Masonry from Flue Gas Desulfurization (FGD) Materials: Dry versus Wet

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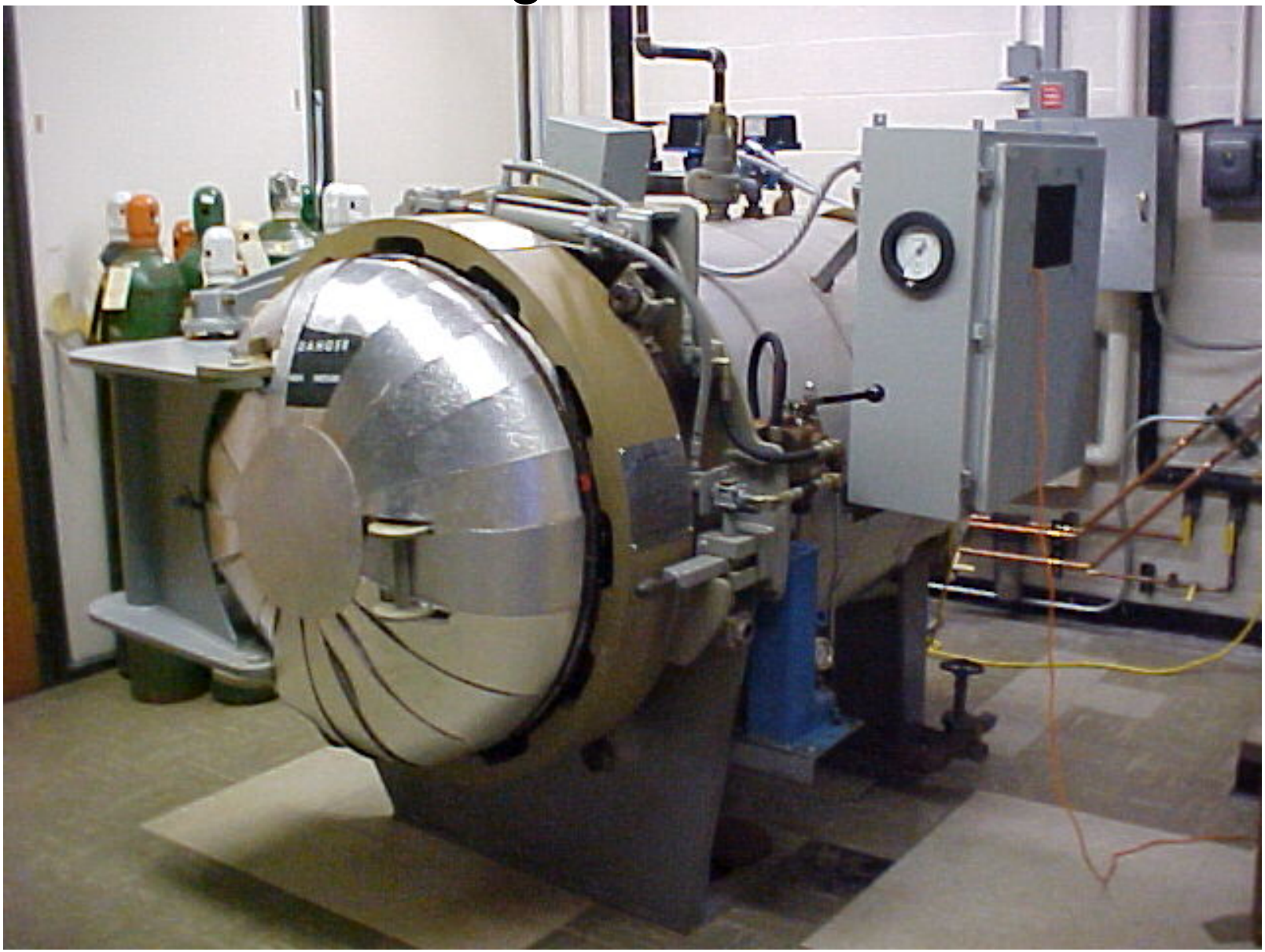
Supported by DOE Grant DE-FG26-04NT42196

Masonry

Masonry construction implies the joining of smaller individual units into a larger whole with or without additional binder between the pieces.

Autoclave Curing Accelerates Reactions



So does Concentrated NaOH

- Fly ash is a recognized pozzolan often used in Portland cement.
- Fly ash will also react with NaOH to produce zeolites.
- Reaction occurs in nature but takes a long time.

- Autoclave curing accelerates the process.

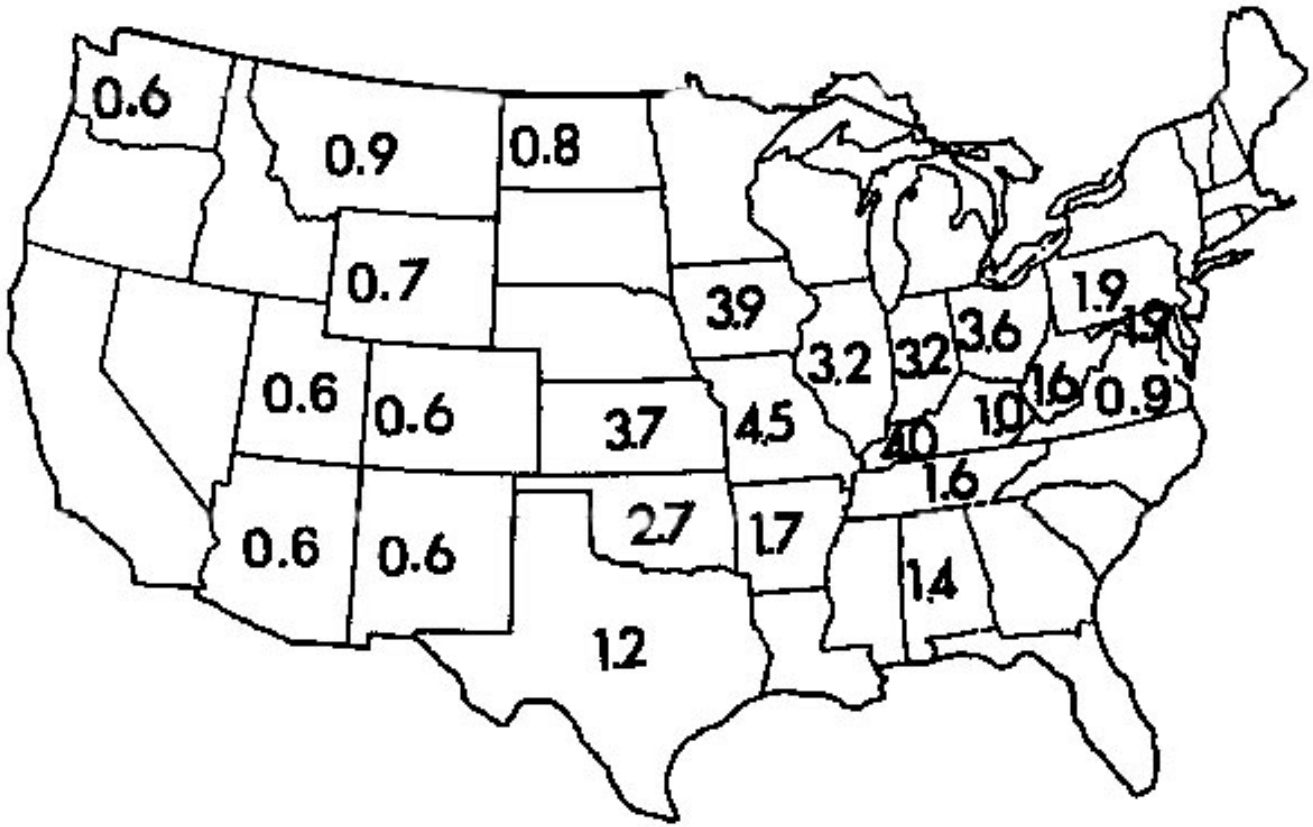
Example of a Fly Ash + NaOH Block

Class F fly ash plus 15 M NaOH cured at 90^{o}C.

Objective

- Optimize the manufacture of masonry block from flue gas desulphurization (FGD) materials:
  - using concentrated NaOH (4-15M) and
  - elevated curing (70^{o} and $185^{o}C$)

It all starts with coal type: Sulfur content of coals by region



Types of FGD (wet and dry)

In the East and Mid West U.S. where power plants tend to burn bituminous coal having 3-4 wt% sulfur, SOx removal is normally achieved by allowing the flue gas to come in contact with a solution containing $CaCO_3$ or $Ca(OH)_2$ mixed with water. The slurry can be injected into the exiting gas or the exiting gas can contact it in a bubble tower or some variant on this theme.

As an alternate, power plants burning sub- bituminous coal which has less sulfur (~1 wt%) than bituminous, these companies are able to use the calcium in their fly ash to sorb the SOx from their flue gases. This process is normally carried out in the dry state. The ash is collected in bag houses and recycled back into the system for a number of cycles. It is then removed and disposed of in land fills. This ash is normally referred to as dry FGD.

Flue Gas Desulphurization (FGD) Products

- Gypsum- $CaSO_4.2H_2O$
  - Produced under oxidizing conditions
  - Relatively soluble
  - Used for wall board (dry wall)
- Hannebachite- $CaSO_3.H_2O$
  - Produced under reducing conditions
  - Relatively insoluble
  - No known use

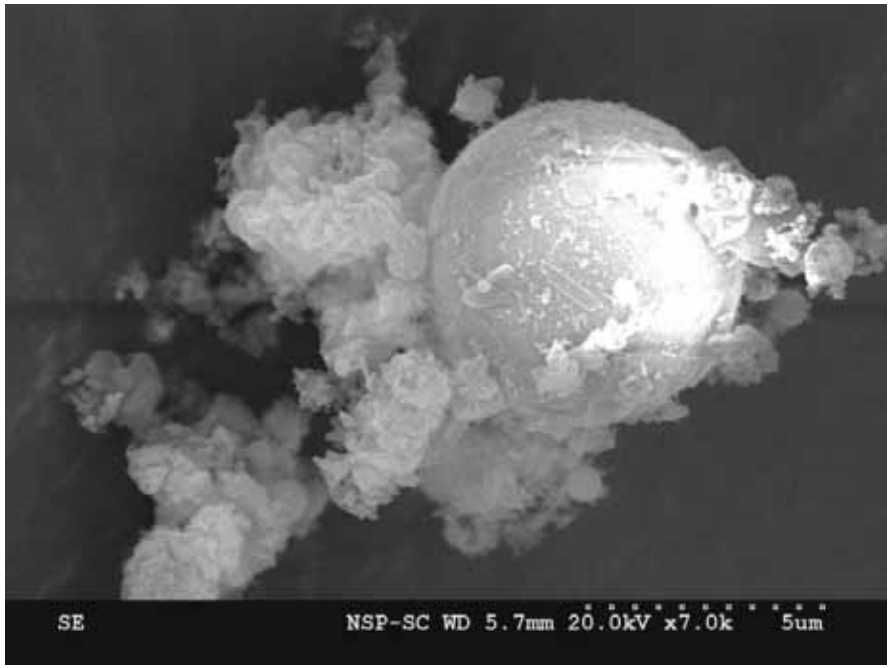
FGD Sources

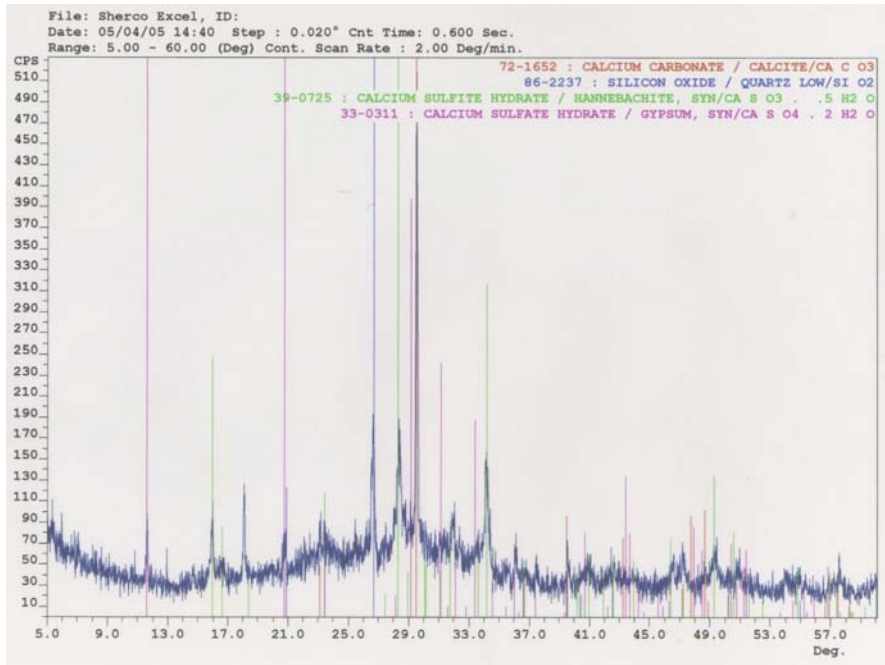
Two FGD materials were tested:

1. A dry FGD from Northern State Power Company (SHERCO) which is a Class C ash coated with calcium sulfate/calcium sulfite hydrates.

2. A wet scrubber filter cake from Indianapolis Power and Light (IPL) that we combined with their Class F fly ash.

Phase chemistry of SHERCO FGD





FGD contains Class C fly ash with overgrowths of sub-micrometer gypsum and hannebachite crystals.

Judging by the X-ray, the amount of FGD is relatively small.

NSP Mixture Design

Because the SHERCO FGD is already a combination of Class C ash and FGD material, no other solid ingredients were used.

Three mixes using SHERCO FGD were made using 15, 8, and 4 molar sodium hydroxide.

The mixes were designed to cover a reasonable span of liquid to solid ratios that could be expected to develop strength: pourable, intermediate, and nearly solid.

The pastes were precured at 70°C overnight and tested, or autoclaved at 180°C for 8 additional hours and then tested.

SHERCO Mixtures

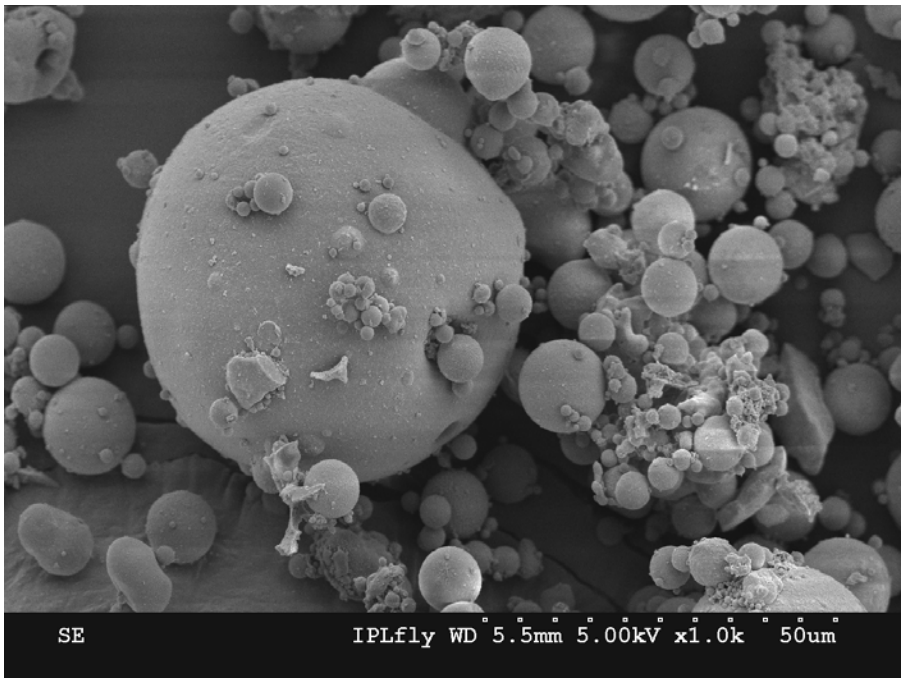
Sample	Solid Mixture		NaOH		NaOH/Solid Ratio	
	FA (g)		M	(g)		
1	700		15	374	0.534	
2	600		15	491	0.818	
3	700		15	622	0.889	
4	800		8	250	0.313	
5	700		8	362	0.517	
6	702		8	635	0.905	
7	840		4	263	0.313	
8	740		4	391	0.528	
9	520.1		4	413	0.794	

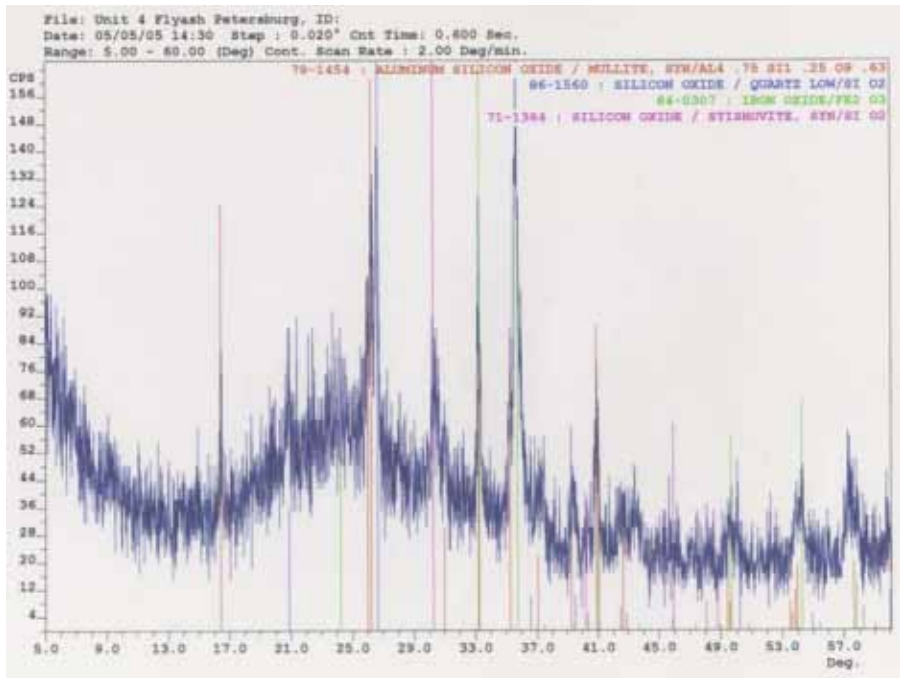
SHERCO Continued

The cubes were hard after precuring at 70^{o}C. They were either tested as is or tested after autoclaving in a steam heated autoclave at 185^{o}C for an additional 8 hours.

The two sets of cubes were tested in a Tinius Olsen screw driven compression testing machine.

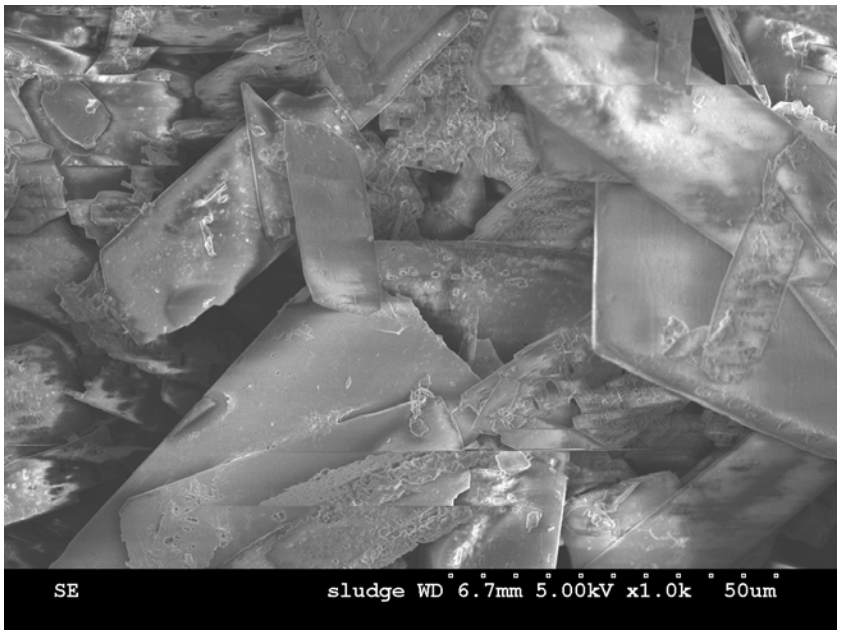
Phase chemistry of IPL fly ash

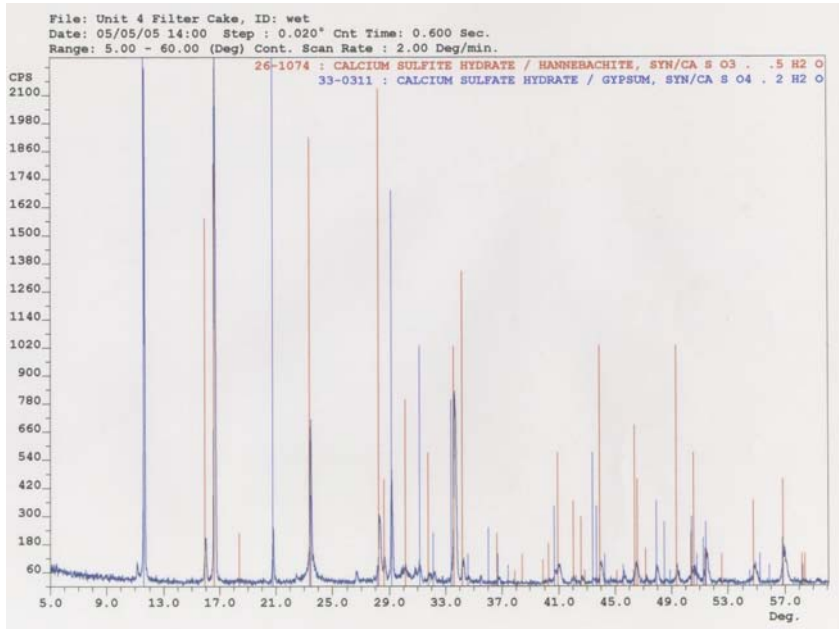




Fly ash is a Class F type. It has the typical rounded shape typical of theses ashes. X-ray suggests that the fly ash contains iron oxide, mullite and a trace of quartz.

Phase chemistry of IPL FGD





IPL sludge consists of large plate-like crystals of hannebachite and gypsum.

IPL Mixture Design

The IPL FGD consists of a mixture of hannebachite and gypsum. In itself, it has no strength when mixed with NaOH and then cured at 70^{o} or 185^{o}C.

However when 10 wt% FGD (optimum amount) was combined with 90 wt% of IPL's Class F fly ash and sodium hydroxide it was possible to produce a block.

Three mixes using 10 wt% IPL FGD and 90 wt% Class F fly ash were made using 15, 8, and 4 molar sodium hydroxide.

The mixes were designed to cover a reasonable span of liquid to solid ratios that could be expected to develop strength: pourable, intermediate, and nearly solid.

The pastes were precured at 70°C overnight and tested, or autoclaved at 180°C for 8 additional hours and then tested.

Indianapolis Power & Light Mixes

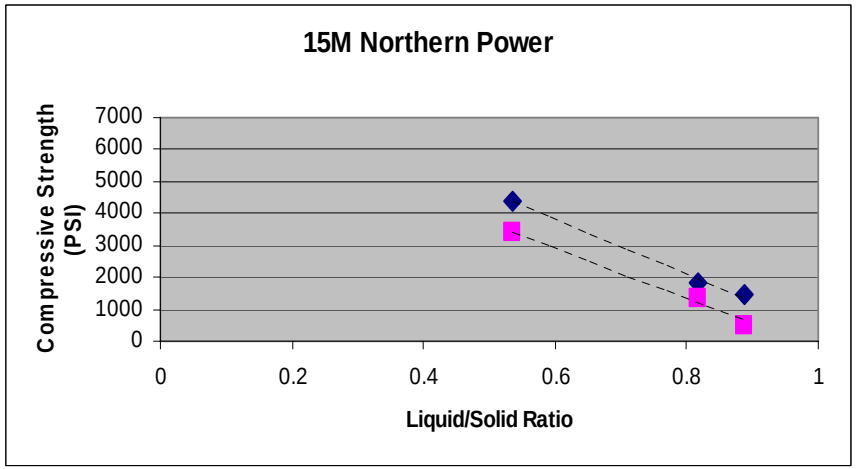
Sample	Solid Mixture		NaOH		NaOH/Solid Ratio
	FA (g)	FC (g)	M	(g)	
1	720	84	15	262	0.326
2	905	105	15	452	0.448
3	723	84	15	440	0.545
4	229	26	8	97	0.380
5	228	26	8	108	0.425
6	228	26	8	120	0.472
7	228	26	4	70	0.276
8	228	26	4	86	0.339
9	228	26	4	100	0.394

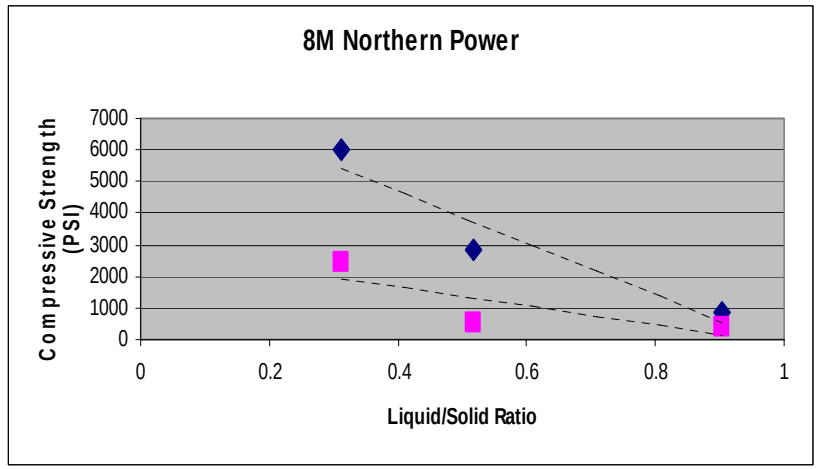
Continued

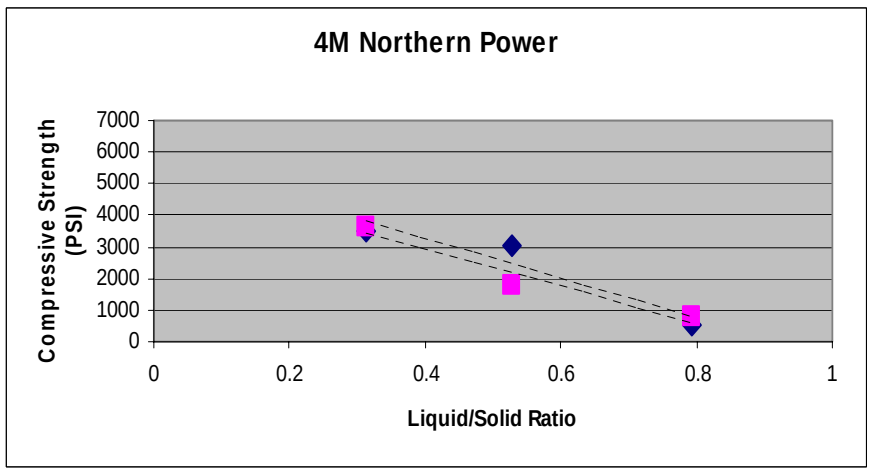
The cubes were relatively hard after precuring at 70^{o}C. They were either tested as is or tested after autoclaving in a steam heated autoclave at 185^{o}C for an additional 8 hours.

The two sets of cubes were tested in a Tinius Olsen screw driven compression testing machine.

Results for SHERCO samples

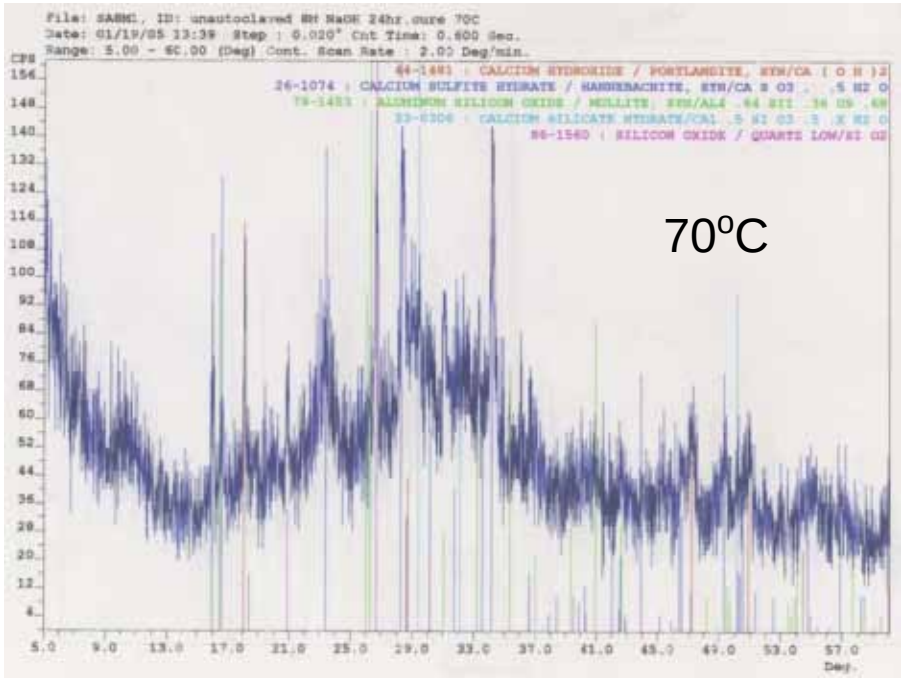


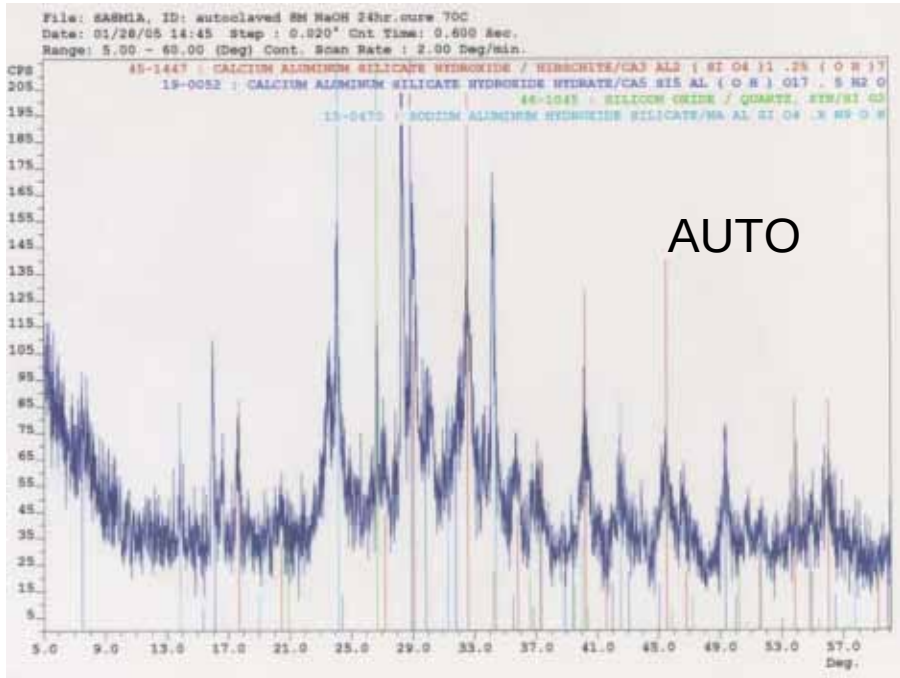




70°C samples are generally stronger than their AUTOCLAVED counterparts.

Phase Analysis by X-ray Diffraction

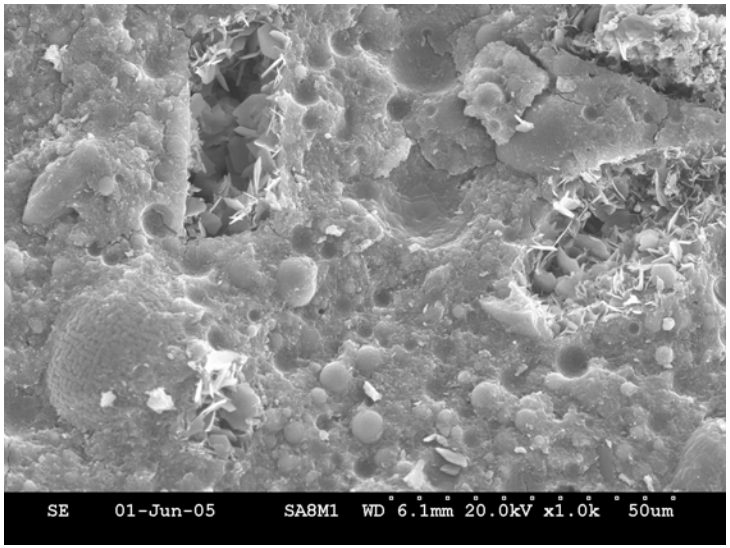


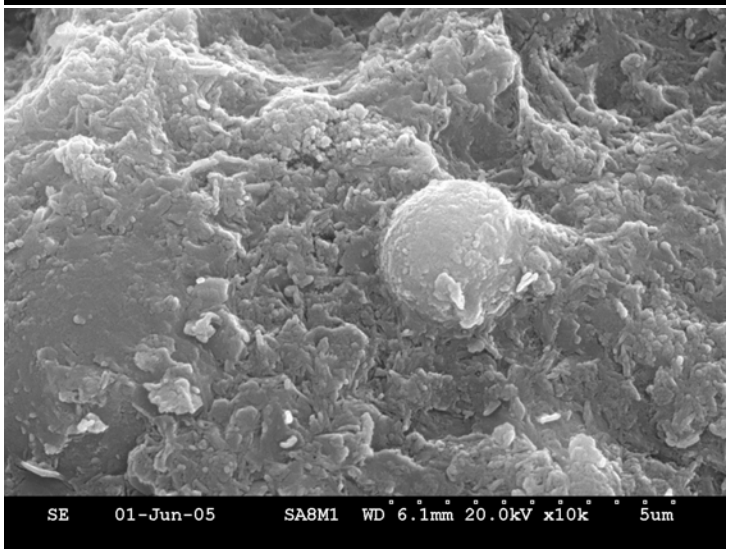


The 70°C sample was stronger. The major difference between the samples is the 70°C sample is far less crystalline than the autoclaved sample.

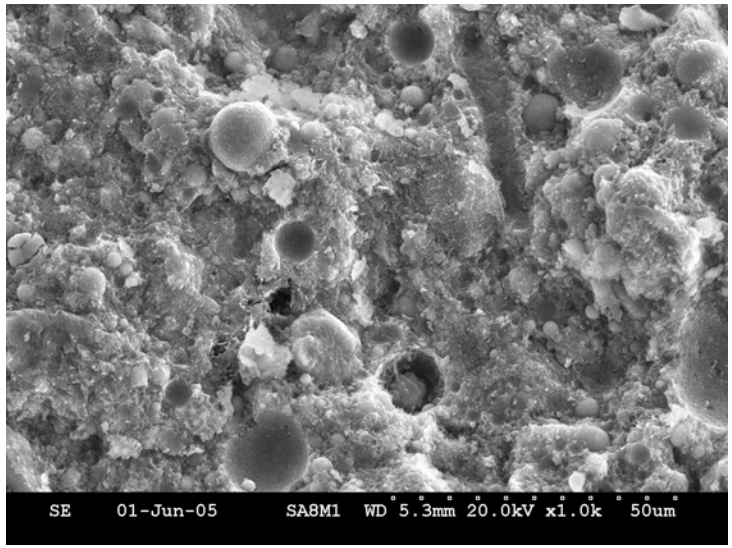
Microstructure of SHERCO samples

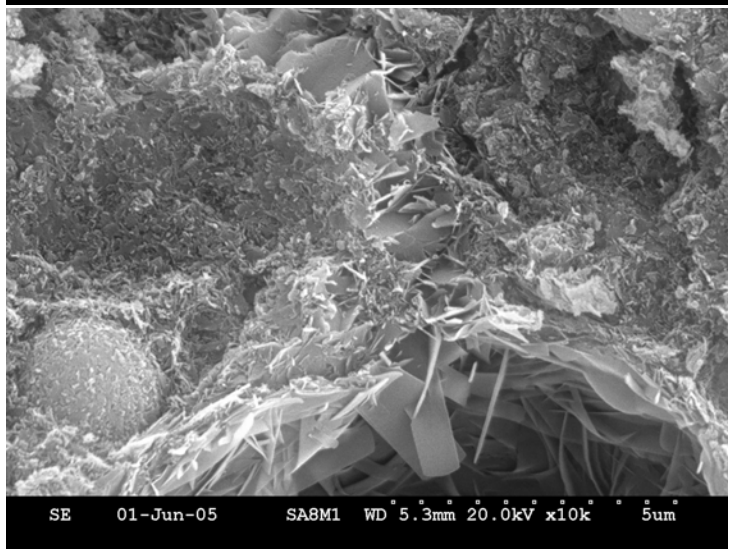
70°C



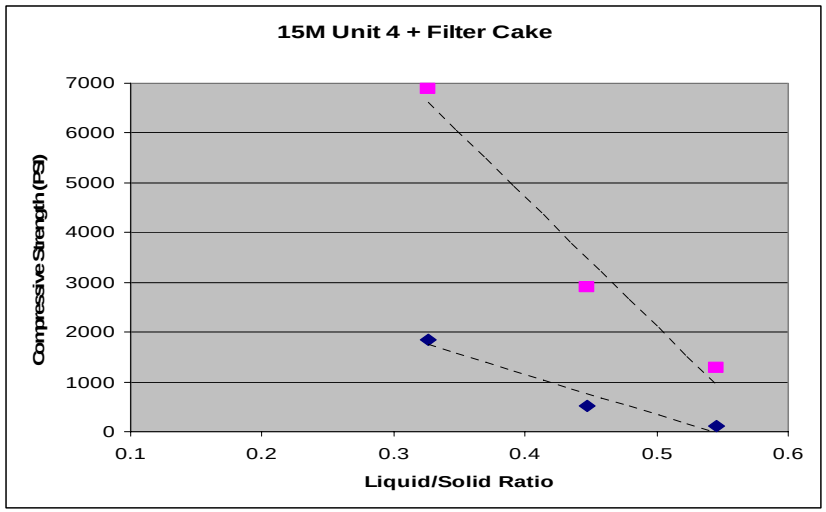


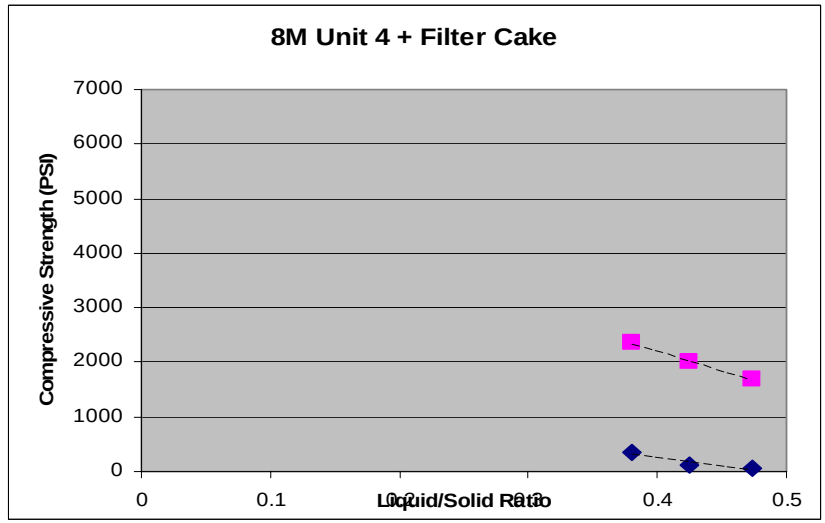
Autoclaved

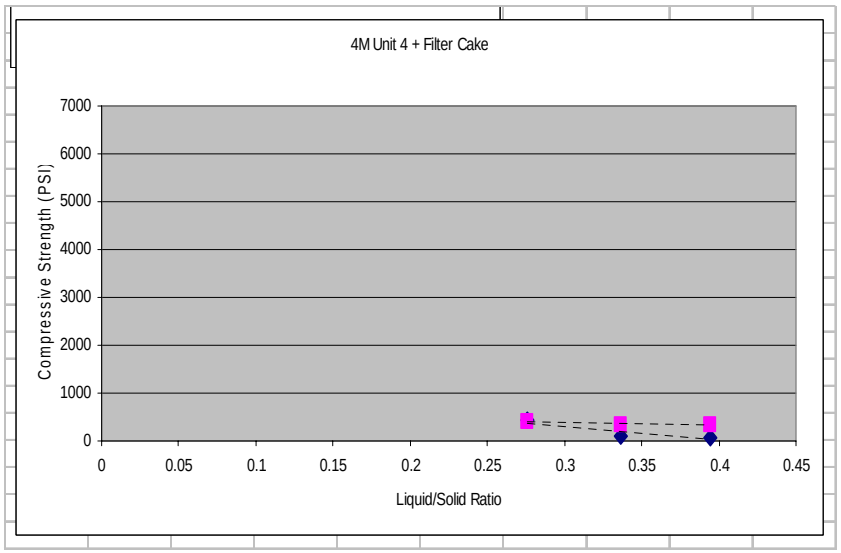




Results Indianapolis Power & Light

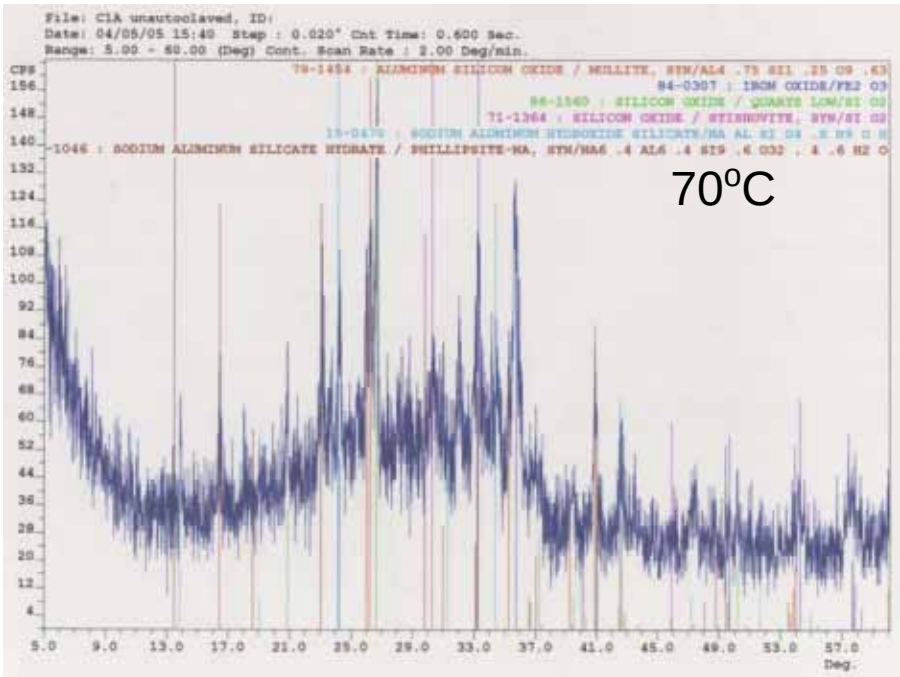


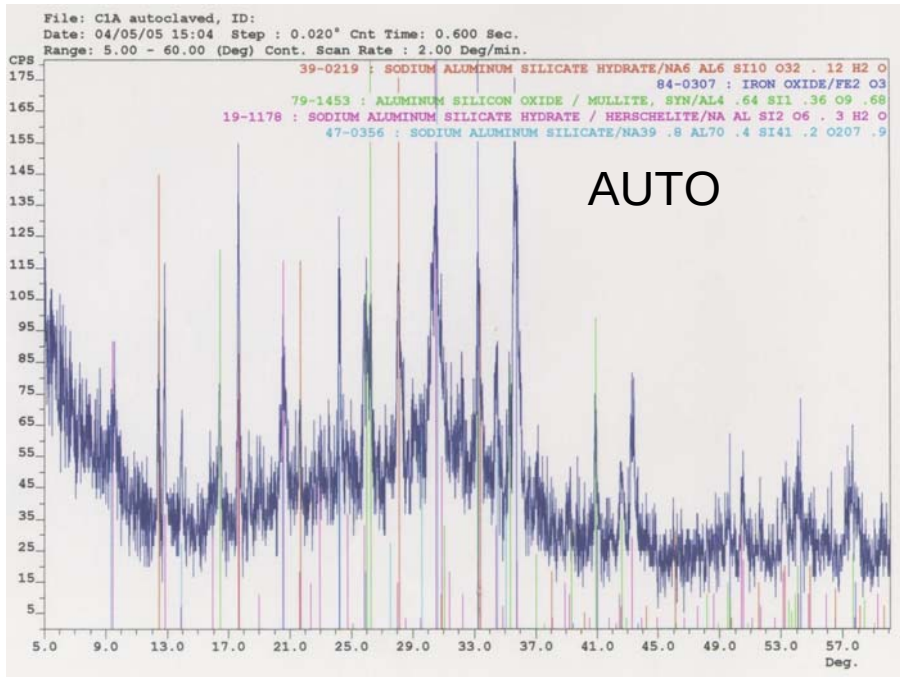




AUTOCLAVED samples are generally stronger than their 70°C counterparts.

Phase Analysis by X-ray Diffraction

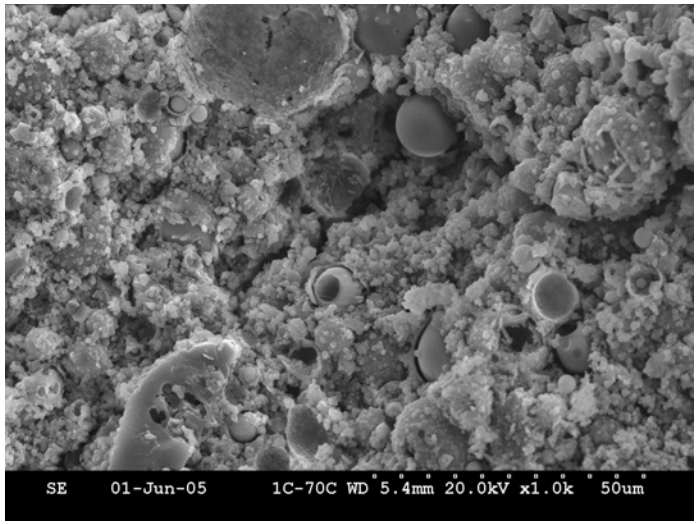


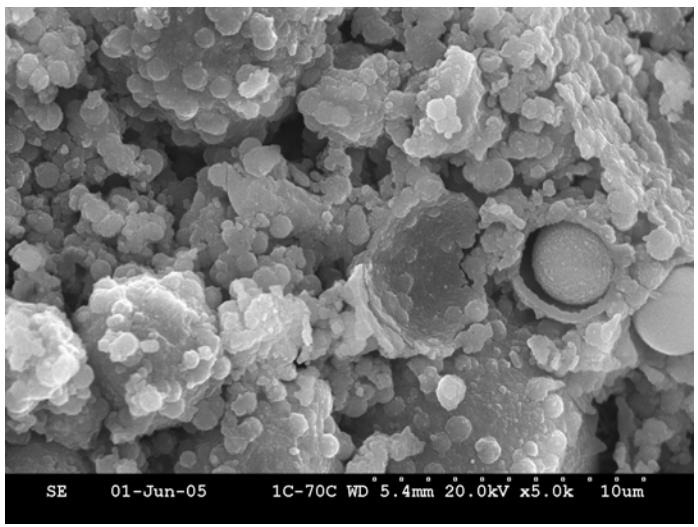


The autoclaved sample was stronger, but by all accounts both patterns look essentially the same.

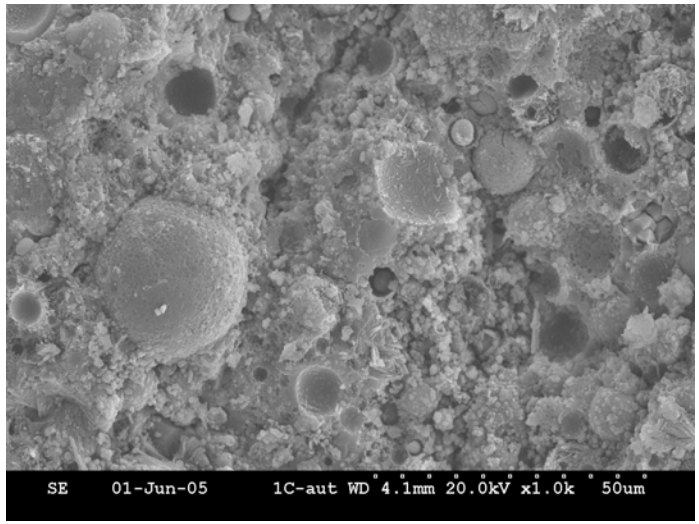
Microstructure of IPL samples

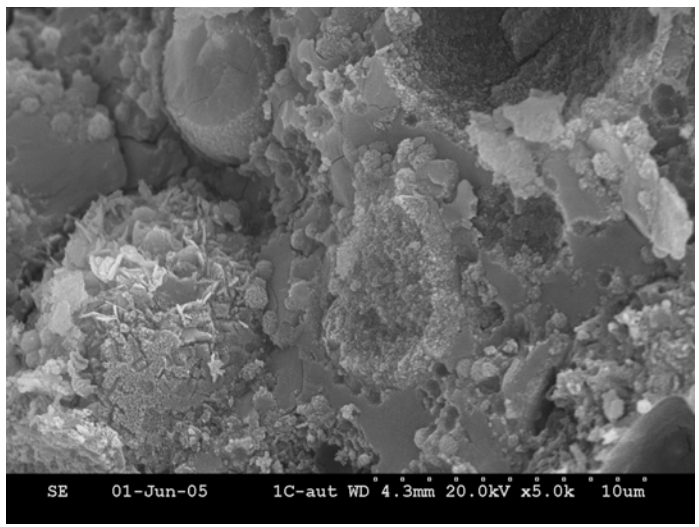
70°C



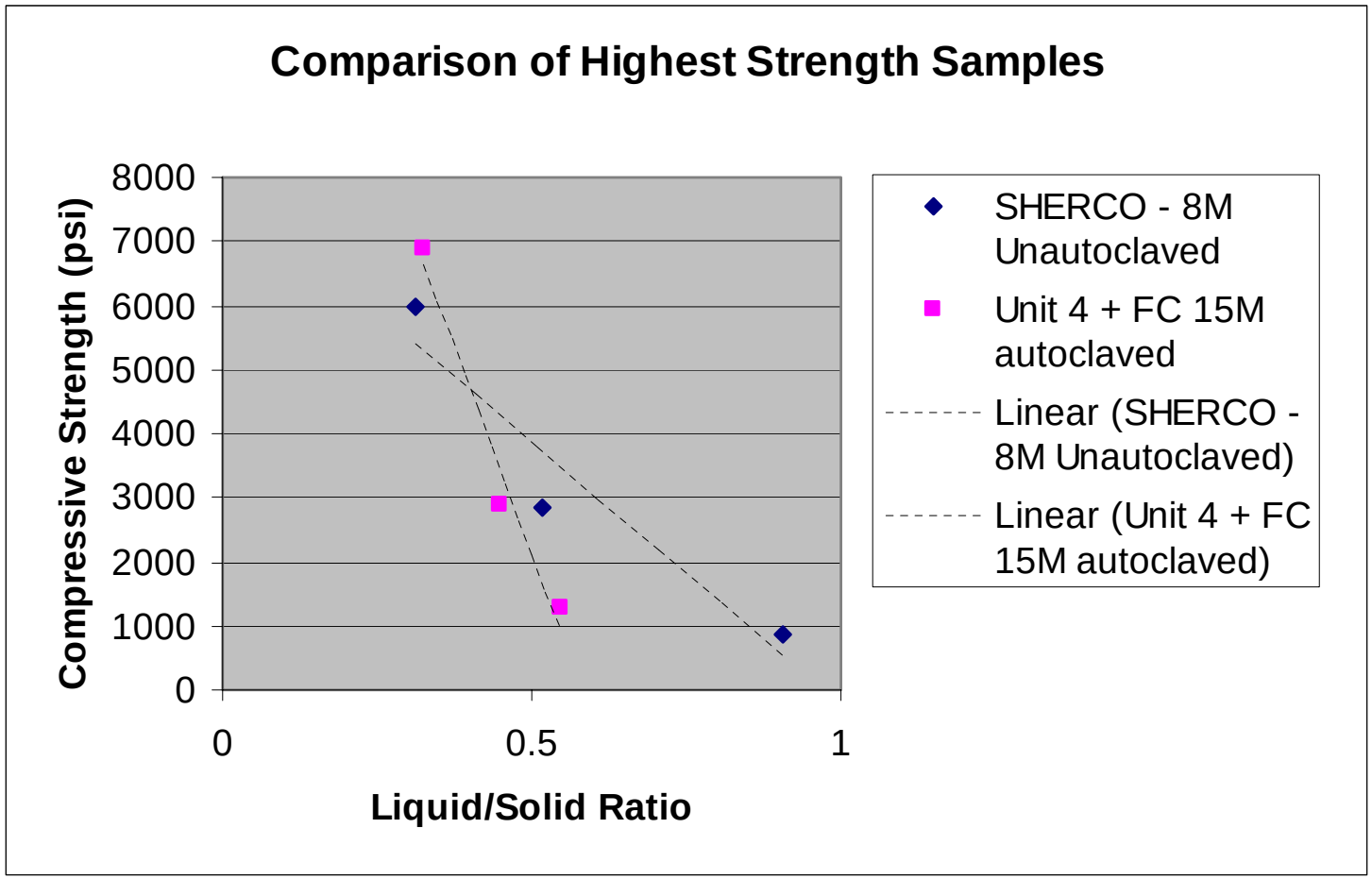


Autoclaved





Discussion


Comparison of Highest Strength Samples
Compressive Strength (psi)
8000
7000
6000
5000
4000
3000
2000
1000
0
0
0.5
1
Liquid/Solid Ratio
SHERCO - 8M Unautoclaved
Unit 4 + FC 15M autoclaved
Linear (SHERCO - 8M Unautoclaved)
Linear (Unit 4 + FC 15M autoclaved)

- A comparison of the maximum strengths attained between the strongest Northern State Power mortar (un-autoclaved) and the strongest IPL Unit 4 Ash with filter cake mortar (autoclaved) is shown here. The 8M un-autoclaved mortar samples displayed the highest strength when using Northern State Power Ash (5995 psi) mixed as a thick paste. The 15M autoclaved mortar tested strongest among the IPL Unit 4 and filter cake specimens (6885psi) also when mixed as a thick paste.

- Although the liquid/solid ratio varies greatly between the two samples, both Northern State Power and IPL Unit 4 Ash + filter cake mortar had the three same consistency states. Each mortar had a fluid, intermediate, and nearly solid consistency. The SHERCO ash was better able to accommodate more water without becoming too thin.

Conclusions

All samples having the lowest solution/solid ratio had the highest compressive strength.

Dry FGD ash consisting of Class C fly ash and FGD can be mixed with 8M NaOH and cured at 70°C to produce a very strong block (5995 psi), in fact stronger than its autoclaved equivalent. This suggests easy adoption by block plants using steam rooms to cure.

Although IPL Class F ash can be made to react with NaOH to form a solid, the solid actually becomes stronger when FGD is mixed with the ash at an optimum ratio of 10 wt% FGD to 90wt% fly ash. When autoclaved, this combination gives the strongest block of all (6885psi).

In this case an autoclave is required to cure the sample, but considering the fact that an utility like IPL has waste steam and a readily available source of Class F fly ash, the production of pavers on site could be profitable endeavor.

In either case waste materials are being used to manufacture a traditionally Portland cement based material. The NaOH activated materials are certainly greener and less destructive to the atmosphere vis à vis Portland cement which emits CO_2 to the atmosphere.

Future Directions

This is a work in progress and it is anticipated that as more samples are received and tested a more coherent picture will evolve. At this point it seems that a Class C ash with FGD additions mixed with minimal amounts of 8M NaOH that is cured at 70^{o}C, and a blend of 90 wt% Class F fly ash containing 10 wt% filter cake FGD mixed with minimal amounts of 15M NaOH and autoclaved give the strongest materials.

It is also noted that a pure Class F fly ash sample mixed with 15M NaOH and autoclaved gave us a block having a compressive strength of 6522 psi, just a few hundred psi below the composite sample. We believe that the hannebachite did not react and that the crystals served as a fiber-like addition strengthening the block.