Use of Calcium Based Products to Stabilize Ponded Coal Combustion Products - Techniques and Results

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Abstract

The prospect of more stringent regulations for coal ash impoundments is leading companies in the power industry to evaluate new processes for stabilizing existing facilities. If ponded ash is disturbed, or if containment is compromised, material can become unstable structurally and it can flow, causing physical damage and/or environmental contamination of adjacent lands and waters. The work presented will demonstrate methods of preparing mixtures of ponded coal ash stabilized with calcium-based products, taking advantage of the pozzolanic properties inherent in fly ash, to produce an engineered structural fill material. This engineered fill material can be used in the construction of dams for impoundments, for structural toe berms for dry ash landfills, as a structural mat to bridge over saturated, low bearing strength, ponded ash, and as a capping material to prevent water infiltration into the ash landfill, thus limiting the leachate from the coal ash. The paper will describe proper steps to be taken in preparation of the fill area and the techniques for proper placement, compaction, and maintenance of the stabilized fill. Data will be presented demonstrating the structural and leachability properties from stabilized pond ash design mixtures.

Problem

The vulnerability of coal combustion product (CCP) impoundments was highlighted in 2008 by the failure of a containment dike at the Kingston Fossil Plant in Roane County, Tennessee. The subsequent coal ash spill cast a spotlight on containment facilities that had previously received little attention from regulators. The spill launched an initiative by regulators and interest groups to revisit the environmental classification (and potentially handling) of CCPs. The regulatory battles and resulting industry uncertainty about how they must manage their containments continues to this day. Issues range from the impacts of unplanned releases from ponds to the potential presence of heavy metals in the combustion residuals.

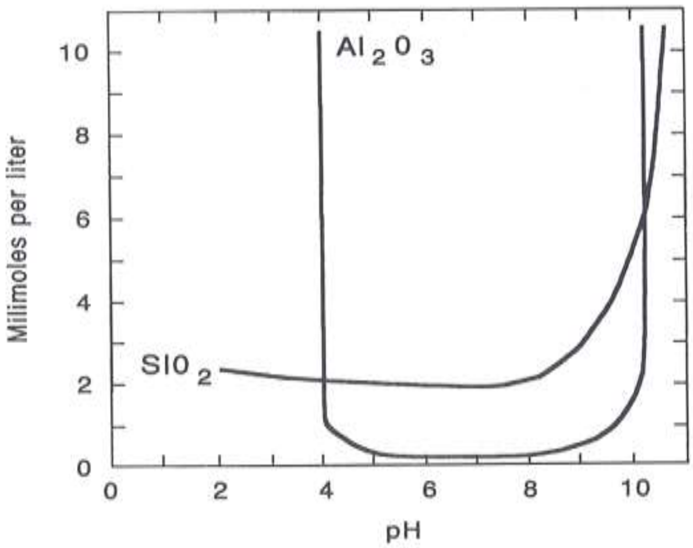
Notwithstanding the regulatory uncertainty there are several issues leading utilities to focus on their containment impoundments. Among those issues are the decommissioning of aging plants which will probably require closure and reclamation of CCP impoundments. In other locations ponds may need to be closed due to changes in the handling of combustion products or the belief that regulatory changes will force closure of liquid impoundments. Finally, some ponds will need to be closed due to the identification of structural problems that require mitigation. The issues driving the decisions to close CCP impoundments are made more complex by uncertainty of where the EPA regulations will ultimately land.

Scope and Strategies

At a recent American Coal Ash Association (ACAA) conference the number of CCP impoundments was estimated to total approximately 630, covering an area of 32,000 acres. The diversity of impoundment designs, their age and range of physical conditions, and the variety of their contents leads to the obvious conclusion that a range of strategies will be required to close and/or reclaim them. Stabilization and remediation in place is an attractive alternative which will be discussed in a later section. In other cases, particularly if the contents of the impoundments can be reused, removal and off-site treatment of the CCPs may be desirable. In fact, beneficiation of excavated CCPs using calcium products may produce materials that can be used to remediate dike problems enabling impoundment facilities to continue operating. Finally, in place stabilization using calcium products may produce pond foundations sufficiently stiff and strong to be used as sites for dry stack landfills.

Lime Solutions

Lime and calcium blends can be excellent choices for stabilizing CCP impoundments. For many decades lime and its co-products have been contributors to geotechnical projects ranging from drying wet construction sites, to stabilizing fine grained soils that are otherwise unsuitable to build upon, to constructing and repairing levees and canals. The chemistry of lime soil stabilization is well known and is based upon the fact that, like coal ash, clay is a pozzolan. Several key characteristics of lime include a strongly exothermic reaction during hydration producing an elevated pH and the presence of highly reactive calcium ions in solution. The combination of calcium ions and available silica and alumina from the clay or fly ash, along with water combine to create strong pozzolanic cements. Coal ash ponds contain ample quantities of the silica and alumina building blocks needed to form pozzolanic cements. However, in virtually all cases the ponds contain far too few calcium and hydroxyl ions to drive the cementitious reactions to completion. For clay stabilization the soil system is flooded with calcium ions and hydroxyls that produce 490 Btu/lb of heat during hydration. The hydroxyl ions resulting from the quicklime hydration elevate the pH to approximately 12. Since the silica and alumina components of clay (or fly ash) are soluble above pH 10 they become available to react with an abundance of calcium ions and water to form the pozzolanic cements, calcium-silicate-hydrates (CSH) and calcium-aluminate-hydrates (CAH). Those cements are water insoluble and can produce strong, permanent matrices. Clay soils (or CCPs) properly stabilized with lime products are transformed into new materials that exhibit significant permanent strength.



Generalized pH Solubility

Like the natural pozzolan clay, coal ash contains significant fractions of silica and alumina that can become available for reaction at an elevated pH. Although coal ash contains a small fraction of calcium hydroxide the percentage is unlikely to be great enough to initiate the formation of significant cementitious products. Consequently, it is necessary to supplement the coal ash with a calcium product based upon lime. When calcium-based products are introduced correctly the water content of the ponded coal ash can be reduced and the solids agglomerated into cementitious products that are stable, have structural properties that improve bearing capacity, and simplify handling of the material. Recent research has confirmed that fine grained soils stabilized with lime can produce foundations and embankments that are durable, highly resistant to erosion and have very low permeability. Consequently, lime stabilized coal ash may be used as foundations for on-site landfills or engineered embankment or backfill applications.

Several attributes of lime stabilization conveniently match the requirements of ponded coal ash stabilization. For example, the strongly exothermic reaction during the hydration of one pound of quicklime (CaO) can raise the temperature of 3.4 lb [1.5 kg] of water from room temperature (70F [21C]) to boiling (212F [100C]), transforming it into steam that dissipates into the air. In addition to that reduction of pond water, the formation of pozzolanic cements consumes water, and the optimum moisture content of the pozzolanic cements created by the reaction of lime with coal ash increases compared to the original material. In other words the solid matrix of the transformed coal ash has an increased moisture holding capacity compared to ash prior to treatment.

Another important characteristic of calcium products based upon lime is that the treated ash can be remixed and manipulated over time as is necessary for the target application. As long as the system's pH remains above approximately 10 soluble silica and alumina will continue to combine with calcium and water to form pozzolanic cements. As has been demonstrated many times when lime has been used to stabilize clays the elevated pH and formation of cements can continue for months, if not years.

Testing

Since the chemistry of coal ash varies according to coal source and the presence of outside contaminants it is necessary to characterize ash to evaluate its potential for structural improvement. Samples should be collected from several locations and depths in each pond to try to capture potentially important material changes that might have occurred over time. At the very least ashes should be tested for percentages of silica and alumina oxides, along with organic (humic) matter and moisture content (percent solids). Generally, available calcium hydroxide in the ash can be disregarded since it is rarely sufficient to produce significant pozzolanic cements. If there is reason to suspect that heavy metals or other contaminants are present in the ponds testing for those concentrations can be included, as well. The characterization testing provides the basis for selecting an additive blend and a strategy that is best suited for the proposed application.

After the coal ash is characterized physical testing basically mirrors the geotechnical tests used to evaluate fine grained soils. Moisture density curves are created to determine the optimum moisture content and unit weight of the ash. Unlike soils coal ash curves are difficult to determine since ash becomes challenging to compact at moisture contents above optimum. It is important to have the moisture-density data as guidance for successful blending of calcium-based products with the coal ash. When lime is added to clay soils those soils are chemically transformed into new materials which have lower unit weights and higher optimum moisture contents. Likewise, coal ash becomes lighter and stronger per unit volume as pozzolanic cements form, and it becomes less sensitive to water (higher optimum moisture content). The following test results using ash from an Eastern power plant and lime from Lhoist North America's St. Genevieve, MO manufacturing facility illustrate the procedures and some typical results.

Characterize the Coal Ash

%	Sample 1	Sample 2	Sample 3	Sample 4
SiO_2	48	47	49	47
Al_2O_3	19	22	21	22
Organic matter	2	3	2	3

The analysis shows that the ash contains ample pozzolanic compounds to form cements. The organic content indicates that some lime will be sacrificed satisfy the cation exchange capacity of the organic material prior to its reaction with the coal ash pozzolans.

Moisture-Density Relationships, Unconfined Compressive Strength (UCS) and California Bearing Ratio (CBR)

Sample 1

Treatment	None	2% Lime	3% Lime	4% Lime
Opt. M.C. (%)	24	26	25	26
Max. Density (lb/ft^3) [kg/m^3]	86 [1378]	84 [1346]	85 [1362]	84 [1346]
UCS (psi) [MPa]	24 [0.17]	147 [1.01]	344 [2.37]	505 [3.48]
CBR (%)	5	33	76	112

Sample 2

Treatment	None	2% Lime	3% Lime	4% Lime
Opt. M.C. (%)	33	36	36	36
Max. Density (lb/ft^3) [kg/m^3]	77 [1233]	75 [1201]	75 [1201]	74 [1185]
UCS (psi) [MPa]	55 [0.38]	174 [1.20]	201 [1.39]	256 [1.77]
CBR (%)	12	39	45	57

Sample 3

Treatment	None	2% Lime	3% Lime	4% Lime
Opt. M.C. (%)	29	32	30	31
Max. Density (lb/ft^3) [kg/m^3]	78 [1249]	79 [1265]	78 [1249]	77 [1233]
UCS (psi) [MPa]	38 [0.26]	122 [0.84]	303 [2.09]	338 [2.33]
CBR (%)	8	27	67	75

Sample 4

Treatment	None	2% Lime	3% Lime	4% Lime
Opt. M.C. (%)	34	38	37	38
Max. Density (lb/ft^3) [kg/m^3]	74 [1185]	72 [1153]	72 [1153]	72 [1153]
UCS (psi) [MPa]	55 [0.38]	133 [0.92]	174 [1.20]	247 [1.70]
CBR (%)	12	30	39	55

The example data demonstrate a dramatic growth of strength with the addition of increasing percentages of lime. In addition, the optimum moisture contents increased and unit weights decreased to lesser extents after the addition of lime. The changes in moisture content and unit weight occurred within the first few hours after mixing. The strength gain was measured after 48 hours of curing in sealed containers at 120F (49C). The accelerated curing provides a prediction of strengths that may be achieved after several weeks of curing at ambient temperatures in the field.

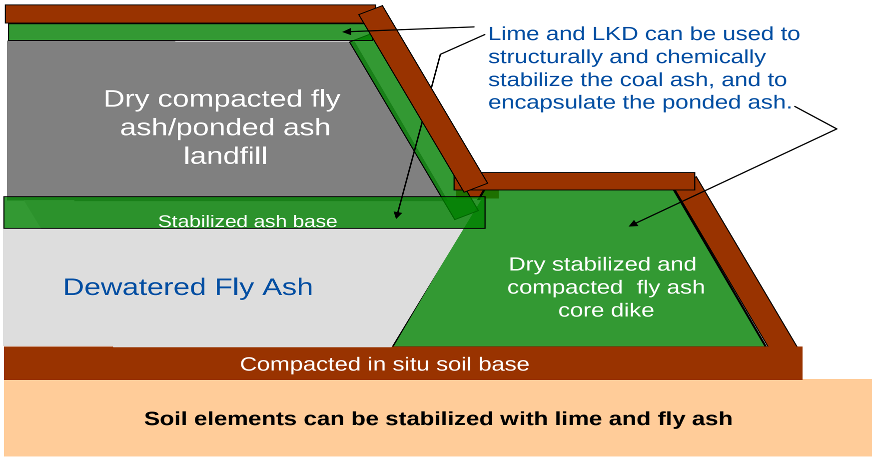
The pH of some of the cured samples was measured to assess the potential for continued strength gain. In each instance the measured pH exceeded 11.75 following 48 hours of accelerated curing indicating that pozzolanic cements would continue to form, further improving the coal ash properties over time. Those observations are corroborated by pH measurements taken on highways months after initial lime stabilization.

Discussion

Uses for Stabilized Coal Ash

Stabilizing coal ash with calcium-based additives can produce products appropriate for several different applications depending upon the ash chemistry and the amount of additive that is used. Fundamentally, the water content of ash ponds can be reduced and the solids increased by the exothermic hydration of calcium oxide and the reaction of the calcium ions with silica, alumina, and water. The combination of drier material and pozzolanic strength can produce a product that can bridge over and contain lower strength coal ash. That improvement will also enable the treated ash to be handled and stacked more efficiently. By increasing the percentage of the calcium-based blend and the intimacy of mixing higher compressive strengths and lower permeability of the stabilized ash can be achieved broadening its potential applications as a structural embankment, fill, or capping material. It is also important to note that the formation of pozzolanic matrices create an efficient means of encapsulating heavy metals or other deleterious materials present in the impoundments.

A potentially attractive option for utilities faced with converting from wet CCP management to dry management strategies would be to stabilize the ponded CCPs in situ and create a foundation for a new dry disposal facility. This would minimize the disturbance of land area and provide an economic solution to the conversion.



Schematic of Lime Stabilized CCP Impoundment

Procedures for Stabilizing Ponded Coal Ash

Procedures used to achieve the target improvements will vary depending upon the accessibility of the ponded ash, its moisture content, and available mixing equipment. To create a working platform or cap on a coal ash impoundment a simple technique is to spread and mix the calcium-based blend into the ponded ash using a low ground pressure excavator operating from the access road on the top of the impoundment dam. The depth of mixing should be based upon laboratory testing and the use of a conservative application rate in the field because of the crude mixing technique. As the ash on the surface reacts with lime and begins to agglomerate, the excavator can proceed out onto the pond expanding the cap. As the treated material solidifies the surface should be kept moist to minimize cracking and light compaction should be applied to improve the contact between particles. That method, though simple, is not very efficient and is likely to waste a significant quantity of the calcium additive.

A much more efficient method to mix lime products into coal ash ponds uses injectors mounted on the boom of an excavator. Lime is metered from a pneumatic trailer through the multiple injectors which can mix up to nine feet deep in a single pass. As the lime and CCPs react with each other the mixture stabilizes allowing the excavator to proceed across the impoundment expanding the stabilized area

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Excavator Spreading/Mixing Lime

Excavator Injecting Lime Into Pond and Mixing

Particularly where there is room to stockpile treated material, coal ash can be pumped from an impoundment and conveyed to a mixing device such as a pugmill where it can be mixed with the calcium blend and stockpiled to partially dry and begin forming pozzolanic cements. When the treated materials have improved enough that they can be easily handled they can be installed in the pond as a working platform or a capping layer. As described above the surface should be kept moist to minimize cracking and lightly compacted to improve contact and bearing capacity. The thickness of the layers should be based upon an engineering design that takes into account the time-dependent strength increase.

Pugmill – Blend Material Off-Site and
Transport to Project

Roto-Mixer – Excellent Mixing Where Foundation is Sound

In areas where the coal ash can be spread and worked outside of the pond conventional soil stabilizing equipment can be used to blend the materials. Dry calcium-based additive can be spread across a mixing table and blended with the ash using commonly available roto-mixers. Additional layers of ponded coal ash can be added to the stockpile, mixed and allowed to cure until they are ready to be transported to their final location. That location could be a capping layer, a structural fill, or an embankment depending on the selection of additive blend and addition rate to achieve appropriate engineering properties. This particular strategy takes advantage of an important property of lime-based additive blends. As noted earlier, the formation of pozzolanic cements and the achievement of permanent material strength is a function of maintaining high pH in the stabilized mixture. There have been many instances when lime has been mixed with clay soils where treated materials have been stockpiled for weeks or months before use. With the addition of an appropriate amount of a calcium-based blend the pH in the stockpile has remained elevated insuring an excellent final product.

In cases where deep mixing is desirable track mounted auger mixers are available that can introduce chemical blends to a desired depth into a pond. That technology is European in origin and was developed, in part, for soft soil engineering. Deep mixing has been used in the U.S. for years and specialty contractors own a variety of types of equipment and are experienced in using the techniques under challenging conditions. It is likely that significant permeability improvements could result from the use of deep mixing.

As the test results from the example coal ash samples demonstrated, with additional engineering many lime coal ash blends can be designed to be incorporated into dam and dike construction to create additional on-site storage. As ponds are filled with lightly treated ash, layers of more heavily stabilized material might be added to provide incremental stability to the total system. Finally, when ponds or landfills are retired it may be possible to cap them with low permeability lime/coal ash layers to minimize water intrusion and leaching.

Finally, given the wide range of strengths that may be achieved by blending lime-based additives with ponded coal ash some engineered products might be used as select fill in embankments or controlled low strength backfill (CLSM) in trenches elsewhere in the construction industry. Naturally, as the importance of the application for which the stabilized coal ash is used increases so too must the extent of engineering design and testing.

Conclusion

The failure of the Kingston impoundment has increased concerns about that common method of coal ash storage. Partly as a result of those concerns new strategies for managing CCP storage facilities and the materials that they contain are emerging. One of those strategies is to stabilize the pozzolanic ash using materials based upon lime. A broad range of applications can be envisioned depending on the target application and the calcium-based blend that is selected. Several construction strategies can be employed depending upon site specific circumstances and the engineering properties that are being sought. As the importance of the engineering application using stabilized coal ash increases more comprehensive tests and evaluations should be conducted. Finally, as more and more attention is given to implementing Green Engineering, new applications will emerge that can take advantage of the chemistry and compatibility of calcium-based additives and coal ash.

References

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World of Coal Ash

Lexington, KY

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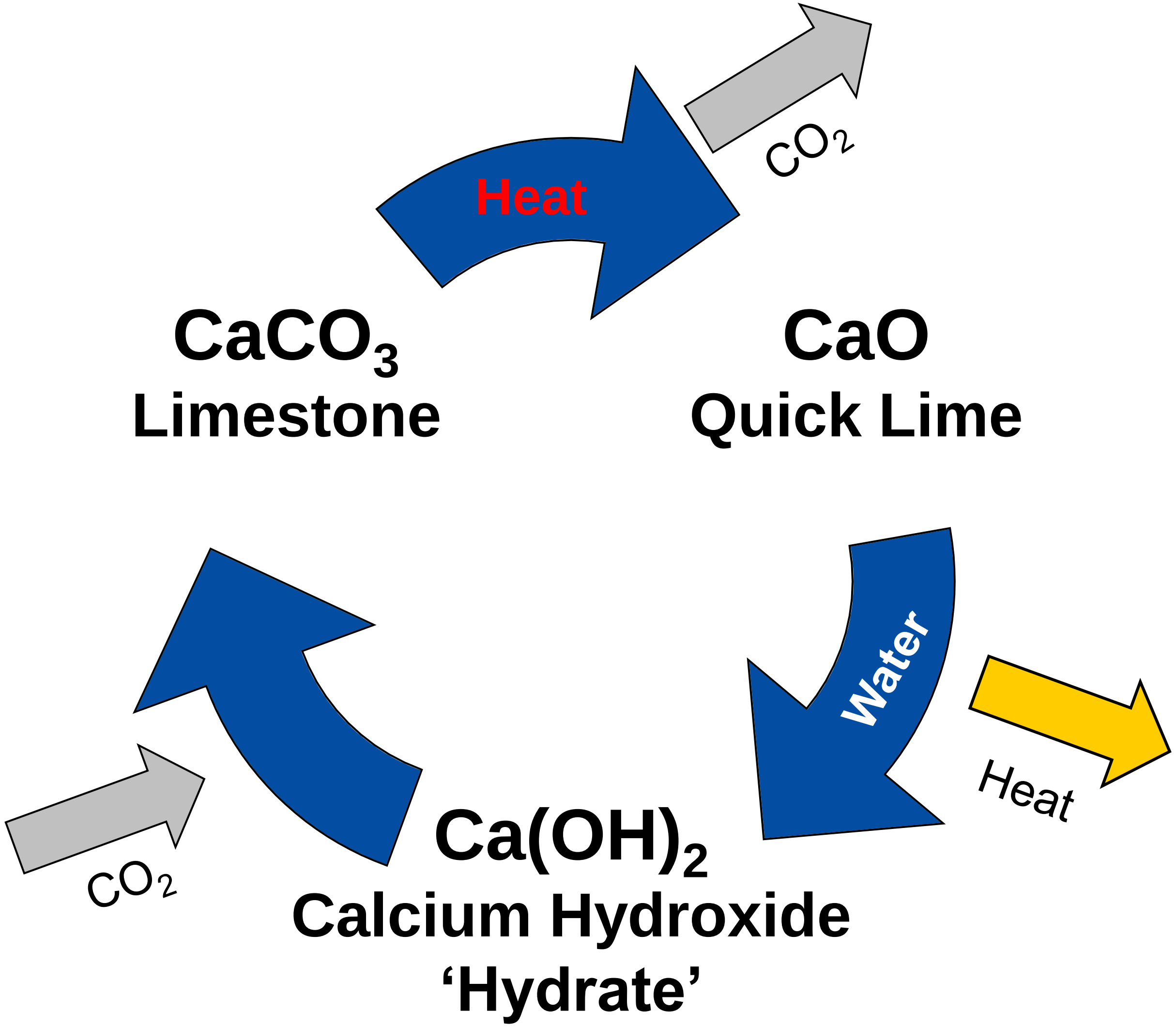
Use of Lime to Stabilize Ponded Coal Ash Techniques, Results, & Proposal

Lime Production



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Lhoist Experience Using Coal Combustion Products for Stabilization

- Highway applications using lime/fly ash blends to stabilize soils are common
  - ✓ Currently engaged with a major fly ash supplier to develop and market high quality blended stabilization products for Civil Engineering activities

Use of Calcium Products to Stabilize Ponded Coal Ash

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Mechanisms

- Heat of lime hydration reduces water content

  $CaO + H_2O \rightarrow Ca(OH)_2 + Heat$
- Elevated pH (pH > 10) solubalizes SiO_2 and Al_2O_3
  - ✓ $Ca(OH)_2$ maximum pH = 12.4
- Chemical reactions – Formation of C-S-H & C-A-H
  - ✓ Ca, Si, Al, OH
- Long term chemical reaction – Improves ash structure by forming agglomerates & pozzolanic cements
- Reduce heavy metal leaching potential
  - ✓ Combination of cementitious matrix and elevated pH

Coal Ash Chemistry

Fly Ash, Bottom Ash and Boiler Slag

Coal Type

Component	Bituminous	Subbituminous	Lignite
SiO_2 (%)	20-60	40-60	15-45
Al_2O_3 (%)	5-35	20-30	20-25
Fe_2O_3 (%)	10-40	4-10	4-10
CaO (%)*	1-12	5-40	5-30
LOI (%)	0-15	0-3	0-5

* Not all CaO in fly ash is chemically available to react with pozzolans

FGD Residue

Up to 99% Gypsum if FGD system is a force oxidation system and uses high purity limestone or lime. FGD residue is primarily $CaSO_4$ and $CaSO_3$.

Calcium Silicate & Aluminate Hydrate Principal (C-S-H & C-A-H)

The hydration products primarily affecting the strength in Portland Cement Concrete are calcium silicate and aluminate hydrates (C-S-H & C-A-H). Fly ash is known as a Pozzolan when used as a partial cement replacement in Concrete.

Component	Typical Class F Fly Ash	Typical Class C Fly Ash	Typical Portland Cement
CaO (%)*	<10	30 - 40	61 - 67
SiO_2 (%)	20 - 60	40 - 60	19 - 30
Al_2O_3 (%)	5 - 35	20 - 30	2.5 - 6
Fe_2O_3 (%)	10 - 40	4 - 10	0 - 6
Typ. Cement Replacement (%)	20	40	-

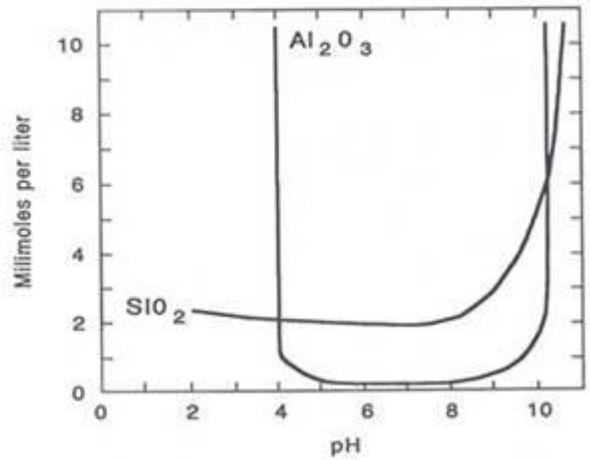
* Not all CaO in FA or cement is available for reaction with pozzolans

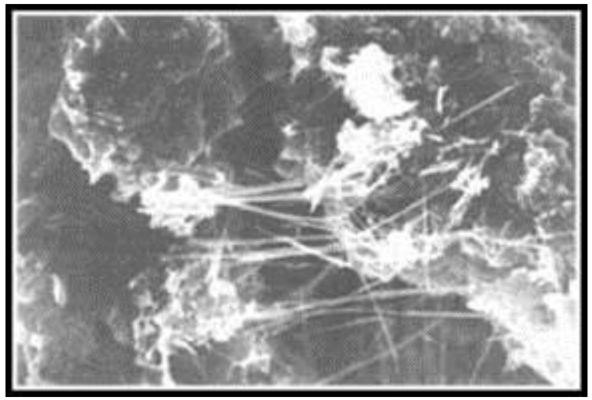
Similar cementitious products are formed when lime reacts with pozzolans

Chemical Reactions for Lime Stabilization of Coal Ash

CaO from the Lime combines with the SiO_2 and Al_2O_3 in coal ash and water (H_2O) to form cementitious C-S-H and C-A-H compounds.

- Hydroxyl Ions (OH^-) elevate pH to range of 11 to 12
- SiO_2 and Al_2O_3 become soluble above pH 10
  - SiO_2 reacts with Ca to form C-S-H
  - Al_2O_3 reacts with Ca to form C-A-H
- Cementitious products agglomerate to form stable matrices
  - Strength continues to increase for months/years





Growth of cementitious crystals in stabilized clay sample

Mechanical Improvements from Lime Stabilized Coal Ash

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- Dramatic increase in unconfined compressive strength (UCR), California Bearing Ratio (CBR) & reduction in permeability of coal ash
- Alteration of ash structure – improved handling
- Increase in optimum moisture content - nominal
- Reduction in maximum dry density - nominal
- Consumption of excess H_2O during hydration
  - ✓ Chemically binds 3.2 lbs of H_2O per 10 lbs of CaO to form $Ca(OH)_2$
- Exothermic reaction dissipates H_2O
  - ✓ Hydration of CaO releases 490 Btu/lb heat (i.e. - raises the temperature of 3.4 lb of H_2O from 70°F to 212°F)
- Cementitious matrix will continue to form as long as pH > 10
  - ✓ Continues to gain strength for months and years depending on lime addition rate
    - Autogenous crack healing

Lab Tests – Short Term Results

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Results after 48 hours accelerated cure

%	Sample 1	Sample 2
SiO_2	48	47
Al_2O_3	19	22
Organic matter	2	3

Sample 1

Treatment	None	2% Lime	3% Lime	4% Lime
Opt. M.C. (%)	24	26	25	26
Max. Density (lb/ft^3)	86	84	85	84
UCS (psi)	24	147	344	505
CBR (%)	5	33	76	112

Sample 2

Treatment	None	2% Lime	3% Lime	4% Lime
Opt. M.C. (%)	33	36	36	36
Max. Density (lb/ft^3)	77	75	75	74
UCS (psi)	55	174	201	256
CBR (%)	12	39	45	57

Lab Tests – Short Term Results (2)

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Sample 3

Treatment	None	2% Lime	3% Lime	4% Lime
Opt. M.C. (%)	29	32	30	31
Max. Density (lb/ft^3)	78	79	78	77
UCS (psi)	38	122	303	338
CBR (%)	8	27	67	75

Sample 4

Treatment	None	2% Lime	3% Lime	4% Lime
Opt. M.C. (%)	34	38	37	38
Max. Density (lb/ft^3)	74	72	72	72
UCS (psi)	55	133	174	247
CBR (%)	12	30	39	55

Heavy Metal Leachate from Coal Ash

- Arsenic
- Barium
- Boron
- Cadmium
- Chromium
- Lead
- Mercury
- Selenium
- Sulfur

Coal ash consistently tests well below Hazardous Waste limits. However, because of the high volumes of waste the concentration of metals has raised concerns for years.

Using Lime to Reduce the Impact of Leachate Containing Heavy Metals from Coal Ash

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- The crystalline structure of the hydrated cementious paste reduces permeability and chemically fixates certain heavy metals.
- Increasing alkalinity of the coal ash reduces the leachability in some heavy metals
- A properly designed and constructed coal ash fill with lime treated encapsulation will reduce leachate production by minimizing infiltration and will confine the coal ash and prevent any unintended release and contamination.

Key Improvements

- Strengthen dike slopes & core

- Solidify pond content to reduce potential movement

Lime's Potential Contributions to Stabilization of Ponded Coal Combustion Products

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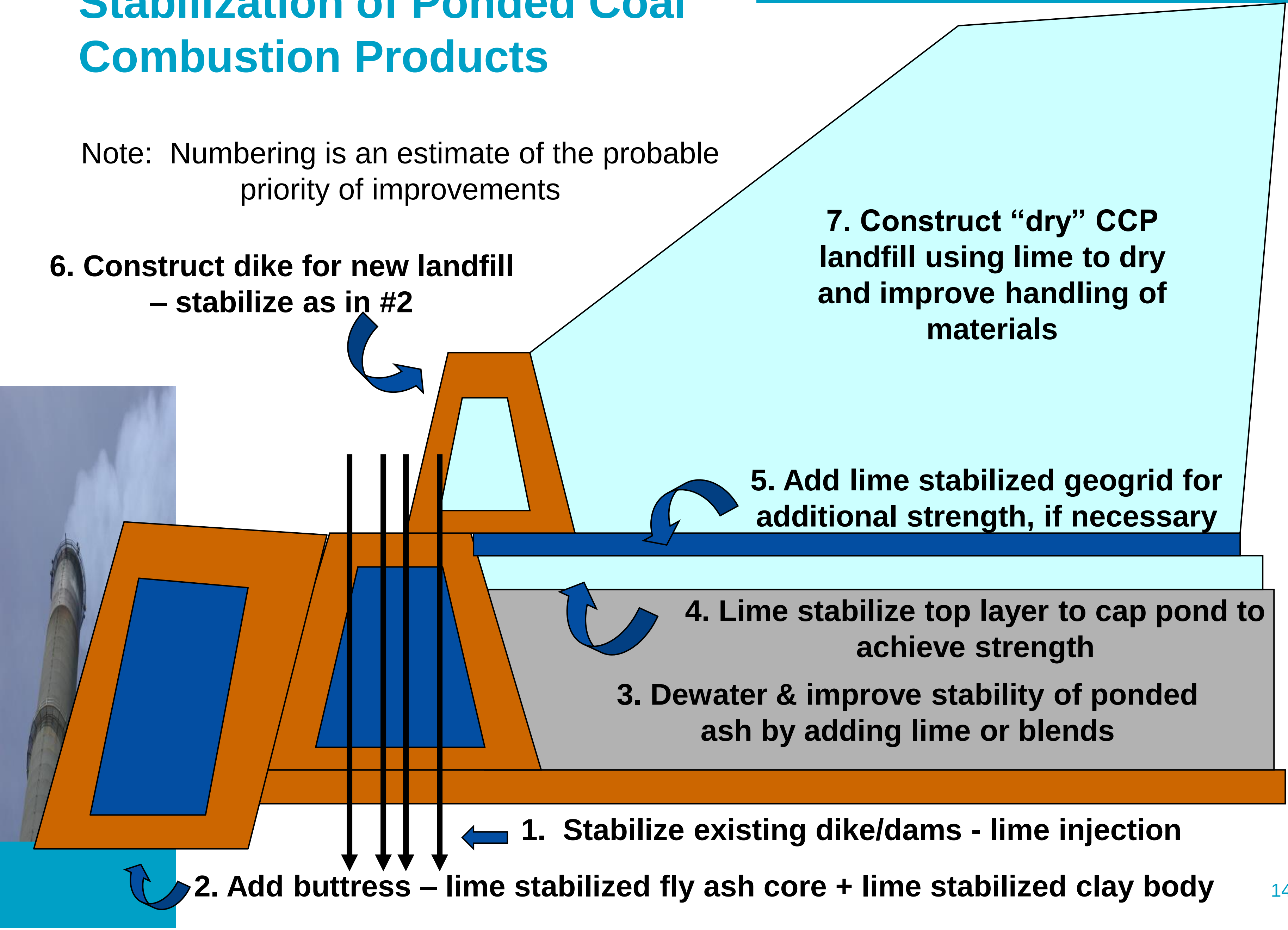
Note: Numbering is an estimate of the probable priority of improvements



Proper Procedures for Stabilizing Ponded Coal Ash

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- Establish project goals
- Characterize ponded ash
- Determine stabilization (mixing) options
- Perform mix designs
- Engineered construction plans
- Prepare construction strategy and logistics

Characterize Ponded Ash

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- Determine pond history
- Grid and core sample ash
- Characterize ash samples
- Identify any poor load bearing areas
- Compare samples to history

Do the cored ash samples logically compare to the history for the ash pond?

Can the discharge locations and settlement patterns be matched to actual operational history for the pond?

Mixing/ Stabilization Alternatives

Track hoe – preliminary access where surface is unstable

Deep mixing injector – follows stabilization across pond

Roto mixer – excellent mixing when surface is sound

Pugmill – blend materials off-site & transport to project

Prepare Construction Strategy & Logistics

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- Establish safety procedures and emergency protocols
- Establish operations procedures
  - ✓ Water maintenance
  - ✓ Dust control
- Preparation of haul roads in pond (if necessary)
- Location(s) for excavation equipment
- Areas for material stockpiling
  - ✓ Necessary if in situ mixing will be inconsistent
- Strategy for QA/QC
- Strategy for performance verification
  - ✓ Short Term
  - ✓ Long Term

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Questions??

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