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## Oxy-co-firing in fluidized beds: control of sulfur emissions and assessment of corrosion issues

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### Abstract

The main objective of this work is to experimentally analyse the effect of firing blends of coal and biomass in oxy-firing atmospheres on SO<sub>2</sub> emissions and deposition/corrosion issues. The research has been conducted in a lab-scale fluidized bed unit, and chemical reactivity of deposited species has been simulated at bench scale.

Two very different Spanish coals were selected for the oxy-combustion experiments: anthracite, with a very low volatile matter, and lignite with high sulphur content. As concerns the biomass, a short campaign was conducted with forest residues, but most effort was done firing corn stover (with three different chlorine levels). The experimental matrix was designed to analyse the effects of the following parameters: atmosphere (air vs. O<sub>2</sub>/CO<sub>2</sub>), coal-to-biomass ratio in the blend (90/10% vs. 80/20%) and bed temperature (850-900°C).

Control of SO<sub>2</sub> emissions was largely dependent on the governing desulfurization mechanism, while chlorine in the biomass plays a role in the condensed alkali sulfates. No significant deposition rates were detected even for the higher biomass shares in the blend (20%). Only when corn stover with the highest chlorine content (2%) was fired, a thick deposition scale was found. For the original corn stover, oxy-firing barely affects the deposition rate and slightly reduces the corrosion risk in comparison to conventional air-firing.

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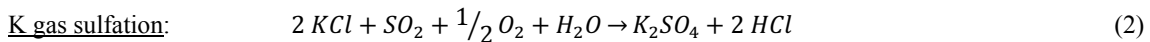
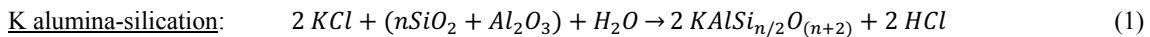
**Keywords:** Oxy-combustion; Co-firing; Emissions; Corrosion

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## 1. Introduction

Oxy-fuel combustion has emerged in the last years as a feasible technology to capture CO<sub>2</sub> from the flue gas in power plants, then avoiding the emission to the atmosphere [1]. Its application to fluidized bed units offers additional advantages: wide fuel flexibility and low pollutant emissions. The use of biomass as fuel (Bio-CCS) is linked to the concept of negative emissions [2], but some operational problems have to be well addressed due to the specificities of biomass composition: alkalis and chlorine have an actual impact on heat transfer degradation due to fouling and on long-term damages by induced corrosion. The risk of corrosion is higher in the case of herbaceous biomass, because KCl from mineral matter volatilizes and then condensed onto heat exchanger surfaces [3]. These problems can be mitigated when co-firing coal and biomass, due to the interactions of the mineral matter of these fuels.

In co-combustion with coal, KCl can react with aluminosilicates in ash and with SO<sub>2</sub> in flue gas:



Then, HCl is released in the gas-phase as result of the KCl transformation and K<sub>2</sub>SO<sub>4</sub> is found in the deposits.

There a number of works reporting co-firing experiences in air-fired units, but few available so far as concerns oxy-fired plants. Hot corrosion due to fouling is expected to be particularly troublesome for oxy-fuel combustion schemes with high-temperature CO<sub>2</sub> recycling, where SO<sub>3</sub> partial pressures are considered threefold those found in conventional combustion [4], and alkali pyrosulphate is formed as in reaction (3).



The corrosion activity of potassium pyrosulphate is due to its high chemical activity towards metals and metal oxides, dissolving them to form alkali trisulfates [5]:



The mechanism of corrosion by trisulfates formation has been proposed as the cause of the metal loss found in corrosion studies in simulated oxy-fuel co-firing conditions [6], with resulting dissolution of protective oxidation scales and final metal loss. Possible retrofitting to oxy-firing of those existing power plants and new configurations such as CFB oxy-co-combustion need experimental data to evaluate the corrosion risk at 500°-560°C [7]. The novel approach is the use of potassium pyrosulfate as simulation of alkaline deposits in HCl and SO<sub>3</sub> rich flow gas as expected in oxy-co-combustion.

## 2. Experimental

### 2.1. Facility

The lab-scale experiments were run in CIRCE fluidized bed reactor (Figure 1): the reactor height is 2.5 m height with an inner diameter of 0.203. The facility can be operated under oxy-firing conditions, feeding O<sub>2</sub>/CO<sub>2</sub> mixtures from commercial gas canisters. Fuel is fed by regulated endless screws and bed temperature is controlled by four water-cooled probes. An air-cooled deposition probe (AISI304) was introduced at 80 cm over distributor to gather the deposits formed during the experiments. Probe temperature was controlled to resemble the performance of a heat exchanger tube in a boiler (450 °C).

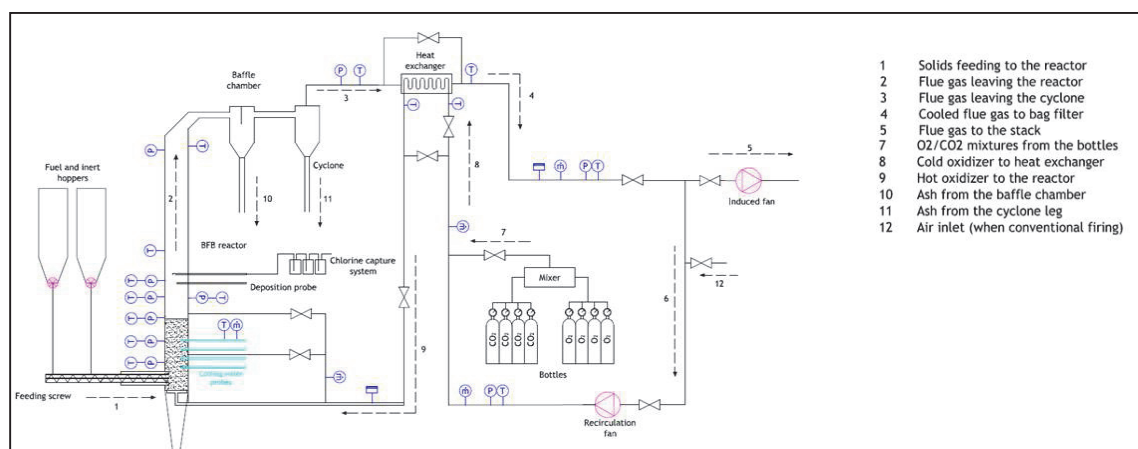


Figure 1.- Lab-scale fluidized bed facility.

## 2.2. Fuels

Anthracite and high sulfur lignite were studied. Biomass resource was corn stover with low Cl content (0.35% as received). The coal particle size ranged 0.3–1 mm, with a mean diameter of 0.7 mm. The corn stover was sieved between 1 and 2 mm. To study the influence of higher chlorine contents, part of the corn stover was doped with KCl. Then, three different contents were finally tested during the experiments: 0.35% (as received), 1% and 2%. In order to control SO<sub>2</sub> emissions, Granicarb limestone was added during the tests with different Ca:S ratios. Limestone mean size was 0.6 mm, as well as the size of the silica sand used as initial inert material in the bed. Table 1 summarizes the information concerning the fuels.

Table 1. Fuels used during the tests.

	Anthracite	Lignite	Corn Stover
<i>Proximate (%)</i>			
Moisture	2.42	13.57	6.18
Ash	31.30	30.30	5.50
Volatiles	6.71	25.72	70.68
Fixed carbon	59.57	30.41	17.64
<i>Ultimate (%)</i>			
C	59.27	40.53	43.3
H	2.01	3.18	5.82
N	0.91	0.28	0.57
S	1.58	6.65	0.11
Cl	–	–	0.35
LHV (kJ/kg)	21 620	14 434	15 438
<i>Ash by ICP (%)</i>			
Al <sub>2</sub> O <sub>3</sub>	24.78	26.01	1.36
CaO	2.83	3.27	8.72
Fe <sub>2</sub> O <sub>3</sub>	8.26	22.23	6.08
K <sub>2</sub> O	3.22	0.92	27.90
MgO	1.56	0.96	3.27
Na <sub>2</sub> O	0.70	0.12	0.22
SiO <sub>2</sub>	47.20	41.06	29.81
TiO <sub>2</sub>	0.99	0.76	0.80
P <sub>2</sub> O <sub>5</sub>	–	–	3.81
MnO <sub>2</sub>	–	–	0.14

### 2.3. Experimental matrix

Air and oxy-fired (30/70% O<sub>2</sub>/CO<sub>2</sub>) tests were completed, for a similar thermal input (around 20 kW<sub>th</sub>). The fuels were blended in 80/20% and 90/10% coal-to-biomass ratios (energy basis), firing three different corn stover samples. Two different Ca:S ratios were also tested (2.5 and 4) to change the availability of SO<sub>2</sub> in flue gas, on-line analyzed by a NDIR sensor, Table 2.

In this way, an ample range of initial elemental composition of inorganic elements is covered. This variation is described in terms of fuel-related indexes, widely used to predict the risk of deposition of alkali chlorides onto the heat transfer surfaces in combustion systems, Table 2. The S/Cl index relates the sulfur and chlorine contents; basic knowledge consider values must be over 4 for alkalis to be sulfated and then chlorine released to the gas-phase as HCl [8]. In the case of a fluidized bed reactor, this index should be reconsidered as that calculated taking into account that sorbent is usually added, and then sulfur availability is reduced. In our case, a modified S'/Cl index has been calculated, taking into account the desulfurization efficiencies.

Table 2. Experimental conditions.

Test #	Experimental			Fuel composition ratios		Deposit on probe (450°C)	Normalized composition of deposits					
	%Cl	Ca/S	mg SO <sub>2</sub> /Nm <sup>3</sup>	S/Cl	S'/Cl		Al'	K'	S'	Na'	Ca'	Cl'
An-A1	0.35	0	2453	14.65		Clean	-	-	-	-	-	-
An-A2	1	0	1822	5.02		Fouled	1	0.32	0.54	0.07	0.16	0
An-O1	1	0	2671	5.02		Fouled	1	1.37	0.85	0.47	0.28	0
An-O2	2	0	2153	<u>2.61</u>		Thick deposit	1	2.11	1.12	0.22	0.93	0.52
An-O3*	1	0	3101	11.35		Fouled (thin)	1	0.49	0.45	0.13	0.23	0
An-O4	0.35	2.5	590	14.65	<u>2.93</u>	Clean	-	-	-	-	-	-
An-O5	1	2.5	168	5.02	<u>1.00</u>	Fouled	1	0.63	0.77	0.14	0.66	0
Lig-A1	1	2.5	2207	31.57	10.78	Clean	-	-	-	-	-	-
Lig-O1	1	2.5	12155	31.57	12.10	Fouled	1	3.66	3.88	0	1.12	0
Lig-O2	2	2.5	11078	15.78	5.85	Fouled	1	11.5	7.52	0	1.85	0
Lig-O3*	1	2.5	13493	74.71	30.25	Fouled (thin)						
Lig-O4	0.35	4	9790	90.21	26.92	Fouled (thin)	1	0.91	0.67	0	0.77	0
Lig-O5	1	4	8671	31.57	9.01	Fouled (thin)						

An: Anthracite      Lig: Lignite

A: Air combustion      O: Oxy-fired combustion (30%O<sub>2</sub>/70%CO<sub>2</sub>)

\*: 10% biomass (the rest of the tests: 20% biomass)

% Cl: Cl in corn (% weight), as received and doped

Ca/S: molar ratio Ca (in limestone) to S (in coal)

mg SO<sub>2</sub>/Nm<sup>3</sup>: SO<sub>2</sub> concentration in flue gas

S/Cl: elemental ratio sulfur to chlorine in fuel blend, as indicative of K-sulfation

S'/Cl: elemental ratio sulfur to chlorine in fuel blend, corrected accounting for the desulfurization efficiency

Al', K', S', Na', Ca', Cl': elemental composition of probe deposits, normalized to Al in atomic basis

## 2.4. Deposits characterization

For each test, a new deposition probe was inserted and surface temperature controlled to 450°C. After two hour of stable operation, the deposition probe was removed and studied. The deposits obtained can be qualitatively classified into three types: (a) clean coupons; (b) thick deposition layer and corrosion scale; and (c) reddish loose fouling in the rest of the tests. This classification is presented in Table 2.

The composition and morphology of the deposits were studied by means of scanning electron microscopy (SEM) in a Hitachi S-3400N microscope equipped with a SDD-EDX detector Rontec XFlash, where the probe was studied as received. For most analysis in %wt elemental, Fe (part), Cr and Ni from SS310 probe material were detected, so a normalisation to Al content was performed to clarify composition. The normalised composition of surfaces is shown in Table 2.

## 3. Results

### 3.1. Sulfur emissions and deposition rates.

Obtained SO<sub>2</sub> emissions in oxy-combustion are higher compared to air combustion, both for anthracite experiments (An-A2 vs. An-O1) and for sorbent-added lignite experiments (Lig-A1 vs. Lig-O1). Direct sulfation conditions worsen desulfurization rates in comparison to indirect sulfation. In the present work, the relationship of SO<sub>2</sub> content in flue gas with chlorine content in the supplied fuels is studied along the experimental matrix, with the main findings following:

- An increase in % Cl in biomass involves a decrease of SO<sub>2</sub> concentration, for all the conditions studied: in air (comparing An-A1 with An-A2), in oxy-combustion (An-O1 vs. An-O2), and in experiments with sorbent addition (An-O4 vs. An-O5, Lig-O1 vs. Lig-O2, Lig-O4 vs Lig-O5), which confirms the reaction (2) of sulfation. In all the cases, this effect involves an increment in fouling in the deposition probe.
- Sulfation extent is determined by SO<sub>2</sub> availability: deposits on An-O1 probe are composed mainly by potassium sulfate, whereas its presence is lower in An-O5, due to the addition of limestone.
- Chlorine in deposits is only detected for test An-O2, which is in agreement with the S/Cl index. The semiquantitative composition indicates that the deposits are rich in KCl and calcium and potassium sulfates. On the contrary, chlorine is not found during tests An-O4 and An-O5, despite the value of the S<sup>o</sup>/Cl index is below 4.

### 3.2. Deposits characterization.

Deposits from An-O2 probe were removed by gently brushing and a sample of loose particles was obtained. It was analyzed by XRD: the assignation by JPDC confirmed the presence of KCl (8%wt sq) but unexpectedly indicated the absence of K<sub>2</sub>SO<sub>4</sub>. The main peaks detected were syngenite K<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub> (47%wt sq) and aphtalite K<sub>3</sub>Na(SO<sub>4</sub>)<sub>2</sub> (23%wt sq).

Under the external loose layer, the probe surface presented not-fused adhered condensed deposits whose nature was studied by SEM-EDX, see Figure 2. They consisted in condensed needle shaped crystals displayed in 30 μm layer as shown by SEM; EDX composition also shown in Figure 2 confirmed the presence of Ca in the initial deposits with K<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub> composition stoichiometry.

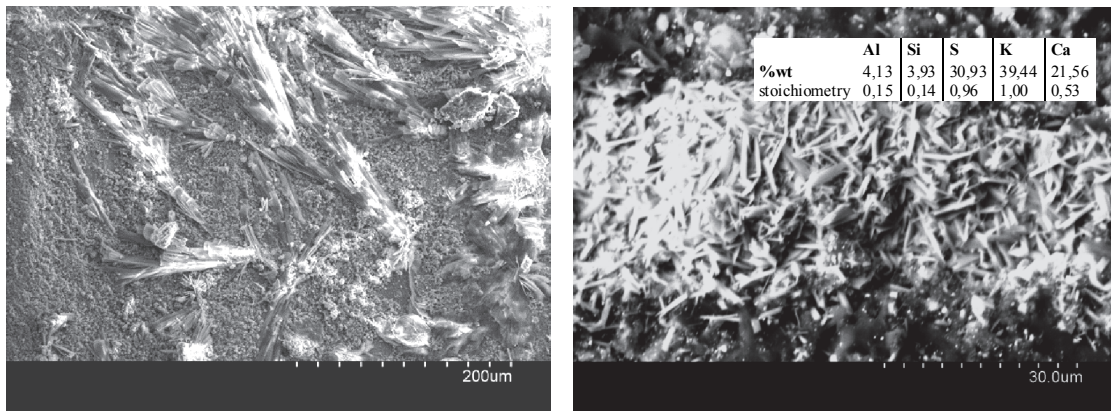


Figure 2.- SEM-EDX of (a) the probe surface under deposits in test Lig- O2, (c) cross-section of deposits and EDX composition

It is generally considered that alkali sulfates are formed in the gas-phase because molten alkali chlorides sulfation is too slow to play an important role on short time scales [10]. KCl aerosols are fast generated in particle combustion and sulfate with  $\text{SO}_2$  in the gas phase, with a mechanism of homogeneous nucleation as the source of alkali sulfate aerosols. On the other hand, the comparison of deposits formation as a function of S/Cl and S'/Cl for those experiments with added calcite as sulfur sorbent, confirms that the gas-phase sulfation is faster than gas-solid Ca-sorbent sulfation. The main finding is that KCl sulfation takes place in the bed dense phase where all the  $\text{SO}_2$  from fuel sulfur is available.

On the other hand, provided that sorbent was not added in test An-O2, calcium in deposits comes from the corn stover mineral matter, where it is finely dispersed as organically bounded or as oxalates in the organic matter. For the combustion temperatures, organic calcium can be transformed into CaO aerosols that may react with available  $\text{SO}_2$  and condense as alkali-alkaline earth double sulfates. In the present study, the formation of CaO aerosols which further sulfate in the vapour-phase is demonstrated; presence of mixed sulfates in deposits indicates co-nucleation of both sulphates as shown by the SEM images.

As mentioned above, the major risk of corrosion in oxy-combustion is the formation of metallic trisulfates following reactions (3) and (4) even at 500°C and 550°C [9]; for that, deposition of  $\text{K}_2\text{SO}_4$  would be the initiation stage. In the presence of CaO, the deposition of  $\text{K}_2\text{Ca}(\text{SO}_4)_2$  would hinder the formation of metallic trisulfates. These results indicate that the risk of hot corrosion by trisulfates can be minimised when burning coal with Cl-rich biomass due to their inherent organic Ca content. The confirmation of low chemical reactivity of syngenite with surface oxides is under study by the accelerated corrosion test proposed in [10].

## Conclusions

An experimental campaign was executed in a lab-scale fluidized bed reactor, oxy-firing blends of coal and biomass. A wide combination of experimental conditions was selected, as for the blends, the firing atmosphere, the chlorine content in the corn stover and the Ca:S molar ratio.

$\text{SO}_2$  emissions were mostly dependent on the desulfurization mechanisms: direct sulfation under oxy-combustion yields lower retention rates than indirect sulfation under air-firing. Molar ratio Ca:S=2.5 is considered adequate for anthracite tests, while Ca:S=4 is still low for lignite tests. The chlorine content supplied with the corn affects emissions, since alkali sulfation is proportionally detected.

Regarding corrosion issues, only a single test showed stubborn deposition and oxidation scale. This was consistent with the high chlorine content supplied. The rest of the oxy-fired tests showed a similar deposition rate and corrosion extent than the observed under air-firing. In consequence, no major corrosion concerns could be expected when shifting from air to oxy-fired conditions.

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