

**BUILDING MATERIALS MADE FROM FLUE GAS DESULFURIZATION  
BY-PRODUCTS**

**FINAL REPORT**

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## **ABSTRACT**

Flue gas desulphurization (FGD) materials are produced in abundant quantities by coal burning utilities. Due to environmental restraints, flue gases must be “cleaned” prior to release to the atmosphere. There are two general methods to “scrub” flue gas: wet and dry. The choice of scrubbing material is often defined by the type of coal being burned, i.e. its composition. Scrubbing is traditionally carried out using a slurry of calcium containing material (slaked lime or calcium carbonate) that is made to contact exiting flue gas as either a spray injected into the gas or in a bubble tower. The calcium combined with the  $\text{SO}_2$  in the gas to form insoluble precipitates. Some plants have been using dry injection of these same materials or their own Class C fly ash to scrub. In either case the end product contains primarily hennobachite ( $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ ) with smaller amounts of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). These materials have little commercial use. Experiments were carried out that were meant to explore the feasibility of using blends of hennobachite and fly ash mixed with concentrated sodium hydroxide to make masonry products. The results suggest that some of these mixtures could be used in place of conventional Portland cement based products such as retaining wall bricks and pavers.

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## EXECUTIVE SUMMARY

The objective of the work has been to find potential uses for flue gas desulphurization (FGD) materials that are now being stored on site or land filled. The scrubbing of flue gases is generally carried out by taking advantage of a mass transport reaction between  $\text{SO}_2$  in the flue gas with a reactive solid to produce an insoluble Ca-compound such as hannebachite ( $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ ) and/or gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Those utilities burning bituminous coal containing 2-4 wt% sulfur have to remove the equivalent amount of  $\text{SO}_x$  from their flue gases. Those burning sub bituminous coal must deal with <1 wt% sulfur and thus a much lower amount of  $\text{SO}_x$ . In either case, in one form or another, lime is the reactant of choice for sulfur removal.

It was proposed that the reactivity of some FGD by-products could be enhanced (activated) by adding caustic (NaOH) to them and then curing the samples at elevated temperatures, in this case  $70^\circ$  and  $185^\circ\text{C}$ . Bituminous coal burning power plants produce large amounts of hannebachite mixed with smaller amounts of gypsum. Mixing it with NaOH and then curing at  $70^\circ$  and  $185^\circ\text{C}$  had no real effect. Pastes remained soft and no additional phases formed. However, it was found that if 10 wt% of dried hannebachite/gypsum was mixed with 90 wt% Class F fly ash and a minimal amount of 8 M NaOH was used to make a paste and the paste was then cured at  $185^\circ\text{C}$ , it was possible to produce a masonry block with a compressive strength of  $\sim 7,000$  psi. Alternately, if the same paste was cured at  $70^\circ\text{C}$  it tested out at  $\sim 2,000$  psi, weaker but still strong enough for paver and retaining wall block. It was surmised that the platy hannebachite crystals were acting much like a fiber reinforcing material.

Similarly, it was found that a dry FGD/Class C fly ash combination produced by a sub bituminous coal burning power plant in the Midwest mixed with the smallest amount of 8M NaOH needed to make a very thick paste could be cured at  $70^\circ\text{C}$  overnight in a sealed container to produce a block having a compressive strength of  $\sim 6,000$  psi. In this instance, if another sample of the same paste was cured at  $185^\circ\text{C}$ , the strength was significantly less.

The work to date suggests that suitable building materials could be produced by a given power plant using its own waste heat sources in an adjacent facility to cure a mixture of fly ash and wet/dry FGD and NaOH and in this way produce a value added product that could tip the financial and environmental balance related to fly ash management in the utility's favor. Manufacturing in an Eco Park setting could provide incubator space for other cottage industries to spring up as well. Fly ash and FGD by-product materials are resources for those entrepreneurs willing to take a chance.

## Introduction

Flue gas desulphurization (FGD) materials such as gypsum and hannebachite are the solid phases remaining after lime based materials have been used to scrub off-gases of a coal burning power plant. Generating plants located in the eastern and mid western United States tend to burn bituminous coal having a 2-3 wt% sulfur content. This is a relatively high value and therefore, these plants are normally required to remove most of the resulting sulfur dioxide ( $\text{SO}_2$ ) that is generated during combustion and then carried out of the plant as part of the exiting flue gas. Scrubbing is the term that is used to describe the cleaning process - a substance is introduced into the combustion chamber or exit gas stream that will combine with the  $\text{SO}_2$  to form particulate matter that can be collected and disposed of in an environmentally sound manner. When the  $\text{SO}_2$  content is relatively large, it has been found that lime based materials are not only inexpensive, but also work quite well. The various oxides of sulfur (a.k.a.  $\text{SO}_x$ ) are removed from the flue gas by allowing it to react in some manner (dry or wet) with  $\text{CaCO}_3$ ,  $\text{CaO}$  or  $\text{Ca(OH)}_2$ . The efficiency of the process is of course a mass transfer problem. Wet scrubbing may be the most widely used process because it is most efficient. A slurry of scrubbing agent e.g.  $\text{CaCO}_3$  and water can be injected into the exiting gas as an atomized mist or the exiting gas can be made to contact the slurry in a bubble tower or some variant on this theme. If the process is carried out under oxidizing conditions, gypsum will be obtained, if it is carried out under slightly reducing conditions, which is most common, hannebachite ( $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ ) will form instead. Alternately a dry powder e.g.  $\text{Ca(OH)}_2$  can be injected into the flue gas on its way to the bag house. Here the scrubbing material becomes part of the solid fly ash waste stream. Because the dry process is less efficient, it is usually reserved for power plants burning coal with low sulfur contents (sub-bituminous).

Byproduct gypsum can be used to manufacture dry wall panels and for other applications normally requiring natural gypsum as a starting material. Plants specifically built for this purpose are now in existence, usually within close proximity of the power plant. Gypsum is generally not a problem, but hannebachite is. Hannebachite is extremely insoluble and thus unreactive in the sense that it could be used as a substitute for gypsum. Because there is no known use for hannebachite, it continues to be a by-product that must be disposed of on a power plant's property or in a land fill. Unfortunately, it is easier to scrub under slightly reducing conditions because hannebachite is less "sticky" and more easily removed from the flue gas treatment facility than gypsum. Also low  $\text{NO}_x$  burners operate in a slightly reducing mode and in order to produce gypsum one would actually have to inject oxygen into the exiting flue gas. Thus, unless there is a factory nearby that can use gypsum, the power plant will normally produce hannebachite. This residual "mud-like" product is normally either pumped into an on-site holding pond or dewatered and then mixed with fly ash and disposed of in a landfill.

As an alternative, power plants burning sub-bituminous coal, which has less sulfur (~1% by weight) than bituminous coal, are able to use the calcium in their fly ash to absorb the oxides of sulfur from their flue gases. Their fly ash is glassy and contains 30-40 wt% calcium oxide ( $\text{CaO}$ ). The glass is by conventional standards a very poor glass-it will dissolve and react with water to form insoluble hydrates. Whereas this is a definite negative if one is making a container glass (bottle) it does have the advantage of making the fly ash reactive enough to combine with the  $\text{SO}_x$  in the gas to produce a combination of hannebachite and gypsum that adheres to the fly ash particles. These ashes are generally called dry FGD Class C fly ashes. These plants are generally located in the western United States. The process of using one's own fly ash or a combination of lime ( $\text{CaO}$ ) and Class C fly ash to scrub exhaust gases is a very economical

solution to dwindling water supplies needed for wet scrubbing and the evolution of CO<sub>2</sub> resulting from the use of calcium carbonate-based scrubbing materials. This process is normally carried out in the dry state. The ash is collected in bag houses and recycled back into the system a number of times. Then the ash is removed and disposed of in land fills. Nevertheless some plants in the West still use lime-based wet scrubbing, and in this case they normally produce hannebachite.

There are a few plants that use alternate scrubbing materials such as sodium carbonate, magnesium carbonate, dolomite (Ca,Mg)CO<sub>3</sub> or alkali solution but these are few are far between. Compared to the volume of lime based scrubbing materials generated annually these materials are nearly insignificant. At this point in time, due to their volumes alone, wet scrubbing, dry scrubbing and dry FGD ash materials are the most damaging to the environment. All are by-products with no real use. All are lime rich, which necessitates the addition of CO<sub>2</sub> to the atmosphere, i.e.  $\text{CaCO}_3 + \text{SO}_x = \text{CaSO}_x + \text{CO}_2$ .

Current research has been directed towards finding uses for these materials, but like fly ash itself the potential uses are ultimately limited by cost. A product can be made, but it has to compete with something that can be found naturally-often at a lower price. Uses in construction as soil amendment or back-fill materials are examples of potential uses. Usually, however, local aggregate is cheaper and more easily obtained. Although the prospects of finding a value added product made from hannebachite itself was slim, there was a prospective processing scheme that had worked for a sample of dry FGD Class C ash that perhaps could be expanded to include wet FGD as well. It had been observed that a sample of dry FGD Class C ash mixed with 15M NaOH as a thick paste would harden with time and then produce a solid with ~4,000 psi strength when autoclaved overnight at 180°C and saturated steam pressure. This process was proposed as a means of making other solids as well using other types of scrubbing materials. With strengths such as these, one could in fact begin to manufacture value added products that could potentially be used as replacements for traditional masonry products and even cast iron. The objective of the work presented here was to evaluate alkali activation with NaOH and autoclave curing to produce a new type of building material from both wet and dry FGD materials.

## Materials

Materials were solicited from a variety of power plants. Plants that provided samples are listed below in Table 1. It is to be noted that other types of coal combustion FGD by-products are produced by utilities using sodium carbonate, magnesium carbonate and alkali solutions to scrub, but regrettably these companies declined (by not providing samples after repeated requests) to participate.

**Table 1. Sources/Types of FGD By-product Materials used in the Study.**

Participants	Scrubbing agent & waste produced
Northern States Power (XCEL)- Sherburne County Unit 3 (Sherco)	Spray alkaline Class C ash and CaO (Dry FGD)
Indianapolis Power and Light- Petersburg 1 & 2 (IPL)	Spray limestone (Wet hannebachite by-product) and Class F fly ash

Non-participation proved to be the major obstacle to expanding the scope of work as originally promised in the proposal. Northern States Power (now XCEL) provided Sherco dry FGD ash and Indianapolis Power and Light (IPL) provided ash and filter cake. All three products

were examined using X-ray diffraction and scanning electron microscopy (SEM) to determine their base properties before being mixed with NaOH solutions to make samples.

On receipt, the two FGD materials listed in Table 1 were characterized. These materials were found to consist of the following. The dry FGD from Northern State Power Company (Sherco) is a Class C fly ash coated with calcium sulfate/calcium sulfite hydrates (Figure 1). The wet scrubber filtercake from Indianapolis Power and Light (IPL) is predominantly hannebachite with ~10 wt% gypsum and ~2 wt% calcite mixed in (Figure 2). This latter material proved to be unreactive when mixed with only NaOH, so it was then combined with IPL's own Class F fly ash and NaOH in an attempt to make a strong solid from it much like the one made from Sherco ash mentioned in an earlier section. Phase chemistry of IPL ash is given in Figure 3. The chemical analyses of the three by-product materials are given in Table 2.

**Table 2. Composition of Sherco dry FGD, IPL Filter Cake and IPL Class F Fly Ash**

	Sherco FGD Fly Ash	IPL Filter Cake	IPL Class F Fly Ash
Al <sub>2</sub> O <sub>3</sub>	13.8	ND	21.71
B <sub>2</sub> O <sub>3</sub>	0.37	ND	ND
BaO	0.48	ND	0.04
CaO	30	44.21	1.72
Fe <sub>2</sub> O <sub>3</sub>	4.82	ND	22.02
K <sub>2</sub> O	0.71	ND	2.40
MgO	2.85	ND	0.90
MnO	0.10	ND	0.02
Na <sub>2</sub> O	1.92	ND	0.55
SiO <sub>2</sub>	30	ND	46.23
SrO	0.58	ND	0.03
P <sub>2</sub> O <sub>5</sub>	ND	ND	0.14
TiO <sub>2</sub>	0.76	ND	1.05
Sulfite as SO <sub>2</sub>	4.43	43.61	ND
Sulfate as SO <sub>3</sub>	4.64	7.04	1.40
Carbonate as CO <sub>2</sub>	ND*	0.88	ND
LOI	2.67	ND	ND
Insoluble Residues	ND	4.25	1.81
TOTAL	98.3	99.99	100.02

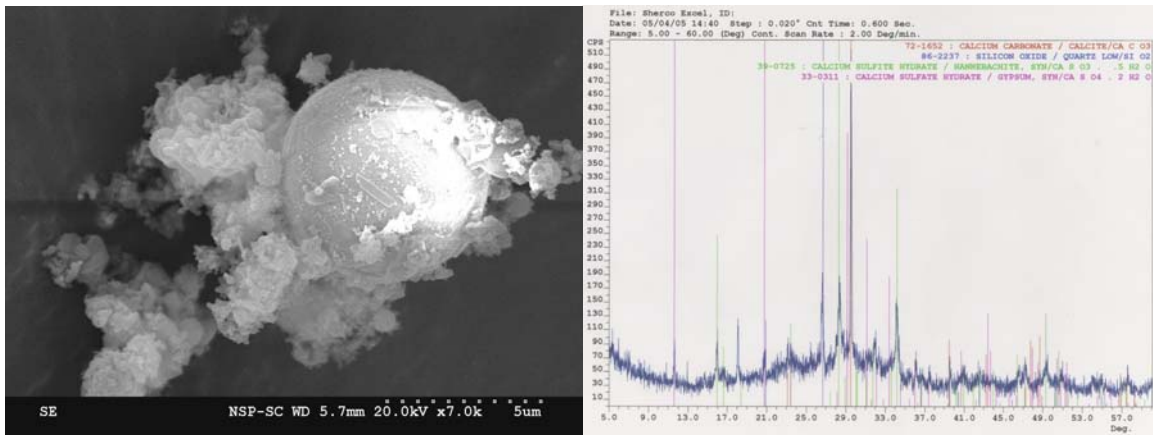
\*ND=not determined

### Formulations --Sherco

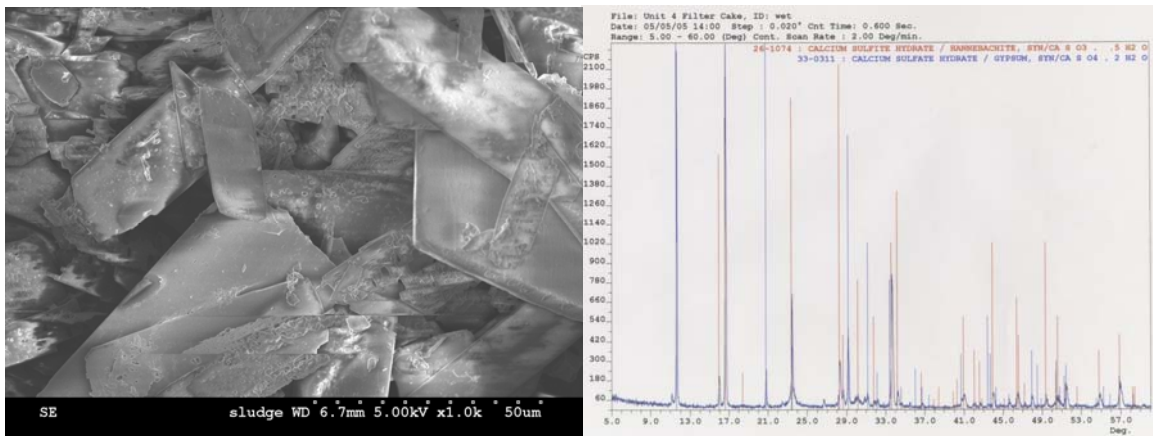
Because the Sherco dry FGD by-product already contains Class C ash and FGD material, initially no other dry ingredients were added to the dry FGD. It was simply mixed with various concentrated NaOH solutions. Three mixes using Sherco dry FGD were made using 15, 8, and 4 molar sodium hydroxide solutions. The mixes were designed to cover a reasonable span of liquid to solid ratios that could be expected to develop strength, i.e. the mixes were formulated with three levels of solution content in order to determine the effect of thickness on final properties. The samples were formulated to be 1) putty-like but placeable, 2) have intermediate viscosity and be pourable, and 3) be easily pourable. The pastes were precured at 70°C overnight and then tested without further treatment. Companion samples with the same amount of precure were also autoclaved at 180°C for an additional 8 hours and then tested. Mixture formulations are given in



Table 3. At a later time, Troy metakaolinite<sup>1</sup> was also used with selected Sherco ash mixtures. The results of testing (compressive strength and phase chemistry) were then compared and used to evaluate the potential of achieving the project’s stated goals.

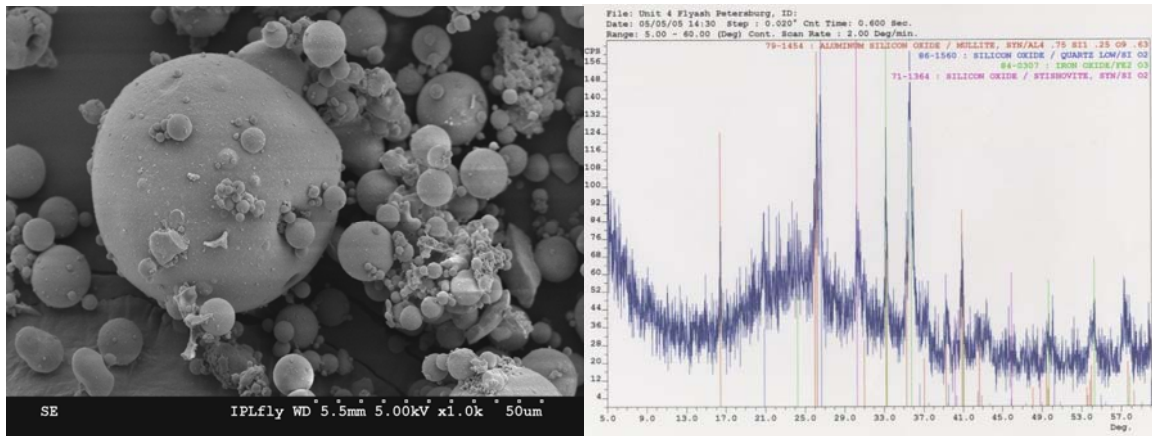


**Figure 1.** The Sherco dry FGD by-product is a Class C fly ash that has been used to scrub SO<sub>2</sub> from flue gas. The spherical fly ash particles are normally coated with a layer of sub micrometer gypsum and hannebachite crystals. The crystalline components of the fly ash can be identified from their characteristic peak spacing on the X-ray diffraction pattern on the right. Judging by the X-ray diffraction pattern, the amount of FGD relative to fly ash is small; peaks are small and the “amorphous hump” (a sign of glassy particles) is large.



**Figure 2.** The wet FGD filter cake from Indiana Power and Light’s plant is a very fine platy material composed predominantly of hannebachite crystals with traces of gypsum. The platy character of the hannebachite suggests that it could act as a reinforcing agent if incorporated into a binder. The accompanying X-ray diffraction pattern is nearly devoid of X-ray amorphous material. Note that the peaks are very large and thin, indicating the presence of well crystallized materials.

<sup>1</sup> Troy metakaolin was made from Troy clay (predominantly kaolinite with traces of quartz and mica hence the name kaolin) which is mined near Troy Idaho. It was heat treated in a rotary kiln for ~2 hours at 700° C and then milled. Troy metakaolin was found to enhance the reactivity of many fly ash based reactions. Metakaolin has a similar composition as a Class F fly ash but is much more reactive. It will easily combine with caustic to form zeolites that act as cement and bind the sample together. Metakaolin additions were used on occasions to ensure rapid reaction at room temperature, as for example, when measuring expansion.



**Figure 3.** The IPL Class F fly ash is spherical, glassy and fairly high in iron oxide. It contains traces of mullite and quartz. It is a rather typical Class F ash. The crystalline components each have distinct peak spacing which here are superimposed on a broad glassy amorphous hump.

**Table 3. Formulations of Sherco plus NaOH Solution Mixtures.**

Sherco Sample	Solid Mixture	NaOH Solution		NaOH solution/Solid Ratio
	(g)	M	(g)	
				--
1	700	15	374	0.534
2	600	15	491	0.818
3	700	15	622	0.889
4	800	8	250	0.313
5	700	8	362	0.517
6	702	8	635	0.905
7	840	4	263	0.313
8	740	4	391	0.528
9	520.1	4	413	0.794

### Formulations --IPL

The IPL (Indianapolis Power and Light) FGD filter cake consisted primarily of hannebachite (hydrous calcium sulfite) mixed with traces of gypsum. In itself, it had no strength when mixed with NaOH and then cured at 70 °C or 185°C in a steam autoclave. However, when 10 wt% FGD (which was determined to be the optimum amount) was combined with 90 wt% IPL’s Class F fly ash and various amounts of NaOH solution and cured as above, it was possible to produce blocks with greater strength than the Sherco mixes.

Three mixtures using 10 wt% IPL FGD filter cake and 90 wt% IPL Class F fly ash were made using 15, 8 and 4 molar sodium hydroxide solution. Once again the mixes were designed to cover a reasonable span of liquid to solid ratios that could be expected to develop strength, i.e. the mixes were formulated with three levels of solution content in order to determine the effect of thickness on final properties. The samples were formulated to be putty-like but placeable, have intermediate viscosity and be pourable, and be easily pourable. The pastes were precured at 70°C overnight and then tested without further treatment. Companion samples with the same amount of precure were also autoclaved at 180°C for an additional 8 hours and then tested. Mixture formulations are given in Table 4. Once again ground Troy metakaolin was used to

supplement some of the mixtures on an as needed basis. These materials were then used for evaluation and comparison of their prepared properties as potential building materials.

**Table 4. Formulations of IPL FGD plus IPL Class F fly ash mixed with NaOH solution.**

IPL Sample	Dry Mixture Blend		NaOH Solution		NaOH Solution/Solid Ratio
	IPL F Fly ash (g)	Dried IPL FGD (g)	M	(g)	
--					--
1	720	84	15	262	0.326
2	905	105	15	452	0.448
3	723	84	15	440	0.545
4	229	26	8	97	0.380
5	228	26	8	108	0.425
6	228	26	8	120	0.472
7	228	26	4	70	0.276
8	228	26	4	86	0.339
9	228	26	4	100	0.394

The cubes were relatively hard after precuring at 70° C. They were either tested as is or tested after autoclaving a companion precured set at 185°C for an additional 8 hours. The two sets of cubes were then tested for strength in a Tinius Olsen screw driven compression machine. Pieces of the broken cubes were characterized using SEM and X-ray diffraction.

## Methods

Mixing procedures were carried out in accordance with ASTM (C305-99) as if the current formulations were Portland cement and water and they were being mixed as a mortar. Mixtures were mixed using a Hobart mixer. Two-inch cube molds were used to cast the samples. The molds were placed in a controlled temperature chamber operating at 70 °C. As an added precaution against drying, sample molds were covered with a glass plate and placed in covered flat plastic storage containers (Walmart) containing a small amount of water. The samples were placed on an elevated platform (plastic or wood) in the container. Here they were allowed to precure overnight. By morning they were often hard enough to demold and test or be allowed to continue curing at 70° C or an elevated temperature (180-185 °C). Unlike Sherco samples, the cubes for IPL ash were relatively soft after the precuring step. However with care they were still demoldable and could be removed from their molds and then allowed to continue curing at 70 °C or in a steam heated autoclave (i.e. autoclaved). All cubes were tested in a Tinius Olsen screw driven compression testing machine per ASTM C109/C 109M-01 test procedures. Curing times were typically on the order of 28 days.

## Results

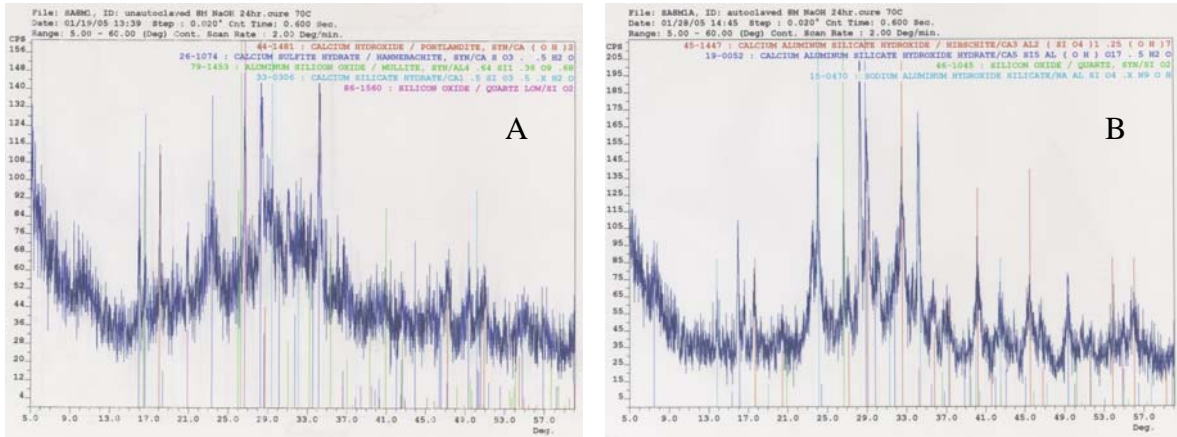
### Phases Present

The chemistries of the starting materials were very different. The Sherco dry FGD material contains a large amount of calcium, lesser amounts of alumina and silica and surprisingly only a small amount of SO<sub>x</sub>. The IPL filter cake was essentially pure calcium sulfite with traces of sulfate and a large amount of occluded water. The Class F fly ash from IPL is rich in iron oxide. This causes it to appear rather dark in color. It is a fly ash that can not be used for

construction purposes. But in as much as it is the only fly ash that IPL has, it was used to successfully formulated block. In fact the data may provide guidance for other companies having less than desirable fly ashes.

The microstructures of the by-product materials were generally nondescript. Except for the fly ashes themselves, the scrubbing products were very fine and long-range crystallinity was difficult to discern. The situation for the cured samples was much the same. This is evident in both the Sherco FGD and the IPL filter cake samples (Figures 1 and 2). The fly ashes were also rather typical. The Sherco ash is very white presumably due to low iron content and the fact that FGD products adhere to the surface of the ash (Figure 1). The IPL ash was almost black due to a relatively large amount of iron oxide and carbon in the ash (Figure 3). The characteristics of the patterns themselves and the nature of the phases present in the X-ray diffraction patterns for the Sherco and IPL ash samples are as follows. The pattern generally contains a predominant amorphous hump with traces of quartz and mullite crystals.

After mixing with NaOH and curing the X-ray diffraction patterns of the cured samples do not change very much. Representative X-ray diffraction patterns for a Sherco and an IPL mix are presented below. Figure 4 represents a Sherco sample mixed with 8 molar NaOH that was cured at 70°C overnight (left) and also autoclaved for an additional 12 hours at 180°C in a steam autoclave (right). The 70°C sample was harder. The major difference between the samples is the 70°C sample is far less crystalline than the autoclaved sample. Figure 5 represents an IPL fly

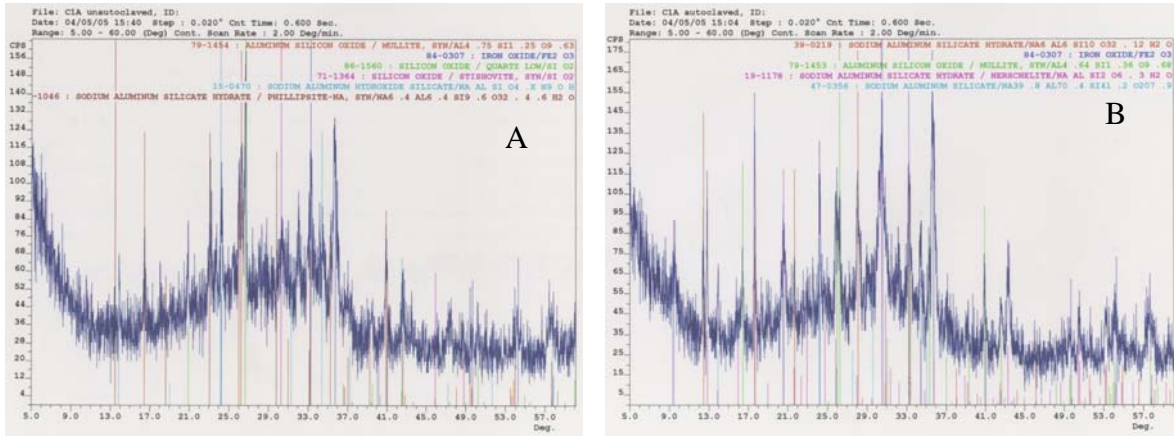


**Figure 4. X-ray diffraction patterns for Sherco samples cured at 70°C (left) and 180°C (right). The 70°C sample has a larger X-ray amorphous hump indicating that it is less crystalline than the autoclaved sample. The heights of the peaks in the autoclaved sample are larger indicating that more crystalline phases formed at the elevated temperature.**

ash + filter cake sample mixed with 8 molar NaOH solution that was cured at 70 °C for 24 hours (left) and also autoclaved for an additional 12 hours at 180°C in a steam autoclave (right). The autoclaved sample was harder, but by all accounts both patterns look essentially the same..

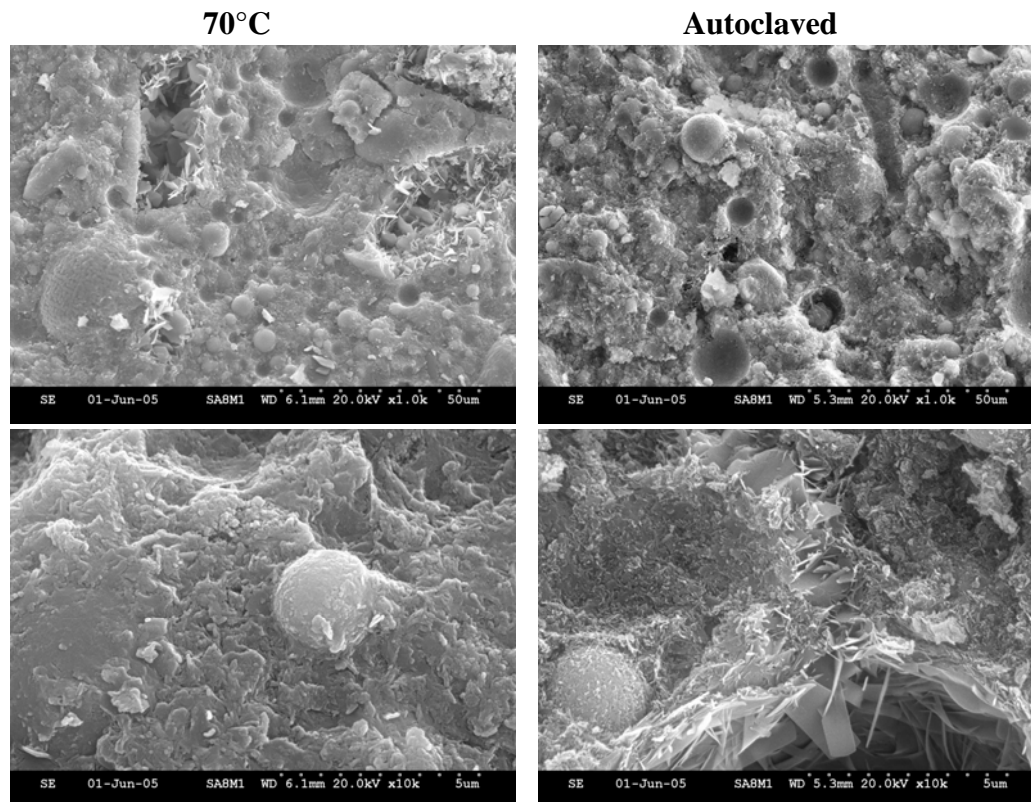
In both sets of patterns one is aware of two things. First, the patterns are of poor quality. Peaks are generally broad and have low count intensities. The baselines are not flat. Each contains a rather broad amorphous hump with traces of superimposed peaks representing newly formed and residual crystalline phases. The unautoclaved Sherco sample (Figure 4A) contains quartz, mullite and hannebachite. The autoclaved Sherco has reacted to a greater extent and now contains traces of zeolite, tobermorite and hydroxycancrinite (Figure 4B). Similarly, the unautoclaved IPL sample (Figure 5A) contains traces of  $\text{Ca}(\text{OH})_2$  and the autoclaved IPL sample

the phases present in the X-ray diffraction patterns for the IPL samples are a large x-ray contains traces of zeolite.



**Figure 5. X-ray diffraction patterns for Sherco samples cured at 70°C and 180°C. Even though the sample on the right (B) has been autoclaved, degrees of crystallinity as judged by the size of the amorphous hump is almost the same as in (A) that was cured at 70°C. Both samples contain traces of zeolites.**

The SEM images collected for these samples are reproduced below as Figures 6 and 7. The Sherco samples are relatively free of porosity. The matrix is generally fine grained and any large crystals present are confined to the insides of voids left over from reacting hollow fly ash spheres (cenospheres). The IPL samples are highly porous. The matrix has evidence of microcracking that could be an artifact of the compressive strength test. The autoclaved sample is far better. It has a finer denser microstructure both at 1000X and 5,000X.



**Figure 6. Two sets of SEM images for Sherco samples. One cured for 24 hours at 70°C (left set) and one cured at 70°C for 24 hours and then overnight at 180°C (right set). The top images are 1,000X and the lower images are 10,000X original magnifications.**

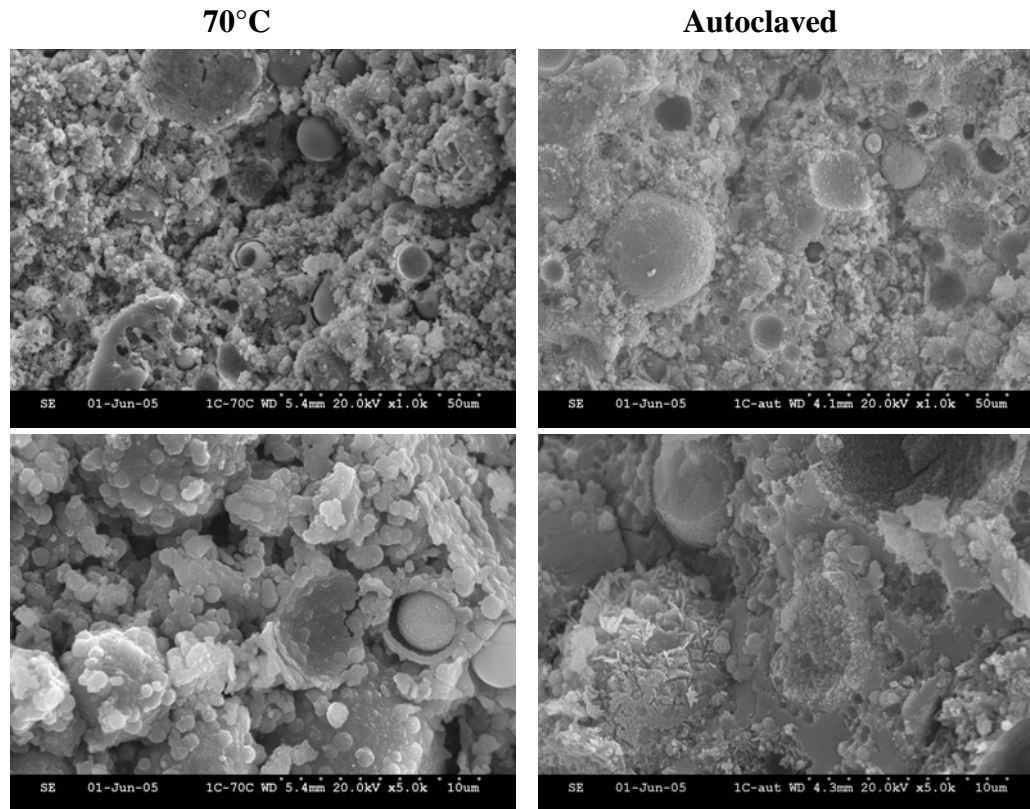
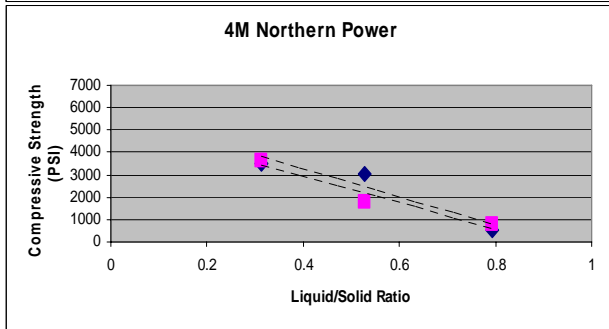
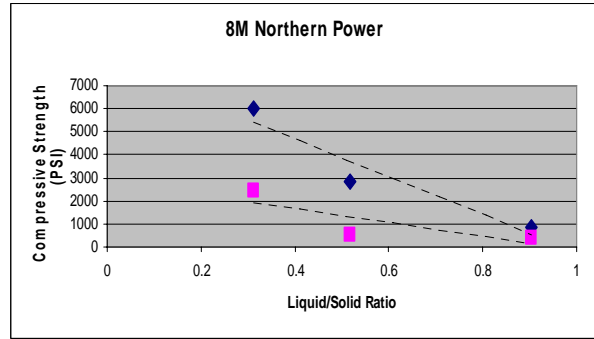
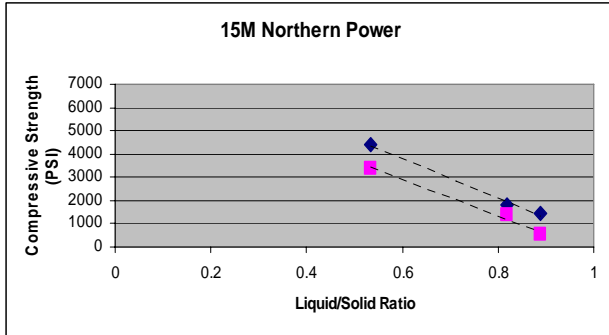


Figure 7. Two sets of SEM images for IPL + by-product samples. One cured for 24 hours at 70 °C (left set) and one cured at 70°C for 24 hours and then overnight at 180 °C (right set). The top images are 1,000X and the lower images are 10,000X original magnification.

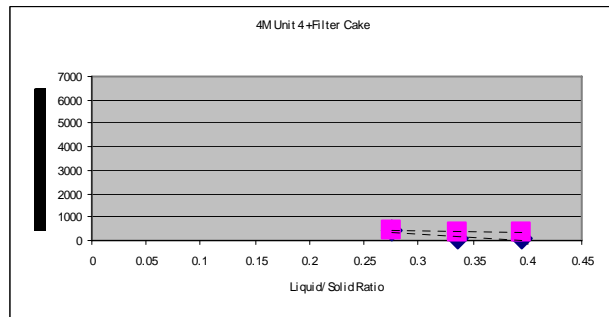
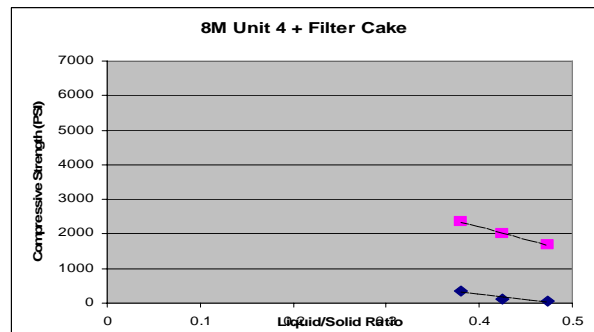
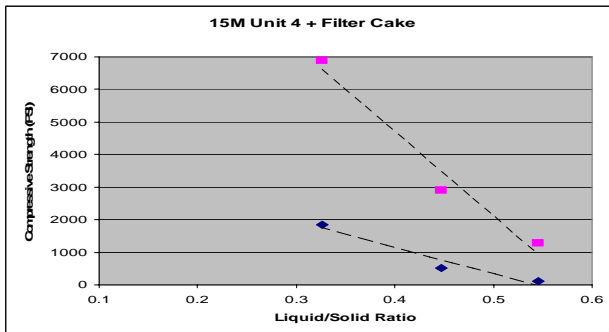
### Compressive Strength

Compressive strengths are summarized below in graphical format as 2 sets of three graphs for the two sample formulations tested. See Figure 8 and 9. It is notable that the two samples behave in radically different fashions. The unautoclaved Sherco samples (Figure 8) made at 70 °C are stronger than their autoclaved counterparts. This may indicate that a disruptive phase change takes place when a 70°C sample is autoclaved. Or more likely since strengths do increase normally, autoclaving does not provide the proper conditions for strength development. It is often the case that very fine grained high surface area substances will crystallize at elevated temperatures and with such crystallization comes an increase in porosity and a reduction in strength. In the case of the IPL mixtures (Figure 9), performance is enhanced by autoclaving. Here the situation may be somewhat different. Both Class F fly ash and hannebachite are non-reactive. Therefore at higher temperatures solubilities are usually increased and as such so is reactivity. Nucleation and growth will occur and the sample may begin to “cement” together. Zeolites that form under these conditions have very large surface areas and this factor could also play a role.

A comparison of the maximum compressive strengths attained between the strongest Northern State Power mortar (unautoclaved) and the strongest IPL Unit 4 ash with filter cake mortar (autoclaved) is shown in Figure 10. The 8 molar unautoclaved mortar samples displayed the highest strength when using Northern State Power ash (Sherco @ 5995psi) mixed as a thick paste. The 15 molar autoclaved mortar among the IPL Unit 4 and filter cake specimens was the strongest (6885 psi) also when mixed as a thick paste. Thick pastes that minimize the amount of liquid present seem to lead to the highest strength development.

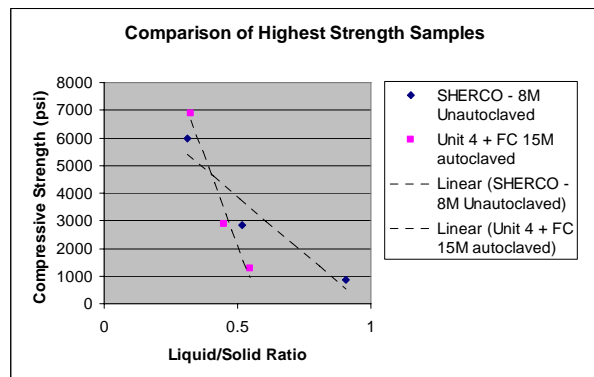


**Figure 8.** Compressive strengths of Sherco samples cured for 24 hours at 70 °C (blue) and overnight at 180°C (purple). Mixtures were made with 15, 8 and 4 M NaOH. All of the thickest samples were strongest regardless of molarity used. The 8M sample cured at 70 °C was the strongest.



**Figure 9.** Compressive strengths of IPL + filter cake samples cured for 24 hours at 70 °C (blue) and overnight at 180 °C (purple). Mixtures were made with 15, 8 and 4M NaOH. All of the thickest samples were the strongest. Autoclaved samples were stronger regardless of the molarity used. The 15 M autoclaved sample was the strongest.

**Figure 10.** A plot showing the best performing mixtures of the two types of FGD by-products. The two types of ash + FGD tested behaved in very different ways. The 70°C cured Class C ash resulted in a very strong product. The Class F ash + FGD required autoclave curing to reach similar strength values.



## Expansion Tests

Expansion tests (ASTM C1038-01) on standard 1x1x11.5 inch bars were monitored as a function of time. The data are preliminary, but important from the standpoint of predicting performance and durability of masonry products made in this fashion. Bars for two types of mixtures were cast. One set consisted of 50:50 mixtures of Sherco dry FGD Class C fly ash and a Class F fly (in this case one from Allegheny Energy's Ft Martin plant) and a second consisting of either 50 wt% Sherco dry FGD ash or 50wt% Ft Martin ash mixed with 50 wt% metakaolin. Mixtures were made to be just pourable (thick), cast as 1 inch bars and allowed to cure at room temperature until they were hard enough to demold. These times varied from 2 days for the 50:50 Ft Martin/metakaolin mixture up to 7 days for the Sherco dry FGD plus Class F Ft Martin mix. See Table 5. All of the depicted mixtures with the exception of the Sherco metakaolin sample cured at room temperature expanded to some degree and then proceeded to shrink. On the average, however, it would seem that volume stability of these materials is quite good. Major expansion (normally 0.1% which is a cut off value beyond which a traditional concrete formulation is deemed unusable as a building material) does not come close to happening. The normalized expansion data are given in Figure 11. It is to be noted that setting and hardening often took 6 days at room temperature but only 2-3 days at 38°C. Any formation of expansive phases would have taken place during the plastic stage thus damage due to their latent formation appears not to occur.

**Table 5. Formulations used to make Expansion Bars.**

Number of bars made	Class C Sherco (wt%)	Class F Ft Martin (wt%)	Metakaolin (wt%)	Amount 8M NaOH added	Curing temperature	Time to 1st measurement
2	50	50	--	pourable	room	6 days
1	50	--	50	pourable	room	6 days
1	50	50	--	pourable	38 °C	3 days
2	50	--	50	pourable	38 °C	3 days
1	--	50	50	pourable	38 °C	2 days

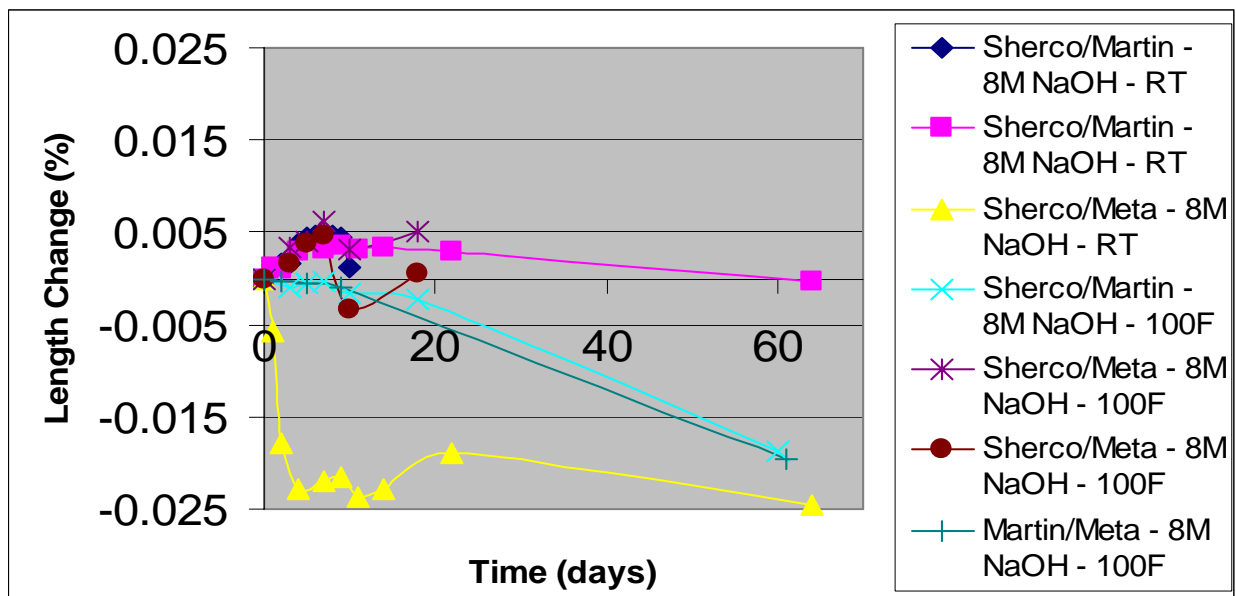


Figure 11. Preliminary length change data as a function of time after initial measurement. Values are normalized to the initial measurement, i.e. all subsequent values have been divided by the initial value in order to calculate % expansion.



## Conclusion

In summary, there is a distinct difference in the performance of a Class F and a Class C ash containing FGD material when they are mixed with different quantities of concentrated NaOH solutions and then heat treated as a function of temperature. The data suggest that the dry FGD ash by-product (Sherco) can be mixed with 15 molar NaOH and cured at 70° C to produce a very strong block, in fact stronger than its autoclaved equivalent. The Class F ash Filter cake mixture (IPL) behaves in just the opposite fashion. The unautoclaved sample is very weak where as the autoclaved sample is very strong. In this case, an autoclave is required to cure the sample, but considering the fact that a utility like IPL has an abundance of by-product steam and a readily available source of Class F fly ash the production of pavers or retaining wall block on-site could be a profitable endeavor for them. This of course expands the scope of what utilities normally do, but in an increasingly polluted world the concept of an eco-park built around a coal burning utility may not be that far fetched.

For sake of comparison, a control sample was made with the IPL Unit 4 Class F ash without adding any hannebachite rich filter cake. It was prepared to have an intermediate consistency with 15m NaOH. It was precured at 70° degrees C, then autoclaved. The strength of this sample was 6522 psi, which is just a few hundred psi less than the equivalent sample made with 90% ash and 10% FGD hannebachite. It is suggested that a blend of ash and FGD provides the chemistry needed to produce a stronger block than the fly ash itself. Thus, a Class F fly ash blended with by-product hannebachite and mixed with 15m NaOH and autoclaved could allow a utility to manufacture a paving material without lime or Portland cement additives. Although an autoclave may be an expensive item to purchase, it could be run in part using waste heat from the generating station. It is suggested that the plates of hannebachite are acting as a reinforcing agent much like a fiber does in conventional concrete masonry.

At this point, it is clear that a Class C ash with FGD additions that is cured at 70° C and a blend of 90 wt% Class F fly ash 10 wt% hannebachite/gypsum FGD by-product that has been autoclaved are two ways of producing a strong material that may be suitable as a substitute for current cement based pavers/retaining wall block. In addition, to the 15M autoclave sample, the 4 molar sample cured at 70° C attained a compressive strength of ~3,000 psi. This in contrast with the finding that a pure Class F fly ash sample mixed with a 15M NaOH and autoclaved at 185° C overnight gave us a block having a compressive strength of 6522psi. Although the strength is about 1/2 that of the autoclaved sample it is produced at near room temperature using a relatively weak caustic and cured at near ambient without using an autoclave. For sake of economy and taking into account the fact that such a block or paver could be made in a conventional concrete block plant it is also recommended.

In either case, by-product materials have been used to manufacture a traditionally Portland cement based material and if adopted this technology could have a positive impact on the environment. The materials are potential “green” building materials. The NaOH activated materials are certainly greener and less destructive to the atmosphere vis à vis Portland cement with emits CO<sub>2</sub> to the atmosphere. However, a missing part of the equation remains. The durability of these materials when exposed to wet and/or humid conditions with freeze thaw and wet dry cycles superimposed over a two or three year period remains to be seen. Testing is recommended before any further commercialization can be made. The economics of manufacture are not yet known. If it is assumed that the material is made by a utility using its own waste steam and coal combustion by-products mixed with 50 wt% NaOH solution delivered by rail car at an estimated cost of \$300 per ton of solution one only has to factor in the cost of raw material.

For the 70°C sample of Sherco ash/FGD by-product an 8M solution is required for optimum strength. A 50:50 wt% NaOH solution is ~15 M. The required liquid/solid ratio (L/S) is ~ 0.4. For a ton of solid by-product one would need ~400 lbs of 15M NaOH and 400 pounds of water. 400 lbs of NaOH would cost ~ \$60.00. The amount of product would exceed one ton. For the 180°C sample of IPL Class F fly ash/FGD filter cake having the same L/S ratio the amount of liquid required is now 800 lbs of 15M NaOH having an estimated cost of \$120 per ton of treated Class F fly ash/filter cake. These values suggest a cost of 3-6 cents per pound of manufactured masonry product. Under the worst of conditions (manufacture at a remote location) price per pound would increase due to cost of buying and shipping by product materials to an off site location and the need to pay for steam generation.