The Utilization of Dry Scrubber Materials for the Production of Calcium Sulfoaluminate Clinkers and Cements

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ABSTRACT:

Dry and wet scrubber flue gas desulfurization (FGD) systems are used to reduce SO_2 emissions in power plants. While the by-products from wet scrubber (FGD gypsum) are widely used in various applications, dry scrubber materials (DSMs) are not, due to the high content of calcium sulfite. This paper summarizes the use of DSMs in calcium sulfoaluminate (CSA) clinker fabrication, and the mechanical performances of the CSA cements. Two types of CSA clinkers are considered: 1- CSA clinker mainly composed of Klein's compound ($C_4A_3\acute{S}$); 2- CSA-belite clinker closely similar to a commercial CSA clinker. The main goals of this study were to use as much DSMs as possible as a source of sulfate for the synthesis of Klein's compound, and obtain a CSA cement made from DSMs to exhibit compressive strength as close as possible to a commercial CSA cement. Three DSMs originating from different plants are used for the production of CSA clinkers, and compared with a CSA clinker made exclusively from reagent chemicals. Both types of CSA clinkers were successfully produced from DSMs. Regarding the mechanical performances, the best CSA clinker exhibited compressive strengths of 26.5 and 30.4 MPa, after 2 hours and 4 hours, respectively. Regarding the CSA-belite clinker, the optimal formulation exhibited strengths of 8.3 MPa after 4 hours, and 39.3 MPa after 1 day. The takeaway from this study is that FGD gypsum can successfully be replaced by DSMs as a source of sulfate for the production of CSA clinkers.

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1. Introduction

Scrubber systems are by definition air pollution control equipment used to remove particulates and/or gases from industrial exhaust streams, such as coal fired power plants, including NOx, SO_2, SO_3, CO_2 gases, hydrochloric acid (HCl), ammonia (NH_3), mercury, etc. Wet and dry (or semi-dry) scrubber flue gas desulfurization (FGD) systems are the two main ways to scrub pollutants out of exhaust to reduce SO_2 emissions in power plants.

Wet scrubbing was the original type of scrubbing system, where the flue gas is scrubbed with a 5-15 wt.% slurry of calcium sulfite/sulfate salts along with calcium hydroxide or limestone. This slurry is sprayed into an absorber tower and the SO_2 is absorbed into the droplets of slurry, and form calcium sulfite hemihydrate (hannebachite) which is converted to calcium sulfate dihydrate, or FGD gypsum with addition of oxygen. This by-product is used in agriculture, wallboard, blended cement, mining applications, and other. [1]

Dry scrubbers are the second most widely used method to control SO_2 emissions in power plants. This alternative to wet scrubbers require less equipment, less capital cost, less space, and no waste water treatment needed. Lime (CaO) or hydrated lime ($Ca(OH)_2$) are used for the dry (or semi-dry) substance. The by-products is a mixture of calcium sulfite hemihydrate and calcium sulfate dihydrate, as only 25 % of calcium reacts to form calcium sulfate. [2] This dry scrubber material (DSM), as opposed to FGD gypsum, is not much utilized.

Several researchers have investigated the influence of these by-products on setting of OPC cement [3, 4], finding a maximum replacement rate of calcium sulfite hemihydrate to calcium sulfate dihydrate in OPC without modifying the mechanical properties. Another suggestion for the reuse of calcium sulfite hemihydrate is as a raw material for the production of calcium sulfoaluminate (CSA) cements. Due to its special clinker composition, the variety of raw materials needed for the production of CSA clinker can be wide, and calcium sulfite hemihydrate would be an excellent source of sulfate in place of FGD gypsum.

The goal of this work was to produce a CSA clinker by using as much DSMs as possible as a source of sulfate, and study the mechanical properties of these CSA cements. Three DSMs originating from different plants are used for the production of CSA clinkers, and are compared with a CSA clinker made exclusively from reagent chemicals. Two types of CSA clinkers were considered: 1- CSA clinker mainly composed of Klein's compound ($C_4A_3\acute{S}$); and 2- CSA-belite clinker closely similar to a commercial CSA clinker. The compressive strength of both of our CSA cements will be compared to a commercial CSA cement.

2. Raw Materials and Clinker Compositions

2.1. Materials

The materials used for this project are:

- Three different DSMs retrieved from three different plants, called DSM-1, DSM-2, and DSM-3;

- Two different bauxite from two different sources, called Bauxite-G and Bauxite-S;
- Flue gas desulfurization (FGD) gypsum;
- Ultrafine limestone;
- Reagent chemicals: calcium hydroxide, hemihydrate, and aluminum hydroxide.

The chemical compositions of all the materials, except the reagent chemicals, are presented in Table 1.

All three DSMs contain anhydrite ($CaSO_4$), portlandite ($Ca(OH)_2$), bassanite ($CaSO_4.1/2H_2O$), and hannebachite ($CaSO_3.1/2H_2O$), with the exception of DSM-3 which contains only anhydrite and portlandite as major phases.

Table 1: Major oxide composition of the three DSMs, calcium carbonate, FGD gypsum, and the two bauxites. (M = moisture, FL = free lime, S = sulfite, all in wt.%; n.d. means not determined)

In wt.%	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	TiO_2	LOI	M	FL	S
DSM-1	43.18	0.76	1.72	0.64	51.72	0.46	<0.1	3.87	1.15	0.11	21.0
DSM-2	47.97	0.93	1.69	0.55	47.96	0.5	<0.1	15.11	0.76	0.92	18.7
DSM-3	53.62	<0.1	1.85	0.61	34.09	0.69	<0.1	3.15	0.06	16.72	2.20
$CaCO_3$	54.11	0.07	0.11	0.32	0.06	0.53	0.06	44.15	n.d.	n.d.	n.d.
FGD gypsum	32.31	1.03	0.22	0.08	45.86	0.17	0.08	20.78	n.d.	n.d.	n.d.
Bauxite-S	0.27	8.09	54.92	5.08	0.49	0.03	1.84	28.89	n.d.	n.d.	n.d.
Bauxite-G	1.25	13.05	54.42	1.04	0.19	0.02	2.42	27.44	n.d.	n.d.	n.d.

2.2. Clinker Compositions and Characterization

Two kinds of CSA clinkers have been formulated, one with high purity Klein's compound (CSA-0, CSA-1, CSA-2, and CSA-3), and another containing 60-65 wt.% $C_4A_3\acute{S}$ and 15-25 wt.% C_2S (CSA-S and CSA-G) similar to a commercial CSA clinker. CSA-0 was produced from only reagent chemicals, while CSA-1, CSA-2, and CSA-3 were produced from limestone, DSMs, and aluminum hydroxide. The influence of each DSM on the formation of high purity CSA clinker will be assessed. CSA-S and CSA-G are belite-CSA clinkers made from limestone, FGD-Gypsum for CSA-S, DSM-2 for CSA-G, and the two bauxites as a source of alumina.

The raw materials for each composition, as presented in Table 2, were mixed together in a mortar and pestle with 10 wt.% of deionized water and pressed into disks under 25000 lbs, and dried at 60°C for a few hours. The disks were fired following this procedure: 1) from room temperature to 800°C at 7.5°C/min; 2) 800°C for 30 minutes; 3) from 800°C to 1250°C at 5.0°C/min; 4) 1250°C for 60 or 120 minutes depending on the composition; and 5) quench rapidly in air. Following the firing process, all compositions were ground in a ball mill. XRD/Rietveld analyses were performed on the final clinkers and the results are presented in Table 3. CSA-0, CSA-1, CSA-2, and CSA-3 clinker are highly pure Klein's compounds (above 90-95 wt.%) with small amount of anhydrite, and traces of free lime. CSA-S and CSA-G contain 69-72 wt.% Klein's compound, 16-21 wt.% belite (C_2S), and small amounts of tricalcium aluminate (C_3A) and brownmillerite (C_4AF). No or traces of free lime have been detected, confirming that the firing procedure was optimal for the production of all clinkers.

Table 2: Raw materials needed for each composition of CSA clinkers.

Compositions (in wt.%)		$Al(OH)_3$	$Ca(OH)_2$	$CaSO_4.1/2 H_2O$	Limestone ($CaCO_3$)	DSM-1	DSM-2	DSM-3	FGD Gypsum	Bauxite-S	Bauxite-G
CSA clinkers High purity Klein's compound	**CSA-0**	54.3	25.8	20	-	-	-	-	-	-	-
	CSA-1	47	-	-	30	23	-	-	-	-	-
	CSA-2	46	-	-	26	-	28	-	-	-	-
	CSA-3	48.7	-	-	13.7	-	-	37.7	-	-	-
Belite-CSA clinkers	**CSA-S**	-	-	-	40.5	-	-	-	17.5	42	-
	CSA-G	-	-	-	37.3	-	22.1	-	-	-	40.6

Table 3: XRD/Rietveld analyses of high purity CSA clinkers and belite-CSA clinkers

Compositions	C_3S	C_2S	$C_4A_3\acute{S}$	C_4AF	$C\acute{S}$	C_3A	Free Lime
CSA-0	High purity $C_4A_3\acute{S}$ (>90-95 wt.%), with small amounts of $C\acute{S}$, and traces of free lime.						
CSA-1							
CSA-2							
CSA-3							
CSA-S	0.3	16.9	71.8	3.0	1.8	5.7	-
CSA-G	0.5	20.1	69.8	3.0	0.9	5.2	0.2

3. Mechanical Properties

3.1. Methods

Set times and compressive strength tests followed ASTM C191 [5] and ASTM C109 [6], respectively. Some modifications to these ASTMs were performed. An amount of 500g of cement (CSA clinker with gypsum) was used with 1375g of the ASTM graded sand, and 240 mL of DI water for all compositions.

3.2. High Purity CSA Clinkers

Each of the high purity CSA clinkers produced in Part. 2.2. were mixed with 20 wt.% of ground FGD gypsum, as a source of calcium sulfate for the formation of ettringite during the hydration process of CSA cements. An admixture was added as a set time accelerator, referred to "Adm" in the figures, for some compositions.

Figure 1 presents the compressive strength results for all high purity CSA cements. After 2 hours, CSA-0 and CSA-3 did not show a significant compressive strength. CSA-1 and CSA-2 did set, and CSA-2 exhibited a compressive strength of 26.5MPa. After 4 hours and 1 day, the compressive strengths of all samples increased, with the exception of CSA-2 which saw a slight decrease of strength from 4-hour to 1-day. Overall, all CSA cements exhibited a compressive strength of at least 25 MPa after 1 day, with the maximum of almost 39.3 MPa for CSA-3 with admixture, which represents a 35% increase in strength. The addition of the admixture helped in increasing the early compressive strength, with the exception of CSA-2.

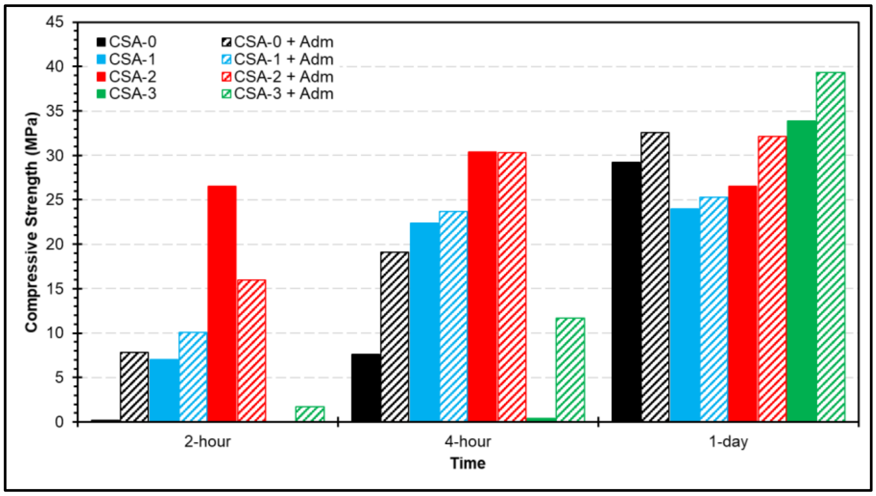

Figure 1: Compressive strength results of high purity CSA cements. 20 wt.% FGD gypsum was added to all compositions. "Adm" refers to an admixture added for acceleration of the set time.

3.3. Belite-CSA Clinkers

Each of the belite-CSA clinkers produced in Part. 2.2. were mixed with 20 wt.% of ground FGD gypsum, for the similar purpose as described in Part 3.2. An admixture was again added as a set time accelerator.

Figure 2 presents the compressive strength results for all belite-CSA cements. After 2 hours, none of the composition gain substantial strength, even with the addition of the admixture. After 4 hours, most of the belite-CSA compositions exhibited strength from 2 to 9 MPa, with the exception of CSA-G. After 1 day, the compressive strength ranged from 34 to 40 MPa through all compositions. As a comparison, a commercial CSA cement have a compressive strength of 25 MPa and 39.7 MPa, after 3 hours and 1 day, respectively. [7]

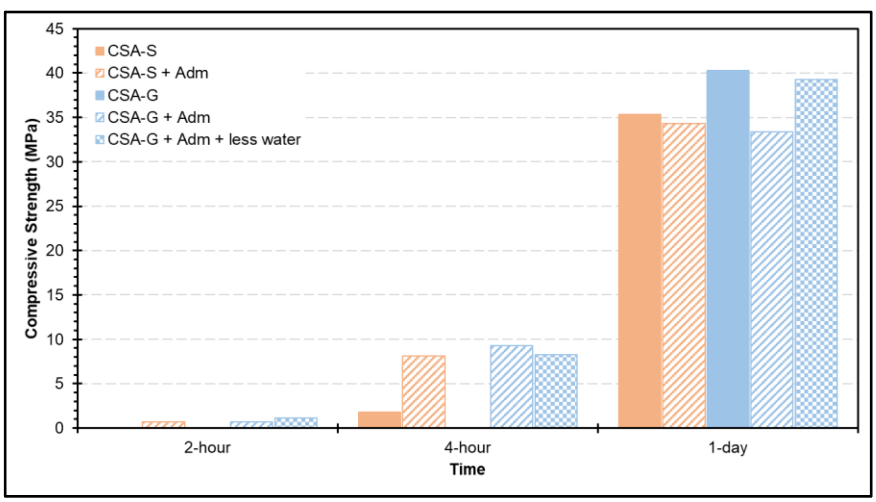

Figure 2: Compressive strength results of belite-CSA cements. 20 wt.% FGD gypsum was added to all compositions. "Adm" refers to an admixture added for acceleration of the set time.

3.4. Set Times

All high purity CSA cement compositions, with and without admixture, set in 7 to 76 minutes. All belite-CSA cement compositions, with and without admixture, set in 15 to 130 minutes. The addition of the admixture did shorten the set time to below 20 minutes for most compositions, which is in comparison, close to a commercial CSA cement which sets in 16 minutes. [7]

4. Conclusions

Based on all this preliminary work, the use of dry scrubber materials for the production of high purity CSA and belite-CSA cements has successfully been demonstrated. Both kind exhibited compressive strength similar to commercial CSA clinker after 1 day. Future work will be dedicated on improving the very early compressive strength.

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