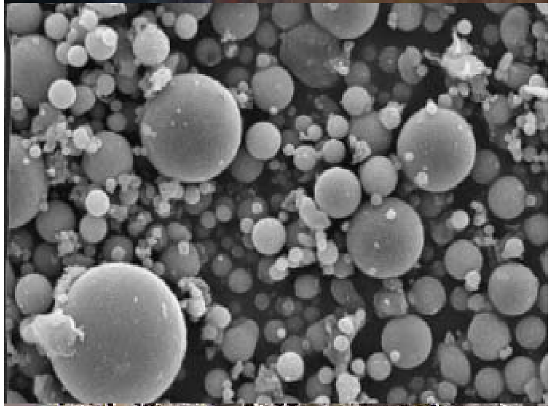
REINHOLD ENVIRONMENTAL Ltd.

2015 Wastewater-Ash Round Table Presentation

September 22, 2015, in Charlotte, NC / Hosted by Duke Energy



Disposal and Treatment Alternatives for Flue Gas Desulfurization Wastewater

Wastewater/Ash Conference

September 22 2015
Charlotte, NC

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Vice President

Research & Development

Headwaters Resources Inc

the leading coal combustion products management company

- Exclusive long-term supply agreements
  - ~100 power plants in 35 states
  - Complete utility service capabilities
- Nationwide infrastructure
  - 22 fly ash terminals
  - Over 50 quality fly ash sources
  - Over 250 trucks/1,000 railcars
- Technology advancements
  - ASM® (ash beneficiation)
  - RestoreAir ® (ash beneficiation)
  - Flexcrete ® (50% ash block)
  - Other building products applications

A construction material and building product company

Affiliated Companies in leading building products market positions:
Eldorado Stone, Southwest Concrete Products, TAPCO group & Entegra roofing

Headwaters R&D and Technical Services

Material Testing and Research Facility (MTRF) in GA

Quality Assurance lab in TX and regional tech support staff.

- **Quality Assurance Testing**: About 3,000 standard tests per year (C618, etc.) to support the sales of fly ash and other CCP's.
- **Technical Support**: Over 50 projects per year to assess impact of sorbent injection, other changes to ash quality, specialty testing and performance evaluation for new products and materials.
- **Research & Development**: Technologies to improve ash quality, mitigate sorbent impact, increase ash utilization and develop new applications.

Background

New EPA power plant effluent limitation guidelines (ELGs) will require treatment of wastewater streams from coal fired plants before release into surface waters.

FGD Waste Water contains high salt concentrations and trace levels of constituents of concern (Se, Cr, As) - challenging to handle.

Utilities may be required to build extensive onsite treatment facilities to comply with ELGs.

Objective

Preliminary lab scale study (ash related) to evaluate options for the disposal or treatment of FGD Waste Water.

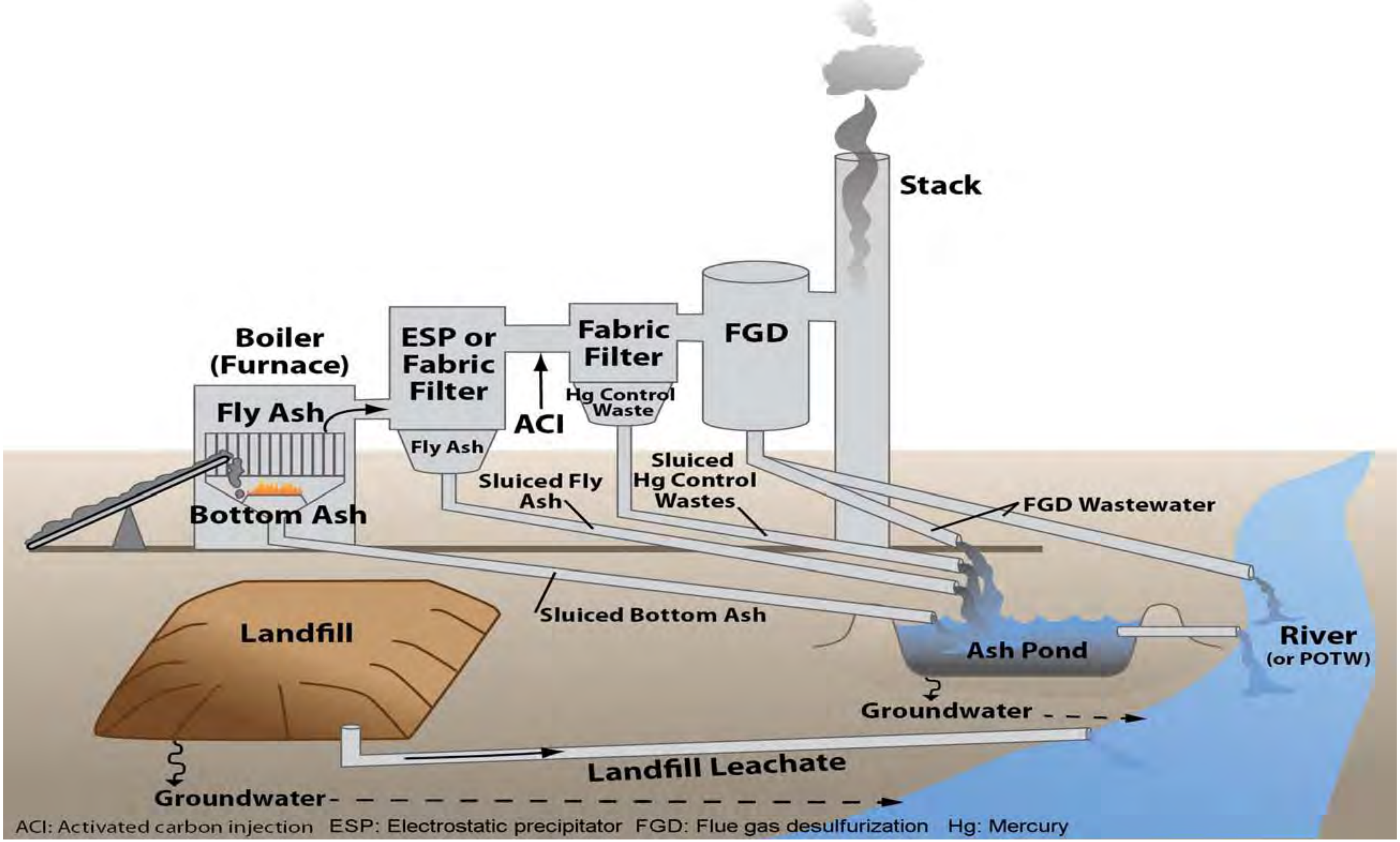
Solidification/Stabilization

Fly ash geopolymer formulation for geotechnical stability and minimize release to environment.

Water treatment with Soda ash (Na_2CO_3)

Recover by-products for beneficial use with ash in concrete.

POWER PLANT WASTEWATER



Source: http://water.epa.gov/scitech/wastetech/guide/steam-electric/proposedimage.cfm

Focus – FGD Waste Water

Chemical Constituent	Concentration [mg/L]
Calcium (Ca)	39000
Chloride (Cl^-)	6000
Magnesium (Mg)	3900
Sulfate (SO_4^{2-})	1200
Bromide (Br^-)	81
Sodium (Na)	52
Potassium (K)	17
Silicon (Si)	16
Manganese (Mn)	1.1
Zinc (Zn)	0.93
Selenium (Se)	0.33
Cadmium (Cd)	0.083
Phosphorus (P)	0.047
Iron (Fe)	0.028
Chromium (Cr)	0.009
Arsenic (As)	0.002

$CaCl_2$

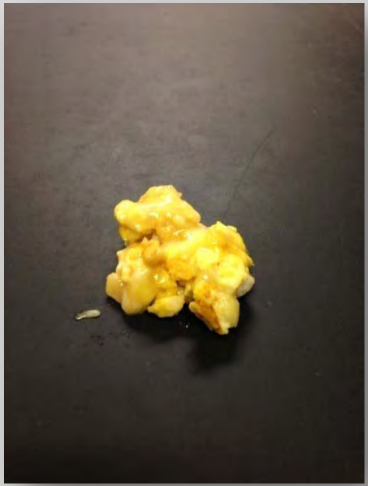
An example of FGD Waste Water from a power plant burning Illinois Basin Coal

*Drying **$CaCl_2$** brine water is:*
Problematic

$CaCl_2$: Extremely hygroscopic and deliquescent
~2g water absorbed per 1g of dry FGDWW

FGD Brine

Dried FGD Brine



After 4 hours exposed to ambient lab conditions

After 24 hours exposed to ambient lab conditions

FGD WW Solidification/Stabilization with Fly Ash and NaOH Activator

A relatively simple concept:

Mix the following to form a solid matrix:

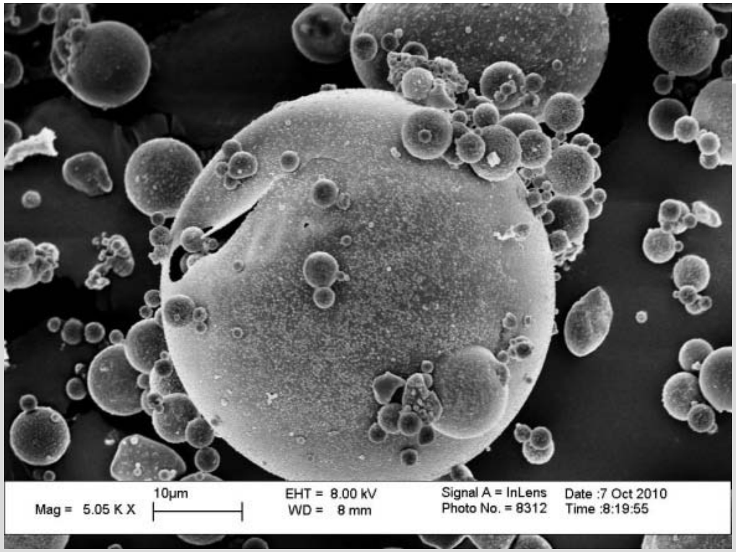
(1) FGD waste water
(2) fly ash
(3) NaOH

Evaluation:

1. **Stability by compressive strength after 3 and 7 days of curing.**
2. **Leaching of chemical constituents: LEAF Method 1315**

Fly Ash Chemical and Physical Characteristics

Major Oxides	% Composition
SiO_2	55.28
Al_2O_3	27.21
Fe_2O_3	7.98
CaO	1.26
MgO	1.23
SO_3	0.07
Na_2O	0.47
K_2O	3.02
P_2O_5	0.19
TiO_2	1.41
LOI	1.40
Total	99.52



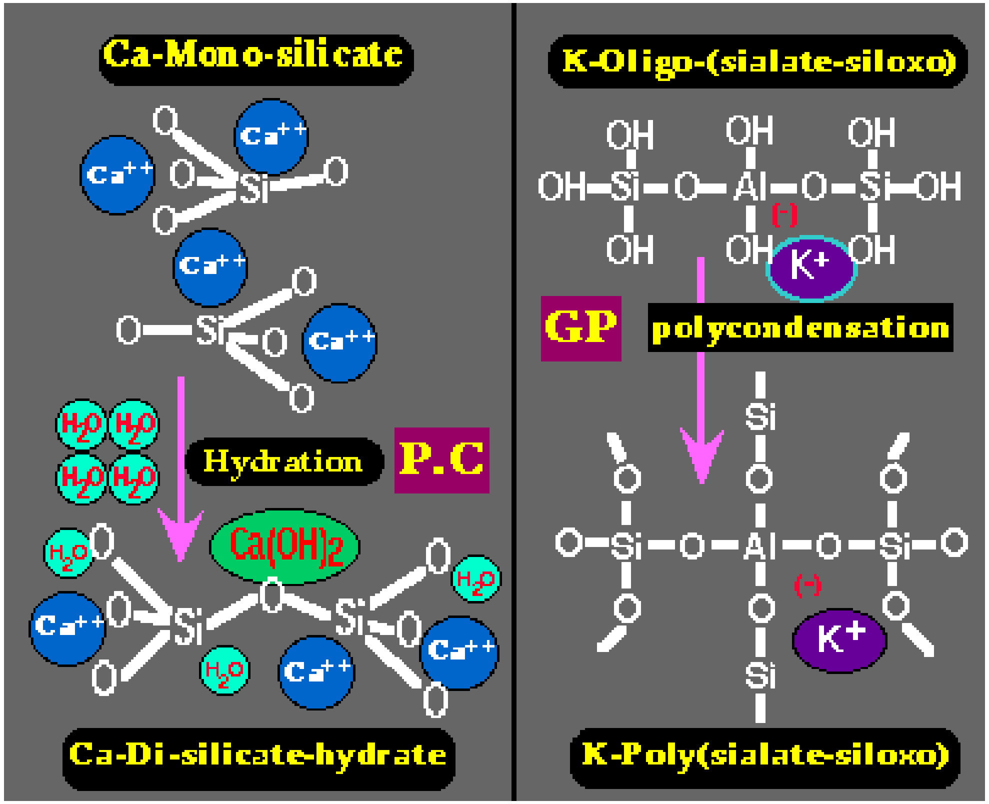
Physical Characteristics	
Total Residual Carbon (%)	1.1
Specific Surface area (m^2/g)	1.27
Specific Gravity	2.63
Median Particle Size (µm)	16.2

Fly Ash ………..How does it work?

The pozzolanic reactivity of ash comes from the rapid-quenching of the molten minerals forming its disordered atomic structure. This amorphous structure allows fly ash to react under certain chemical conditions.

The pozzolanic reaction requires "chemical activation" by an alkali such as:

- **$Ca(OH)_2$ in portland cement systems**
- **NaOH, KOH, etc. in "geopolymer" systems**



Solidification/Stabilization

Results

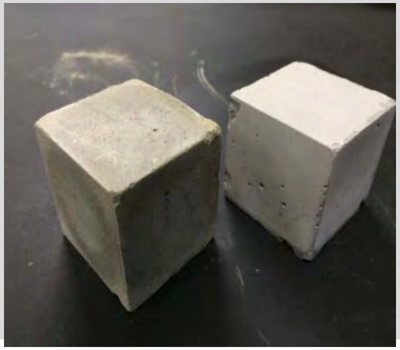
Mix #	3 Molar NaOH Activator	FGDWW/FA	3 Day Strength (psi)	7 Day Strength (psi)
1	12 Mol. NaOH solution diluted with FGDWW to make 3 Molar solution	0.33	**965**	**1,240**
2	NaOH (solid) introduced directly into FGDWW (to make 3 Molar solution.	0.45	**914**	**1,020**

Conclusions:

Direct dissolution of dry NaOH in the FGD WW is effective

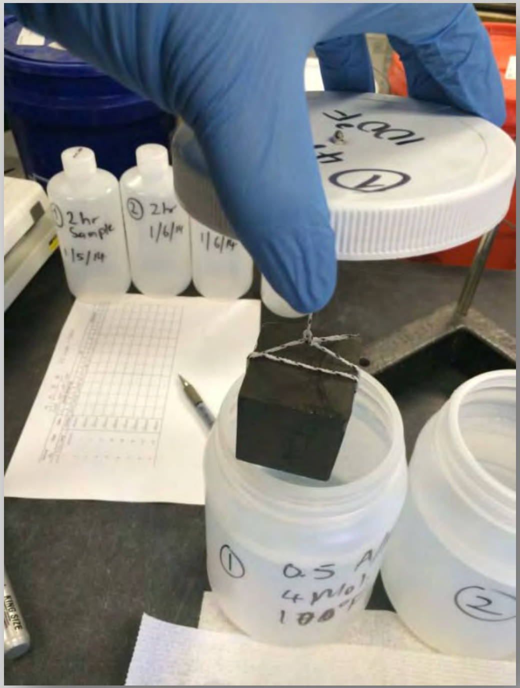
Stable geopolymer blocks are formed

Heating will accelerate geopolymerization.



LEACHING FROM SOLIDIFIED FGDWW

LEAF Method 1315

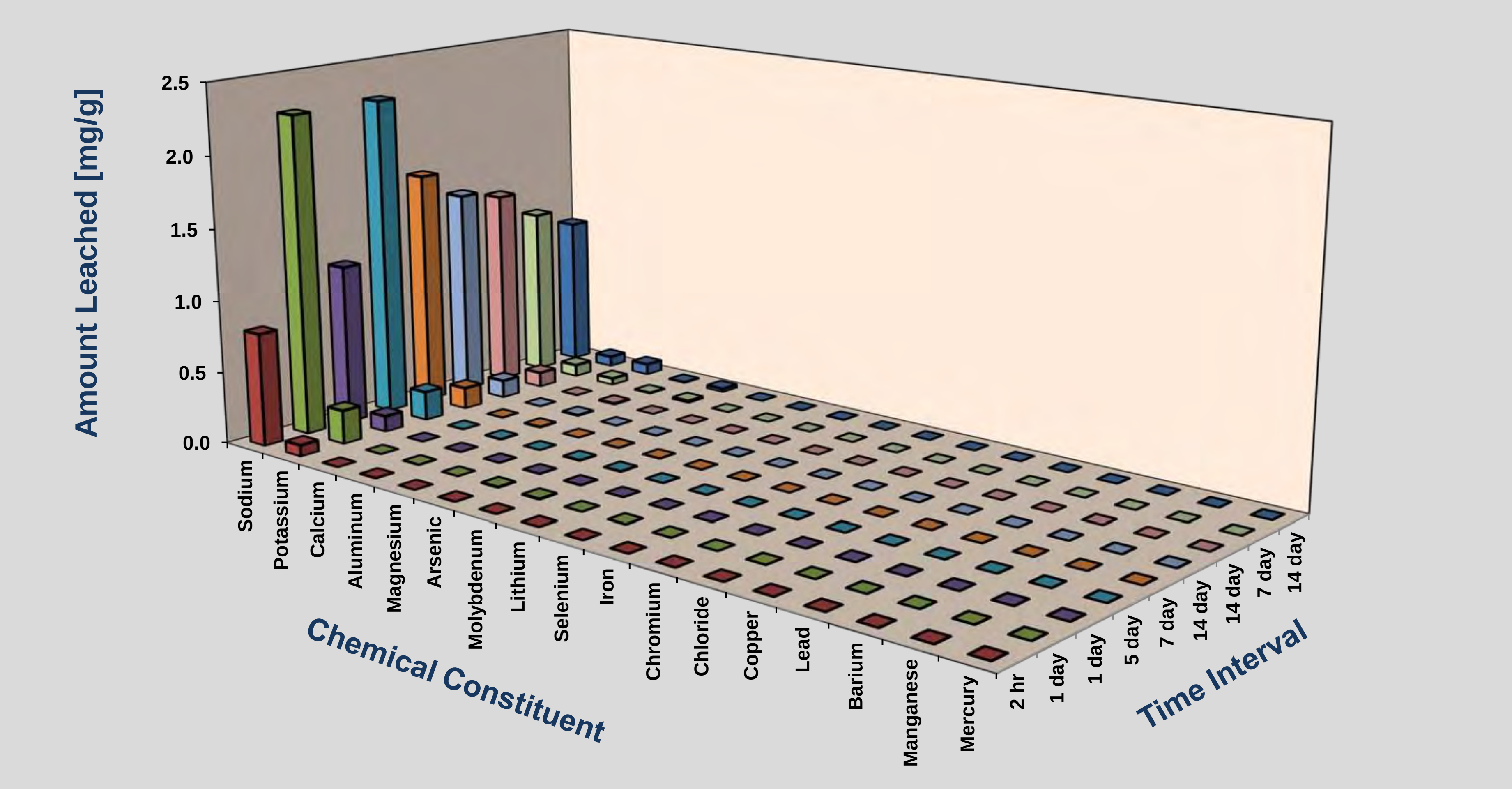


Laboratory setup for LEAF leaching test. Geopolymer blocks suspended in DI water.

Chemical Constituent	Total Amount Leached [mg/g]	
	Mix #1	Mix #2
Sodium	13.13	9.69
Potassium	1.17	0.39
Calcium	0.14	0.10
Aluminum	0.04	0.06
Magnesium	0.04	0.04
Arsenic	0.02	0.02
Molybdenum	0.02	0.02
Lithium	0.01	0.01
Selenium	4.5E-03	3.9E-03
Iron	2.8E-03	2.8E-03
Chromium	1.5E-03	2.2E-03
Chloride	9.9E-04	1.3E-03
Copper	5.7E-04	3.0E-04
Lead	4.9E-04	8.6E-05
Barium	1.0E-04	1.0E-04
Manganese	2.2E-05	4.2E-05
Mercury	6.4E-06	5.3E-06

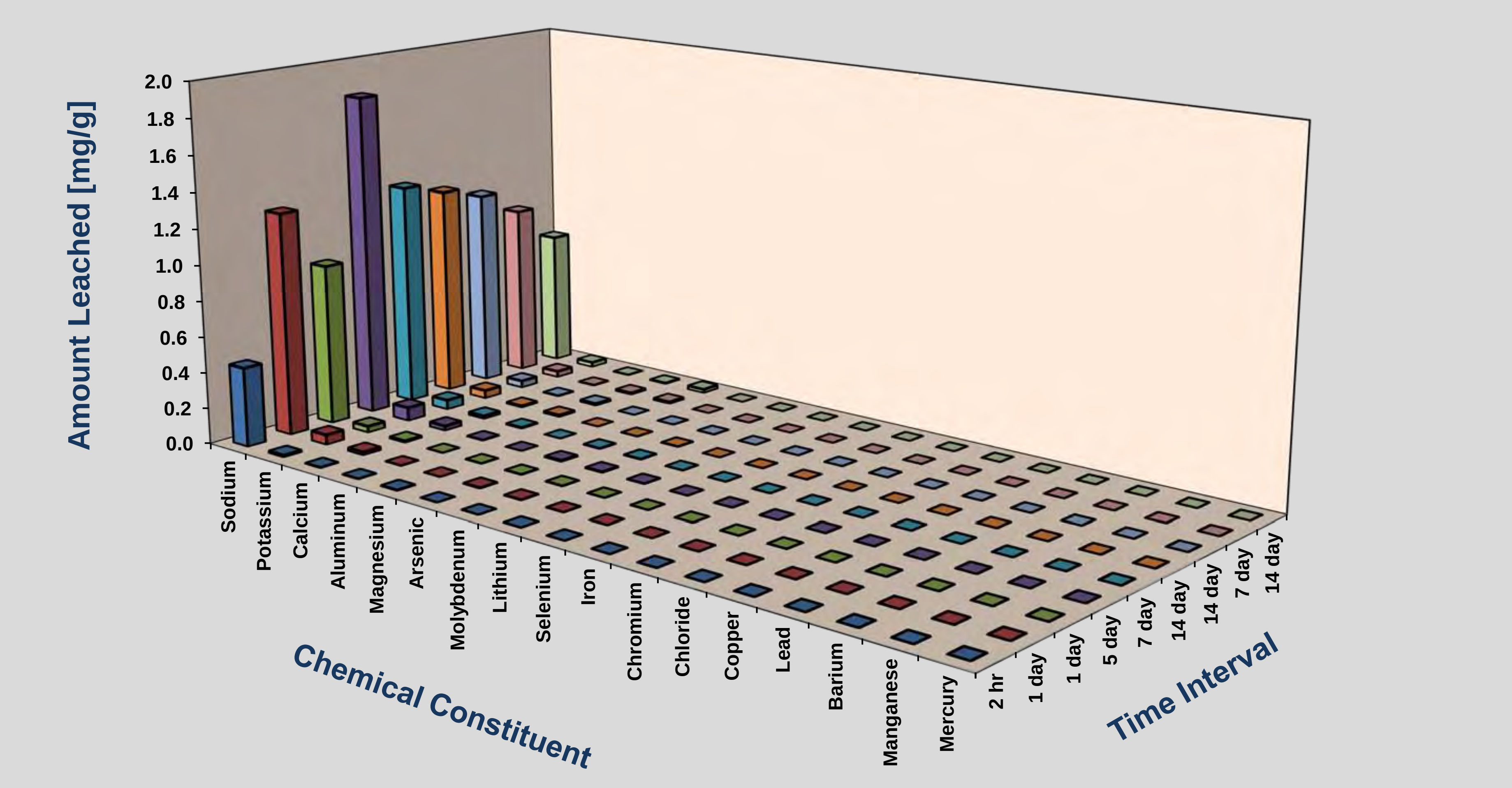
LEAF Results

Geopolymer Mix #1



LEAF Results

Geopolymer Mix #2



Solidification/Stabilization

Material Cost

Cost		
Fly ash	20	$/ton
NaOH	0.70 1360	$/lb $/ton

Technically feasible
Cost prohibitive

Component	Mix #1	Mix #2
Activator	FGDWW+ NaOH pellets	FGDWW + 12 M NaOH
NaOH Concentration	3 Mol.	3 Mol.
Activator/Ash Ratio	0.5	0.5
FGDWW/Ash Ratio	0.33	0.45
NaOH (per 1000 gallon FGDWW)	$ 990	$ 750
Ash (per 1000 gallon FGDWW)	$ 270	$ 200
Total (per 1000 gallon FGDWW)	$ 1260	$ 950

Treating FGDWW with Soda Ash

Basic chemical reaction involved in the process:

$$CaCl_{2\ \text{aqueous}} + Na_2CO_{3\ \text{solid}} \rightarrow CaCO_{3\ \text{solid precipitate}} + 2NaCl_{\text{aqueous}}$$

FGDWW

Filter, dry and collect

Easier to handle than $CaCl_2$

Evaluation:

Beneficial use of $CaCO_3$ precipitate in concrete, similar to Portland Limestone Cement (PLC) – *Patent pending*

- Particle size distribution of OPC/$CaCO_3$ blends
- ASTM C311 – Strength Activity Index
- Isothermal calorimetry

Laboratory Scale Procedure

FGDWW as received

FGDWW treated with Na_2CO_3

Filtered FGDWW after Na_2CO_3 treatment

Filtered and dried

Dried

Solid Byproduct #1
Primarily $CaCO_3$
D_{50} = 13 µm

Solid Byproduct #2
Primarily NaCl

Water quality comparison before & after precipitation of calcium carbonate

	Concentration [mg/L]	
Chemical Constituent	**FGDW (CaCl aqueous)**	**Treated FGDW (NaCl aqueous)**
Calcium	39,000	6.2
Chloride	6,000	6,200
Magnesium	3,900	39
Sulfate	1,200	910
Bromide	81	62
Sodium	52	26,000
Potassium	17	140
Silicon	16	5.3
Manganese	1.1	0.043
Zinc	0.93	0.035
Selenium	0.33	0.21
Cadmium	0.083	ND
Phosphorous	0.047	1
Iron	0.028	ND
Chromium	0.009	0.029
Arsenic	0.002	0.011
Aluminum	ND	ND
Copper	ND	ND
Lead	ND	0.026
Mercury	ND	ND

Note:

ND = non-detect

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Solid Byproducts
Calcium Carbonate and Sodium Chloride

Chemical Constituent	Concentration [mg/kg]	
	Precipitate ($CaCO_3$ solid)	Dried Filtrate (NaCl solid)
Calcium	220,000	4,300
Chloride	69,000	560,000
Sodium	65,000	290,000
Magnesium	12,000	14,000
Boron	6,700	6,600
Bromide	2,100	11,000
Potassium	1,600	7,700
Selenium	70	93
Cadmium	29	ND
Barium	13	1.6
Arsenic	5.3	ND
Chromium	3.6	6.30
Lead	2.3	1.9
Mercury	1.0	2.8
Iron	ND	54
Aluminum	ND	44
Copper	ND	ND

Precipitation and dewatering process can be optimized to reduce chlorides in $CaCO_3$ and reduce constituents of concern from water soluble NaCl

Note:
ND = non-detect

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Potential Beneficial Uses
Calcium Carbonate and Sodium Chloride

Applications	$CaCO_3$	NaCl
ASTM C595-12 acknowledges 15% limestone thershold in portland cement – type IL, portland limestone cement.	portland limestone cement	Leather tanning brine
	Adhesives, Paint and Coatings	Deicing salt
	Carpet backing	Extinguishing agent in fire extinguishers.
	Paper	Chlorine source - for chlorine used in PVC and pesticide production.

Why portland limestone cement?

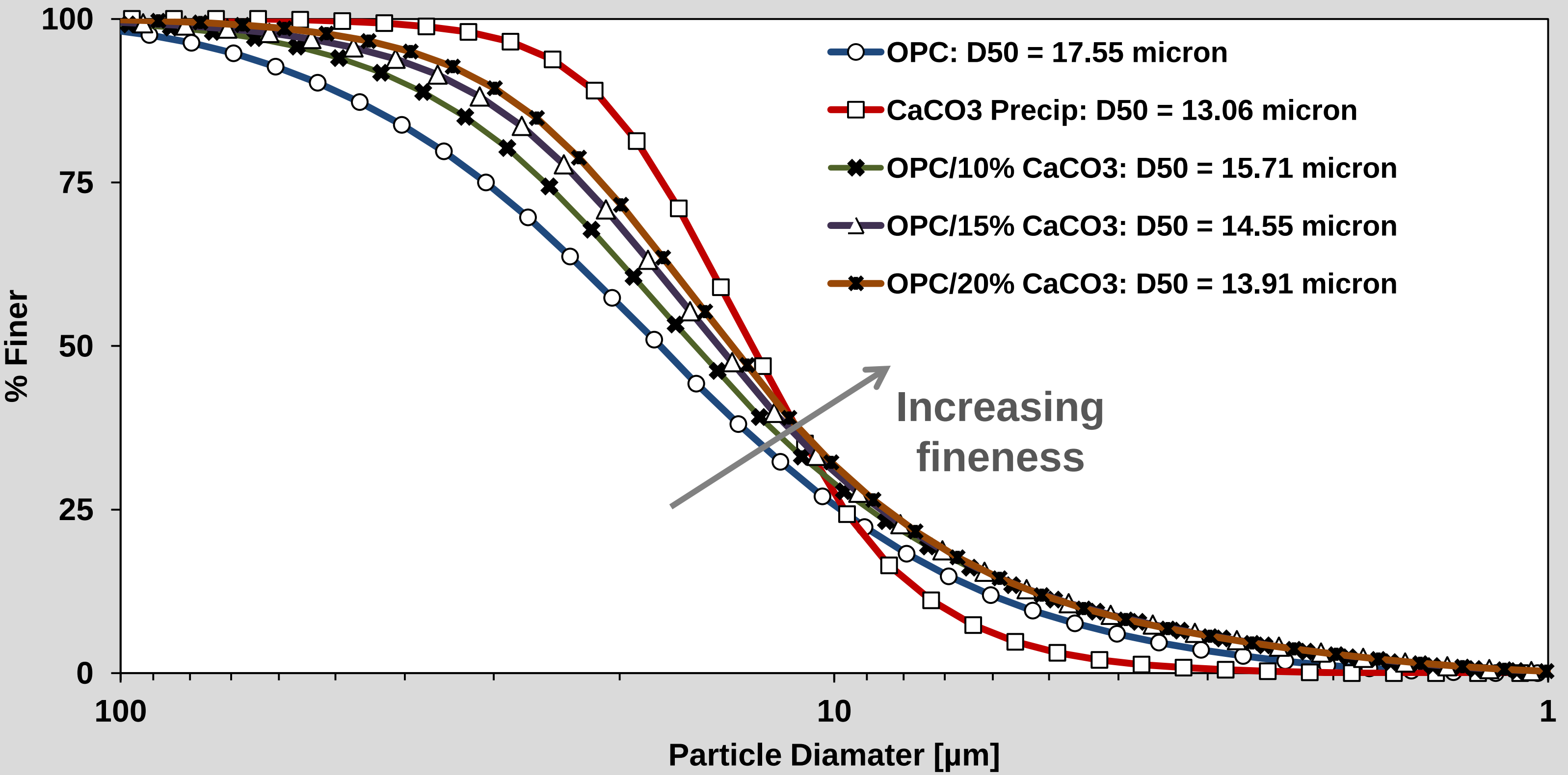
When OPC's w/ up to 5% limestone are replaced with PLC's containing 10% to 15% limestone, the resulting impact per million tons of cement produced equates to:

- 443,000 to 664,000 million BTU less clinkering energy
- millions of pounds less SO_2, NOx, and CO emissions
- 189,000 to 283,000 tons reduction of CO_2emissions
- Improvements in permeability and other concrete durability parameters are possible

Potential for ash/limestone blend at power plants

Constituents of concern are immobilized in concrete

Particle Size Distribution of Cement/CaCO3 blends



Strength Activity Index

ASTM C311

ASTM C311 Parameter		OPC Control	10% $CaCO_3$	15% $CaCO_3$	20% $CaCO_3$
Water in mortar	**Mass [g]**	242	242	242	242
	% of Control	-	100%	100%	100%
Flow	**Diameter [mm]**	211	205	201	193
	% of Control	-	97%	95%	91%
7 day Compressive Strength	**[MPa]**	34	29	26	24
	[% of control]	-	86%	78%	69%
28 day Compressive Strength	**[MPa]**	38	33	32	28
	[% of control]	-	88%	84%	74%

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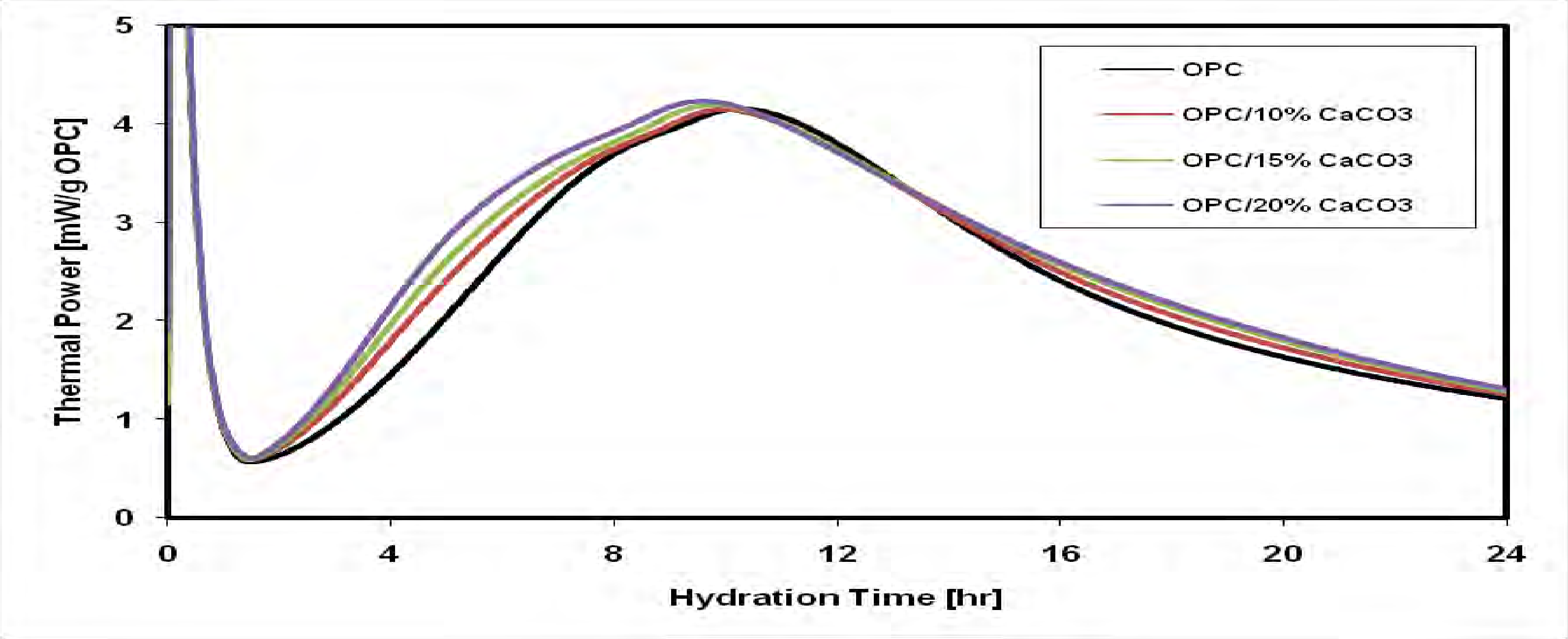
Isothermal Calorimetry



Hydration time and heat release of OPC paste compared with OPC/$CaCO_3$ blends of 10%, 15%, and 20% OPC substitution rates at water/cement of 0.4%

Soda Ash, CaCO3 Precipitate Quantities:

	Cost	
Soda Ash	$ 290.0	per ton

IB Coal Power Plant	
400	gal/min
40,000	mg/L Cl
136	Ton/day $CaCO_3$
158	Ton/day NaCl
144	Ton/day $NaCO_3$
Cost of	**Reagent**
$ 72	per 1000 gal

PRB Coal Power Plant	
50	gal/min
1,000	mg/L Cl
0.42	Ton/day $CaCO_3$
0.50	Ton/day NaCl
0.45	Ton/day $NaCO_3$
Cost of	**Reagent**
$ 1.8	per 1000 gal

Do not include other costs such as CapEX and OpEX (processing, drying, etc.)

Conclusions and Recommendations

Solidification/Stabilization of FGD waste water using ash based geoplymerization is technically feasible but cost prohibitive.

It could have a role in solidification of concentrates in conjunction with evaporative drying of wastewater.

Converting calcium chloride to calcium carbonate and sodium chloride by soda ash treatment is an interesting approach.

Recovery of calcium carbonate and sodium chloride for beneficial use might be an option for some power plants waste water streams.

Further studies addressing process scale up, economic feasibility, balance of plant, fate of constituents of concern, as well as market acceptability of recovered materials are recommended.

COMMENTS/QUESTIONS?

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