

# Carbonation of Coal Ash under Oxy-fuel Combustion Conditions

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## INTRODUCTION

Ash carbonation under oxy-fuel combustion conditions was reported by IFK (Institute of Combustion and Power Plant Technology) at the University of Stuttgart [1]. Studies by ALSTOM Power Inc. [2] on oxygen firing in circulating fluidized bed boilers showed that carbonation could occur at 871 °C when the CO<sub>2</sub> partial pressures were in the 0.6-0.7 atmosphere range, which caused poor fluidization and led to a pluggage in the cyclone. However, the mechanisms of ash carbonation in pulverized coal oxy-combustion has little been investigated, which may induce more severe fouling problems due to strength development in deposits.

This work aims to investigate the effects of water vapor and SO<sub>2</sub>, important flue gas constituents, on carbonation of two high-Ca coal ashes (especially CaO) in simulated oxy-coal combustion gases. Explanations for the observations are provided.

## EXPERIMENTAL

### 1. Fuel Properties

Two high-Ca coals (bituminous coal and sub-bituminous coal) were used. Their properties are shown in Table 1 & 2.

Table 1 Proximate and Ultimate analysis (wt%, ad)

	Proximate analysis				Ultimate analysis				
	Moisture	Volatiles Matter	Fixed Carbon	Ash	C	H	N	S	O (by diff.)
Coal A	6.41	30.52	55.67	7.40	45.72	3.84	0.81	2.94	32.88
Coal B	23.69	33.36	38.01	4.94	53.72	6.22	0.78	0.23	34.11

Table 2 Ash Composition (wt%)

	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	MnO	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	SiO <sub>2</sub>	Na <sub>2</sub> O	SO <sub>3</sub>	TiO <sub>2</sub>
Coal A	14.18	25.57	9.5	1.13	0.33	0.68	0.39	29.17	2.19	16.07	0.46
Coal B	14.78	22.19	5.2	5.17	0.01	1.07	0.35	30.46	1.94	8.83	1.3

### 2. Ash Generation

Ash samples were generated on a high-temperature drop tube furnace (DTF) under oxy-fuel combustion conditions: (1) 32vol%O<sub>2</sub>/68vol%CO<sub>2</sub>; (2) 1300 °C. Ash particles were cooled and diluted at a water-cooled sampling probe with N<sub>2</sub> injection at the tip. Samples were collected on glass-fiber filters.

### 3. Ash Carbonation

The carbonation tests were carried out at a horizontal tube reactor (HTR), as shown in Fig. 1. For each coal ash, carbonation tests were conducted under six different conditions, according to Table 3. The reaction temperature was 650 °C and the reaction time was 2 h.

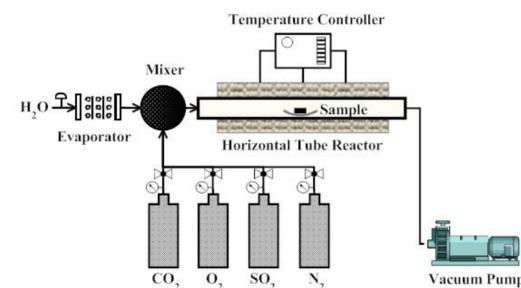


Table 3 Carbonation Conditions

Condition	Gas Composition (% Volume basis)					
	CO <sub>2</sub>	H <sub>2</sub> O	SO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	
HTR00	0	0			19	
HTR01	8	0			11	
HTR02	16	0			3	
HTR03	80	8	0.2	1	10.8	
HTR04	8	0.5			10.5	
HTR05	16	0.2			2.8	
HTR06	16	0.5			2.5	

Fig. 1. Combustor and sampling systems

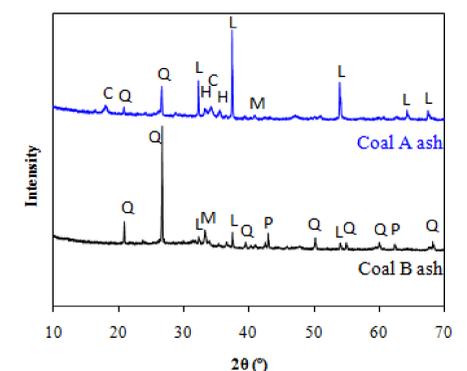
### 4. Sample Analysis

The coals and their DTF ashes were characterized by X-ray powder diffraction (XRD). X-ray photoelectron spectroscopy (XPS) was used to identify elements (especially carbon and sulfur) with different chemical states and electronic states. By XPS, the inorganic carbon (as carbonate) and the organic carbon can be readily distinguished. The molar ratios, C/Ca and S/Ca, were used to describe carbonation and sulfation, respectively.

## RESULTS & DISCUSSION

### Fig. 2 Key Results

- Coal A ash: mainly Lime and Quartz;
- Coal B ash: mainly quartz;
- Ca in Coal A ash is primarily present as lime (CaO) and some calcium hydroxide (Ca(OH)<sub>2</sub>) is also identified;
- However, only a small fraction of Ca occurs as lime in Coal B ash. Most of Ca is likely present as amorphous Ca-containing silicates. Some periclase (MgO) is detected.

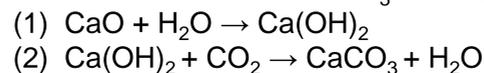


C – Calcium hydroxide; H – Hematite; L – Lime; M – Mullite; P – Periclase; Q – Quartz

Fig. 2. XRD spectra of DTF ashes

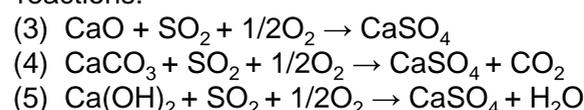
### Fig. 3 Key Results

- Longer reaction time leads to a higher carbonation (comparing DTF (~1s) and HTR00 (2 h));
- The presence of H<sub>2</sub>O tends to enhance ash carbonation, and ash carbonation increases with increasing H<sub>2</sub>O concentration. This is attributed to the formation of the transient species Ca(OH)<sub>2</sub> in the system, so that the conversion of CaO to CaCO<sub>3</sub> is accelerated.



### Figs. 4 & 5 Key Results

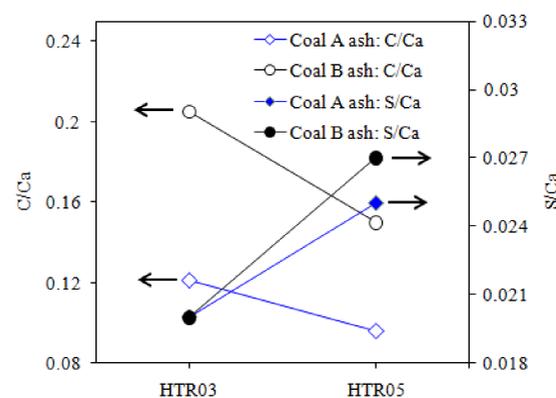
- The presence of SO<sub>2</sub> enhances sulfation while suppresses carbonation. With increasing the SO<sub>2</sub> concentration, sulfation increases while carbonation decreases.
- The observations are attributed to the following three reactions:



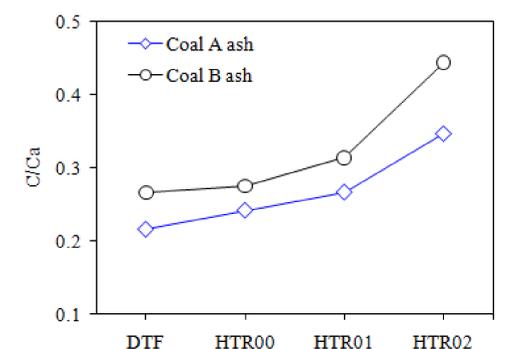
- Due to the above reactions, SO<sub>2</sub> competes with CO<sub>2</sub> for free CaO in coal ash, leading to increase in sulfation while decrease in carbonation.

### Fig. 6 Key Results

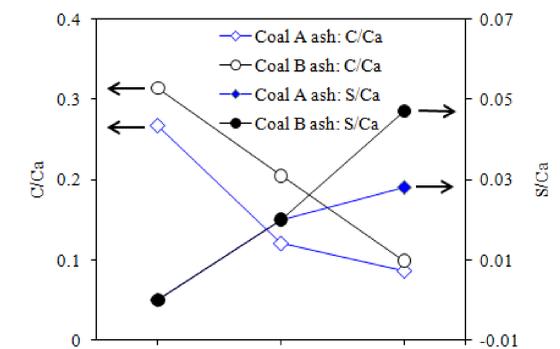
- H<sub>2</sub>O also has important effects on sulfation. At the same SO<sub>2</sub> concentration (0.2%), increasing H<sub>2</sub>O enhances sulfation, resulting in a decrease in carbonation. It is proposed that Reactions (1) and (5) play important roles.



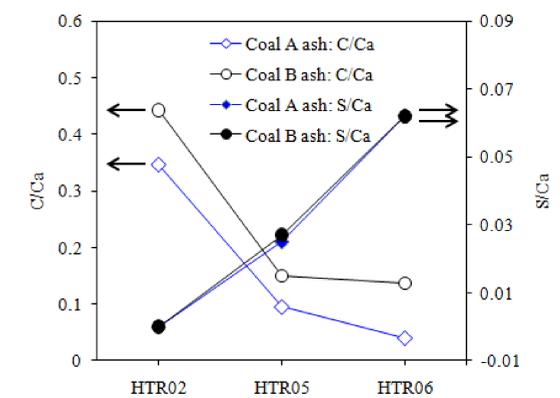
HTR03: 8% H<sub>2</sub>O; HTR05: 16% H<sub>2</sub>O  
Fig. 6. Effects of H<sub>2</sub>O on carbonation and sulfation at 0.2% SO<sub>2</sub>



HTR00: 0% H<sub>2</sub>O; HTR01: 8% H<sub>2</sub>O; HTR02: 16% H<sub>2</sub>O  
Fig. 3. Effects of H<sub>2</sub>O on carbonation without the presence of SO<sub>2</sub>



HTR01: 0% SO<sub>2</sub>; HTR03: 0.2% SO<sub>2</sub>; HTR04: 0.5% SO<sub>2</sub>  
Fig. 4. Effects of SO<sub>2</sub> on carbonation and sulfation at 8% H<sub>2</sub>O



HTR02: 0% SO<sub>2</sub>; HTR05: 0.2% SO<sub>2</sub>; HTR06: 0.5% SO<sub>2</sub>  
Fig. 5. Effects of SO<sub>2</sub> on carbonation and sulfation at 16% H<sub>2</sub>O

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