Masonry Products made from FGD Materials Grant # DE-FG26-04NT42196

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OBJECTIVE

Our objective has been to find potential uses for FGD materials that are now being land filled. The scrubbing of flue gases in the United States and elsewhere in the world is generally carried out using a mass transport reaction between SO_2 in a flu gas with a reactive solid to produce an insoluble Ca-compound such as hannebachite ($CaSO_3 \bullet 1/2H_2O$) and/or gypsum ($CaSO_4 \bullet 2H_2O$). Those utilities burning bituminous coal containing 2-4 wt% sulfur have to remove the equivalent amount of SOx from their flue gases. Those burning sub bituminous coal must deal with <1 wt% sulfur and thus a much lower amount of SOx. In either case, in one form or another, lime is the reactant of choice for sulfur removal.

ACCOMPLISHMENTS TO DATE

Samples of FGD materials and fly ash were obtained from Allegheny Energy, Indiana Power and Light, Algona Municipal Utilities and Northern States Power. The fly ashes were of two types: Class F (Indianapolis Power & Light and Allegheny Energy) and Class C (Northern States Power and Algona Municipal Utilities). The FGD materials were obtained from Northern States Power (dry FGD mixed with Class C fly ash), Indianapolis Power & Light (spray limestone filter cake) and Allegheny Energy (spray dolomite mixed with Class F fly ash). Most FGD materials consist of nearly pure hannebachite or pure gypsum. Gypsum is used for wall board and other applications, but hannebachite is considered a waste product that has no use and therefore must be land filled. Hannebachite is a better scrubbing material because it does not gum up and coat the insides of reactor vessels like gypsum tends to do. For this reason, unless a utility is making secondary gypsum for wall board or some other use, hannebachite is the predominant FGD material produced in the United States.

All FGD materials resulting from the burning of bituminous coal with its 2-4 wt% sulfur content are produced by exposing the resulting flue gas to a reactive caustic. Although some utilities report using sodium based adsorbents, the majority of utilities use a calcium compound of some type. Generators that burn sub-bituminous coal have less sulfur to deal with. They also produce a high Ca-fly ash (typically Class C) that has the ability to scrub SOx from the flue gas without adding additional scrubbing compounds.

The sources and nature of the starting materials used in this study are given in Table 1. Typical recipes developed using these materials are summarized in Tables 2 and 3. The mixtures were used to study the effect of: 1) Concentration of caustic solution used to make the mix, 2) Solution/solid ratio and 3) Curing temperature on the properties of the masonry made from them. Other studies were carried out using a hannebachite FGD+Class F fly ash mix from Allegheny Energy (Harrison Plant) that was mixed with additional Class F (Ft. Martin Plant) or Class C fly ash (Algona Neal #4 Plant) and 15M NaOH. In this case FGD was gradually substituted for fly ash in 5 wt% steps, i.e. hannebachite content varied from 5 to 30 wt %.

Samples were prepared by mixing FGD material with fly ash (NSP dry FGD was the exception-it already contained Class C fly ash) and the various molar NaOH solutions to obtain different consistencies (thick, intermediate and thin). The samples were compacted in 2” molds and allowed to cure for 24 hours at 40°C. After demolding the cubes were cured at 70°C or autoclaved at 185°C and saturated steam pressure for 24 & 12 hours, respectively. Hannebachite by itself was unaffected by mixing with NaOH and autoclaving. It is very insoluble and thus not readily available for reaction. However the thickest samples made with the dry FGD from NSP and 8M NaOH (Table 2 mixes) tended to develop superior strengths at 70°C versus autoclave curing, whereas the thickest 15 M NaOH Class F fly ash plus FGD samples (Table 3 mixes) tended to benefit from autoclave curing. The experiments carried out with Allegheny Energy’s Harrison FGD mixed with Ft. Martin Class F or Neal Class C ash and 15 M NaOH cured at 70° and 185°C suggest that: 1) Both the 70° and 185°C cured samples containing 10 wt% FGD were the strongest, and 2) Autoclave curing increased strengths of both mixtures 3 to 4 times.

Table 1. Sources and nature of the starting materials used in our experiments

Source	**Ash**	**FGD**	**Phases present in FGD**
Northern States Power	NA	Dry FGD adsorbed on Class C ash, Sherburne County #3 Plant	30 wt% gypsum, 70 wt% hannebachite
Indianapolis Power & Light	Class F fly ash, Petersburg #4 Plant	Spray Limestone Filter Cake, Petersburg #4 Plant	80 wt% Hannebachite, 30 wt% gypsum
Allegheny Energy	Class F, Ft. Martin Plant, Maidsville, West Virginia	FGD + Class F mix, Harrison Plant, Haywood, West Virginia	--
Algona Utilities	Class C fly ash (27 wt% Ca), Neal #4 plant, Algona, Iowa	NA	--

Table 2. Class F fly ash plus filter cake from Indianapolis Power & Light

Sample	Solid mixture		NaOH		NaOH/ Solid Ratio	Consistency
	FA (g)	FC (g)	M	g		
1	720	84	15	262	0.3	thick
2	905	105	14	452	0.4	intermediate
3	723	84	15	440	0.5	thin
4	229	26	8	97	0.4	thick
5	229	26	8	108	0.4	intermediate
6	229	26	8	120	0.5	thin
7	229	26	4	70	0.3	thick
8	229	26	4	86	0.3	intermediate
9	229	26	4	100	0.4	thin

Table 3. Class C fly ash plus adsorbed FGD from Northern States Power.

Sample	Dry FGD (g)	NaOH		NaOH/ Solid Ratio	Consistency
		M	g		
1	700	15	374	0.5	thick
2	600	14	452	0.4	intermediate
3	700	15	440	0.5	thin
4	800	8	250	0.3	thick
5	700	8	362	0.5	intermediate
6	702	8	635	0.9	Thin
7	840	4	263	0.3	thick
8	740	4	391	0.5	intermediate
9	520	4	413	0.8	thin

FUTURE WORK

We will obtain different FGD materials and test them for their performance.

LIST OF PAPERS PUBLISHED

Poster at World of Coal Ash April 11-15, 2005. Abstract #8 in Program for Meeting

STUDENTS SUPPORTED

I am using an undergraduate student supported by an NSF REU to work on the project. His name is Paul Brenner. His expenses are being paid from the grant, but his salary is not. He is a Civil Environmental Engineering student. He is responsible for most of the work reported here.