B.H.; Shekhawat, D.; Berry, D. The reactivity of cuo oxygen carrier and coal in chemical-looping with oxygen uncoupled (clou) and in-situ gasification chemical-looping combustion (ig-clc). *Fuel* **2018**, *217*, 642–649. [\[CrossRef\]](#)
- Adanez-Rubio, I.; Abad, A.; Gayan, P.; de Diego, L.F.; Garcia-Labiano, F.; Adanez, J. Performance of clou process in the combustion of different types of coal with co<sub>2</sub> capture. *Int. J. Greenh. Gas Control* **2013**, *12*, 430–440. [\[CrossRef\]](#)
- Abad, A.; Adanez-Rubio, I.; Gayan, P.; Garcia-Labiano, F.; de Diego, L.F.; Adanez, J. Demonstration of chemical-looping with oxygen uncoupling (clou) process in a 1.5 kw(th) continuously operating unit using a cu-based oxygen-carrier. *Int. J. Greenh. Gas Control* **2012**, *6*, 189–200. [\[CrossRef\]](#)
- Adanez-Rubio, I.; Abad, A.; Gayan, P.; de Diego, L.F.; Garcia-Labiano, F.; Adanez, J. Biomass combustion with co<sub>2</sub> capture by chemical looping with oxygen uncoupling (clou). *Fuel Process. Technol.* **2014**, *124*, 104–114. [\[CrossRef\]](#)
- Adanez-Rubio, I.; Arjmand, M.; Leion, H.; Gayan, P.; Abad, A.; Mattisson, T.; Lyngfelt, A. Investigation of combined supports for cu-based oxygen carriers for chemical-looping with oxygen uncoupling (clou). *Energy Fuels* **2013**, *27*, 3918–3927. [\[CrossRef\]](#)
- Azimi, G.; Leion, H.; Mattisson, T.; Ryden, M.; Snijders, F.; Lyngfelt, A. Mn-fe oxides with support of mgal<sub>2</sub>o<sub>4</sub>, ceo<sub>2</sub>, zro<sub>2</sub> and y<sub>2</sub>o<sub>3</sub>-zro<sub>2</sub> for chemical-looping combustion and chemical-looping with oxygen uncoupling. *Ind. Eng. Chem. Res.* **2014**, *53*, 10358–10365. [\[CrossRef\]](#)
- Pour, N.M.; Leion, H.; Ryden, M.; Mattisson, T. Combined cu/mn oxides as an oxygen carrier in chemical looping with oxygen uncoupling (clou). *Energy Fuels* **2013**, *27*, 6031–6039. [\[CrossRef\]](#)
- Adanez-Rubio, I.; Gayan, P.; Abad, A.; Garcia-Labiano, F.; de Diego, L.F.; Adanez, J. Kinetic analysis of a cu-based oxygen carrier: Relevance of temperature and oxygen partial pressure on reduction and oxidation reactions rates in chemical looping with oxygen uncoupling (clou). *Chem. Eng. J.* **2014**, *256*, 69–84. [\[CrossRef\]](#)
- Clayton, C.K.; Whitty, K.J. Measurement and modeling of decomposition kinetics for copper oxide-based chemical looping with oxygen uncoupling. *Appl. Energy* **2014**, *116*, 416–423. [\[CrossRef\]](#)

14. Peterson, S.B.; Konya, G.; Clayton, C.K.; Lewis, R.J.; Wilde, B.R.; Eyring, E.M.; Whitty, K.J. Characteristics and clou performance of a novel sio<sub>2</sub>-supported oxygen carrier prepared from cuo and beta-sic. *Energy Fuels* **2013**, *27*, 6040–6047. [CrossRef]
15. Hu, W.T.; Donat, F.; Scott, S.A.; Dennis, J.S. Kinetics of oxygen uncoupling of a copper based oxygen carrier. *Appl. Energy* **2016**, *161*, 92–100. [CrossRef]
16. Matzen, M.; Pinkerton, J.; Wang, X.M.; Demirel, Y. Use of natural ores as oxygen carriers in chemical looping combustion: A review. *Int. J. Greenh. Gas Control* **2017**, *65*, 1–14. [CrossRef]
17. Wang, K.; Tian, X.; Zhao, H.B. Sulfur behavior in chemical-looping combustion using a copper ore oxygen carrier. *Appl. Energy* **2016**, *166*, 84–95. [CrossRef]
18. Wang, K.; Zhao, H.B.; Tian, X.; Fang, Y.F.; Ma, J.C.; Zheng, C.G. Chemical-looping with oxygen uncoupling of different coals using copper ore as an oxygen carrier. *Energy Fuels* **2015**, *29*, 6625–6635. [CrossRef]
19. Zhao, H.B.; Wang, K.; Fang, Y.F.; Ma, J.C.; Mei, D.F.; Zheng, C.G. Characterization of natural copper ore as oxygen carrier in chemical-looping with oxygen uncoupling of anthracite. *Int. J. Greenh. Gas Control* **2014**, *22*, 154–164. [CrossRef]
20. Tian, X.; Zhao, H.B.; Wang, K.; Ma, J.C.; Zheng, C.G. Performance of cement decorated copper ore as oxygen carrier in chemical-looping with oxygen uncoupling. *Int. J. Greenh. Gas Control* **2015**, *41*, 210–218. [CrossRef]
21. Wen, Y.-Y.; Li, Z.-S.; Xu, L.; Cai, N.-S. Experimental study of natural cu ore particles as oxygen carriers in chemical looping with oxygen uncoupling (clou). *Energy Fuels* **2012**, *26*, 3919–3927. [CrossRef]
22. Calcutt, V. Introduction to Copper: Mining & Extraction. Copper Development Association Inc., 2001. Available online: [https://www.copper.org/publications/newsletters/innovations/2001/08/intro\\_mae.html](https://www.copper.org/publications/newsletters/innovations/2001/08/intro_mae.html) (accessed on 12 October 2018).
23. Baba, A.A.; Ayinla, K.I.; Adekola, F.A.; Ghosh, M.K.; Ayanda, O.S.; Bale, R.B.; Sheik, A.R.; Pradhan, S.R. A review on novel techniques for chalcopyrite ore processing. *Int. J. Min. Eng. Miner. Process.* **2012**, *1*, 1–16. [CrossRef]
24. Teck-Metals-Ltd. Andacollo Copper Concentrate Safety Data Sheet. 2015. Available online: <https://www.teck.com/media/Andacollo-Copper-Concentrate-SDS.pdf> (accessed on 10 September 2018).
25. Gayan, P.; Adanez-Rubio, I.; Abad, A.; de Diego, L.F.; Garcia-Labiano, F.; Adanez, J. Development of cu-based oxygen carriers for chemical-looping with oxygen uncoupling (clou) process. *Fuel* **2012**, *96*, 226–238. [CrossRef]
26. Wang, B.; Yan, R.; Zhao, H.; Zheng, Y.; Liu, Z.; Zheng, C. Investigation of chemical looping combustion of coal with cufe<sub>2</sub>o<sub>4</sub> oxygen carrier. *Energy Fuels* **2011**, *25*, 3344–3354. [CrossRef]
27. Cao, Y.; Pan, W.-P. Investigation of chemical looping combustion by solid fuels. 1. Process analysis. *Energy Fuels* **2006**, *20*, 1836–1844. [CrossRef]
28. Wang, P.; Howard, B.H.; Means, N.; Shekhawat, D. Bimetallic cu-fe Oxygen Carriers for Coal Chemical-Looping Combustion. In Proceedings of the 255th American Chemical Society National Meeting & Exposition, New Orleans, LA, USA, 18–22 March 2018.
29. Fastmarkets-MB. Copper Concentrate tc/rcs Decline Further as Traders Bid Aggressively for Tonnes. 2018. Available online: <https://www.metalbulletin.com/Article/3787933/Copper-concentrate-TCRCs-decline-further-as-traders-bid-aggressively-for-tonnes.html> (accessed on 9 March 2019).
30. Fastmarkets-MB. LIVE Futures Report 08/03: Comex Copper Price Suffers Further Losses in Final Session. 2018. Available online: <https://www.metalbulletin.com/Article/3863299/LIVE-FUTURES-REPORT-0803-Comex-copper-price-suffers-further-losses-in-final-session.html> (accessed on 10 March 2019).

