

## Fate of sulfur in chemical looping combustion of gaseous fuels using a copper-based oxygen carrier

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### ABSTRACT

The development of the chemical looping combustion technology for gaseous fuels has reached a point where it has been demonstrated in several pilot units for several thousands of hours using a variety of oxygen carriers. So far, a lot of experimental work was focused on fuel conversion performance and life time of oxygen carrier particles. In addition to the general performance of an oxygen carrier regarding fuel conversion, it is of special interest how it interacts with fuel impurities or contaminants like sulfur. Here, it is not only of interest if and how impurities affect fuel conversion performance, but also in which composition and in which reactor stream (air reactor or fuel reactor) they leave the CLC system. This knowledge is of great importance when it comes to the requirements of exhaust gas treatment facilities in large scale units.

In the present study, the fate of sulfur in chemical looping combustion has been investigated in a 120 kW<sub>th</sub> pilot unit consisting of two interconnected circulating fluidized beds using a copper based oxygen carrier prepared by impregnation on an inert alumina support. Natural gas from the grid, originally without sulfur, was used as fuel. To investigate the influence of sulfur, H<sub>2</sub>S has been added to the fuel stream up to a concentration of 2000 ppmv. In order to close the mass balance of sulfur, the exhaust gas streams of air and fuel reactor are analyzed against H<sub>2</sub>S and SO<sub>2</sub>. Further, solid samples of the oxygen carrier particles were taken on a regular basis to investigate potential interaction of sulfur with the particles.

The contribution shows how sulfur affects the general fuel conversion performance of the oxygen carrier as well as how much H<sub>2</sub>S is converted to SO<sub>2</sub> and in which exhaust gas stream it leaves the reactor system. Measurements were performed for several temperatures in the range of 800–850 °C.

### 1. Introduction

Chemical Looping Combustion (CLC) represents a sustainable and innovative combustion technology with a great potential to inherently capture CO<sub>2</sub> from the flue gas. The energy intensive gas/gas separation step is not needed and thereby results in a reduction of costs and energy penalties in an industrial application. The steadily expanding knowledge on CLC gained by the continuously growing community (Lyngfelt, 2011) leads to a constant increasing number of lab scale and pilot scale reactor systems. Today there are a number of publications, investigating different of oxygen carriers (OC) under specific conditions within these reactor systems. By now chemical looping combustion has proven to be a robust and effective technology. Further effects of fuel pollutants, such as SO<sub>2</sub>, NO<sub>x</sub> or higher hydrocarbons, are of great interest and there are a few studies with thermodynamic analysis of impurity impacts on metal oxides. It is noted that only little literature is available, which study the reaction behavior in a CLC reactor system on this subject (Adánez et al., 2012).

Table 1 shows an overview of published literature focused on adsorption behavior of fuel impurities such as sulfur or nitrogen of different metal oxide materials with relevance to the current study. To our knowledge, this is the first experimental work carried out with a copper-alumina based material and sulfur impurities under relevant CLC conditions.

Without taking into account the singularity of different oxygen carriers, general changes in performance and life time of OC particles with sulfurous fuel impurities are rather sparsely illuminated. Comparable results were obtained by Penthor et al. (2014b) by examining the effect of nitrogen in the CLC process using a nickel-based oxygen carrier.

From an operational point of view, the sulfur compounds may react with the active metal oxide to form metal sulfides and sulfates that are poisonous to the oxygen-carrier and decreasing their reactivity. This process is especially important when Ni-based oxygen-carriers are used (Díaz-Castro et al., 2012). The degree of conversion from H<sub>2</sub>S to SO<sub>2</sub> is enhanced at high temperatures and low pressures. Both SO<sub>2</sub> and H<sub>2</sub>S

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Nomenclature		XRD	X-ray diffraction
<i>Abbreviations</i>		<i>Symbols</i>	
AR	Air reactor	$m_{\text{tot}}$	Total solids inventory of the pilot plant [kg]
CLC	Chemical looping combustion	$\dot{n}_i$	Molar flow of species $i$ [mol/s]
DCFB	Dual circulating fluidized bed	$P_{\text{th}}$	Fuel power input based on the lower heating value [W]
DFB	Dual fluidized bed	$T_{\text{FR}}$	Fuel reactor temperature [°C]
EDS	X-ray spectroscopy	$X_{\text{CH}_4}$	Methane conversion [–]
FB	Fixed bed	$Y_{\text{H}_2\text{S,FR,feed}}$	$\text{H}_2\text{S}$ molar concentration in the fuel reactor feed [mol/mol]
FR	Fuel reactor	$Y_{\text{CH}_4,\text{FR,exh}}$	$\text{CH}_4$ molar concentration in the fuel reactor exhaust [mol/mol]
FTB	Fire tube burner	$Y_{\text{H}_2\text{S,FR,exh}}$	$\text{H}_2\text{S}$ molar concentration in the fuel reactor exhaust [mol/mol]
LLS	Lower loop seal	$\gamma_{\text{CO}_2}$	$\text{CO}_2$ -yield [–]
OP	Operating point	$\lambda$	Air-to-fuel ratio [–]
SEM	Scanning electron microscope		
TGA	Thermo gravimetric analysis		
ULS	Upper loop seal		

Table 1

Published literature focused on adsorption behavior of different metal oxide materials.

OC material	Impurity	Concentr.	Fuel	$P_{\text{th}}$	Facility	Ref
CuO, $\gamma\text{-Al}_2\text{O}_3$	$\text{SO}_2$	2000 ppmv	$\text{CH}_4$	–	FB	Buelna and Lin (2004)
CuO, $\gamma\text{-Al}_2\text{O}_3$	$\text{H}_2\text{S}$	800–1300 ppmv	$\text{CH}_4$	0.5 kW	DFB	Forero et al. (2010)
CuO, $\gamma\text{-Al}_2\text{O}_3$	$\text{SO}_2$	10 000 ppmv	$\text{CH}_4$ , $\text{H}_2$	–	TGA	Deng and Lin (1996)
$\text{CuAl}_2\text{O}_4$ , $\text{Cu}_2\text{Ti}_2\text{O}_4$	$\text{H}_2\text{S}$	800 ppmv	$\text{H}_2$	–	TGA/FB	Pishahang et al. (2016)
$\text{FeTiO}_3$	S, N	–	Coal	71 kW	DFB	Linderholm et al. (2014)
CuO, $\text{CuFe}_2\text{O}_4$	$\text{H}_2\text{S}$	4000 ppmv	$\text{H}_2$	–	TGA	Wang et al. (2016)
NiO, $\text{MgAl}_2\text{O}_4$ , $\text{NiAl}_2\text{O}_4$	$\text{H}_2\text{S}$	48 56 ppmv	$\text{CH}_4$	110 kW	DFB	Díaz-Castro et al. (2012)
Ni, NiO, $\text{MgAl}_2\text{O}_4$ , $\text{NiAl}_2\text{O}_4$	$\text{H}_2\text{S}$	4100–16 000 ppmv	$\text{CH}_4$	120 kW	DFB	Penthor et al. (2014b)

could react with the copper based materials. Cu particles are used e.g. for hot gas cleaning in large-scale industrial production and showing potential benefits for desulfurization (Buelna and Lin, 2004; Pishahang et al., 2016).

The experiments, conducted in the present study, have the aim to quantify the effects on the process with different concentrations of sulfur added to the fuel feed of a 120 kW<sub>th</sub> CLC pilot unit.

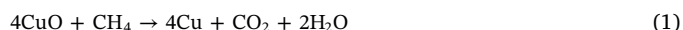
### 1.1. Sulfurization of a copper based oxygen carriers

The typical CLC system consists of two separated reactor units. The combustion step occurs in the fuel reactor (Fig. 1), where the oxygen carrier interact with the introduced fuel and is reduced from  $\text{MeO}_x$  to  $\text{MeO}_{x-1}$ . On the contrary, the oxidation step takes place in the air reactor (AR), where the OC reacts with the atmospheric oxygen. Leakages from the fuel reactor (FR) to the air reactor are prevented, thus no nitrogen is involved into the combustion step and only  $\text{CO}_2$  and  $\text{H}_2\text{O}$  exit the FR.

Among the typical OC materials, Ni, Cu, Fe or Mn (Adánez et al., 2012; Cho et al., 2004; Jerndal et al., 2009; Mayer et al., 2014) a copper-alumina based material is used in this work. Conventional fuels such as natural gas, refinery gas and coal contain variable amounts of sulfur. Usually natural gas contains a very low quantity of up to 20 ppmv  $\text{H}_2\text{S}$ , compared to coal, where the amount can diverge according to the origin up to 10 000 ppmv (Adánez et al., 2012). In various works the sulfurization and regeneration properties of copper-alumina sorbents were investigated for hot gas cleaning (Buelna and Lin, 2004; Deng and Lin, 1996; Pishahang et al., 2016) or in chemical looping combustion (Buelna and Lin, 2004). Among others, in Pishahang et al. (2016), a similar copper-alumina sorbent was used for hot gas cleaning of  $\text{H}_2\text{S}$  through chemical swing adsorption.

Using sulfur as a fuel impurity, different reactions may occur.

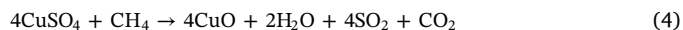
During CLC operation with  $\text{H}_2\text{S}$  impurities in the fuel feed, hydrogen sulfide has the affinity to form copper sulfide according to sulfurization reactions in the fuel reactor:



In the oxidizing atmosphere of the air reactor, the oxygen transforms copper sulfide to copper sulfate according to the following reaction:



Back in the FR the copper sulfate is reduced back to copper oxide and forms  $\text{SO}_2$ :



Furthermore, it is assumed that the sorption chemistry of CuO in the presence of  $\text{SO}_2$  follows the following main reaction routes (Buelna and Lin, 2004; Centi et al., 1992; Deng and Lin, 1996):

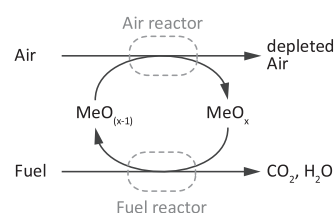


Fig. 1. Basic scheme of the chemical looping combustion process.

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