Options to Stabilize and Utilize Tomorrow's Fly Ash: Approaches and Initial Results

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INTRODUCTION

The characteristics of fly ash are changing as coal-fired power plants respond to increasingly stringent air pollution regulations. Activated carbon injected into the flue gas for mercury control will impact the utilization of fly ash for concrete admixture. Dry sorbent injection (DSI) for acid gas control will alter the characteristics of the combined fly ash and spent sorbent. Sodium-based sorbents (trona or sodium bicarbonate) increase soluble sodium and sulfate species, increase ash and leachate pH, and increase concentration and mobility of some metal species, in particular selenium and arsenic, in the collected fly ash and in the leachate or any water discharge from impoundments.[1,2]

Long-term physical performance of mixtures of DSI sorbent and fly ash placed in geotechnical or disposal settings may also be affected. Loss of soluble bulk constituents if exposed to water over time could lead to mass loss from materials in landfills and contribute to subsidence, settling and instability as voids develop in the underlying solids.

Disposal of coal combustion residuals (CCR) for many plants will be changing from sluiced wet ash handling and wet surface impoundments to dry landfills as a result of both state regulations and the recently enacted CCR disposal regulation. Furthermore, as plants consider options to address future discharge effluent standards in response to the Steam Effluent Limitation Guidelines (ELG), many are considering reduction of waste water discharge volume or zero liquid discharge (ZLD). However, concentrated flue gas desulfurization (FGD) wastewater solids from ZLD processes may require stabilization of heavy metals and soluble halides and nitrates prior to landfill disposal. Fly ash may provide stabilization options.

The forthcoming conversion from wet to dry fly ash handling and disposal may be an industry opportunity to reevaluate the entire solid waste handling process. In particular, fly ash and other FGD byproduct streams could be partially diverted to stabilization of

FGD wastewater solids for long-term immobilization of metals and overall reduced water penetration and leaching. Some higher risk fly ash such as ash enriched with DSI sorbent may also benefit from stabilization prior to landfill placement.

HIGH CARBON ASH UTILIZATION

ADA has been testing fly ash from plants using activated carbon injection (ACI) for mercury control in end uses other than concrete admixture. When used as a replacement for cement in concrete, there are a number of technologies to mitigate the impact of activated carbon on the air entraining reaction, but variability in the amount of activated carbon is still problematic for concrete batch mix control. Alternate uses where carbon is not reactive could help to maintain ash marketability once ACI for mercury control is implemented. One such use would be incorporation of higher carbon ash into non-concrete masonry building materials. ADA provided some ash containing activated carbon to CalStar, an innovative building products company that incorporates recycled material such as fly ash into their bricks, blocks, and masonry products. According to CalStar's website, "Traditional masonry products use clay or Portland Cement and require firing in kilns at thousands of degrees. Our innovative technology and manufacturing processes use 81% less energy, emit 84% less CO_2, and utilize up to 37% post-industrial recycled material." If ash containing activated carbon did not impact use by CalStar, this would represent a valuable reuse of this combustion byproduct.

Class C PRB fly ash samples taken during injection of activated carbon at a rate of 1.75 lb/MMACF were tested for suitability in CalStar Products. This level of injection is typical of efficient ACI mercury control for MATS compliance and yields a fly ash with about 1% LOI and visibly darker fly ash. Preliminary results using this ash suggest the ash is compatible with the CalStar technology, although some adjustments in color might be necessary to accommodate the darker ash. The brick manufacturing process does not use concrete or apply air entraining chemicals, so there are not the same constraints as for activated carbon in fly ash for concrete admixture. Prior to any introduction into the masonry market, further testing is required to see if, among other things, the variability in activated carbon can be managed over longer term.

FGD WASTEWATER ENCAPSULATION

ADA has been developing and testing techniques to use fly ash as a matrix material for scrubber wastewater solids encapsulation. Waste brines produced in high recycle wet scrubbers can be combined with fly ash and additives to produce a stable and manageable material that exhibits reduced leaching of certain metals. Depending on availability, scrubber byproducts such as gypsum can also be incorporated. Potential benefits from this approach include reduced leachability of problematic metals from both materials and lower or zero wastewater treatment volume.

Formed solids incorporating high-salt waste could be used for a variety of disposal purposes, including wet discharge as slurry to landfill or pond enclosure, as an intermediate barrier layer in a dry landfill, or as formed, transportable aggregate. For most plants the FGD blowdown liquid will require volume reduction to achieve a practical mix ratio of liquids to waste and matrix solids.

The recently enacted CCR Rule sets a standard of 1 x 10^{-7} cm/sec hydraulic conductivity (permeability) for flexible geomembrane liners for new CCR landfills. However, even with this liner in place there may be reason to further inhibit moisture penetration into CCR landfills as increased protection to:

1) Ensure long-term immobilization of soluble contaminants such as chlorides, bromides, nitrates and metals;
2) Minimize subsidence from leaching of bulk species such as soluble sodium and sulfates; and
3) Reduce or eliminate the need for leachate water treatment

One possible method to reduce water penetration into landfilled CCR is via placement of a self-cementing solid layer of plant fly ash. If combined with the FGD wastewater brines, this approach is analogous to what Muntingh has described as "pasting" of industrial process brines with fly ash.[3] During testing of options to co-dispose of industrial brines and fly ash, results indicated that fly ash mixed with highly saline brine hardened and exhibited low leaching characteristics. During ADA testing, permeability of a Class C fly ash mortar was tested to compare the relative hydraulic conductivity to an engineered liner. These results, presented later in this paper, suggest that the hydraulic conductivity standard was not achieved with fly ash alone.

Pelletization of FGD brine solids using fly ash or fly ash and FGD gypsum is another encapsulation option. Pelletization may require less fly ash or fly ash/gypsum as matrix material compared to slurry mixers. However, pelletization with fly ash alone may not prevent moisture from reaching the high solubility salts and subsequent mobility and leaching. Additional binders may be required to minimize mobility and leaching.

Fly ash with sodium-based DSI could be stabilized by the same encapsulation methods prior to landfill placement to fix metals and ensure long-term physical stability.

Pelletization Testing

ADA conducted a series of tests to determine the effectiveness of pelletization with fly ash to stabilize simulated ZLD solids. ZLD solids are comprised of high solubility chemicals that are either present in coal or added to the process that become concentrated in the FGD solution. Halogens such as chlorides are often a major constituent. Prepared liquid mixtures to simulate a high recycle FGD wastewater were spray dried in an experimental pilot process for FGD wastewater disposal via zero liquid discharge. Two batches of these "ZLD solids" were evaluated for solidification/stabilization (S/S). Two types of samples were prepared: formed mortar cubes and pellets. The sample for pelletization tests had lower chloride than the sample used for mortar testing (14.2% vs. 37.9%). Samples were mixed with a variety of potential encapsulation material at various liquid:solid ratios to determine the best mixes for solidification and stabilization. Liquid waterproofing additives and binders were also added to some batches.

Mortar samples for final testing were prepared using a 1:5 mass ratio of fly ash to FGD waste solids and 20% liquid with a waterproofing additive. Samples were mixed to a highly homogeneous state using a high speed laboratory mixer then poured into cube molds.

Pellets were produced in a lab-scale pan pelletizer Pellets were made using a 1:1 mass ratio of fly ash to FGD waste solids and approximately 25% liquid. Binder or waterproofing additives were introduced with the water spray. Two-layer pellets were produced with an inner core of ZLD solids with binder and an outer layer of PRB with binder coating the surface. The same ingredients were pre-mixed dry and homogeneous pellets were formed with liquid/binder. This method is expected to be functionally equivalent to spray contact of high-solids waste brine with fly ash (wastes need not be fully dried for pelletization).

A final pellet batch was completed with just ZLD solids and binder. However, it reverted to liquid within 24 hours due to liquefaction of the very hydroscopic calcium chloride and could not be tested further.

Batch Leaching

Leaching was performed by the standard toxicity characteristic leaching procedure (TCLP)[4] for a suite of Resource Conservation and Recovery Act (RCRA) heavy metals followed by a simple generic leach test with deionized (DI) water, the synthetic groundwater leaching procedure (SGLP)[5]. The SGLP leachate was analyzed for metals and for chloride. The pellet samples were analyzed for only select metals: arsenic, mercury and selenium.

TCLP leaching of solids requires pre-crushed or powdered samples, so it is of limited value for leaching characterization of larger monolithic samples. For all tests in this project, cubes were first broken during the crush test and intact pieces sieved to the largest size range allowable for TCLP, 3/8” to + ¼” mesh. Material fines below this size fraction were discarded.

For the DI water leach (SGLP), 20 g of solid and 400 ml of water (20:1 ratio) were combined in a spinning leach bottle. The water was deionized with a pH of about 6.3-6.5. In all of the leaching tests with cubes, the cubes were broken and sieved to the largest size allowable size, - 3/8” mesh. Pellets were left intact and screened to -3/8” mesh. Leach bottles were set up and tests were run for 24 hours and 30 days for both the pellets and the mortar cube samples. The bottles were then stopped from spinning and filtered. The samples were preserved with nitric acid and then run on the instrument within 48 hours. Chloride leach with DI water was performed on duplicate leachate samples without the acid preservation.

Analytical and batch leaching results for the ZLD solids and mortar cube samples waste solids are shown in Table 1. Metal leaching was non-detectable to low for all metals except barium. Selenium was non-detectable in the 24-hour test, but present at low concentration in the 7-day test. Essentially all the chloride leached in the SGLP test, despite addition of a waterproofing additive.

Table 1. Analytical and leaching results for ZLD solids and mortar encapsulation

Constituent	Ag	As	Ba	Cd	Cr	Hg	Pb	Se	Cl
Concentration in solid (µg/g)									
ZLD Solids (dry)	<2	30	91	4	51	1.7	30	48	379,000
Encapuslated Solids	<1.9	33	5600	6.4	75	4.3	39	92	110,700
TCLP Leach, mg/L									
ZLD Solids (dry)	<0.1	0.4	0.7	0.5	0.1	<0.1	<0.1	3.5	--
Encapuslated Solids	<0.1	<0.1	24	<0.1	<0.1	<0.1	<0.1	<0.1	--
SGLP Leach (24 hour, mg/L)									
ZLD Solids (dry)	<0.01	0.38	1.1	1.6	0.04	0.23	<0.01	24	16,000
Encapuslated Solids	<0.01	0.04	20	<0.01	<0.01	<0.01	<0.01	<0.01	1,600
SGLP Leach (7-day, mg/L)									
ZLD Solids (dry)	<0.01	0.32	1	1.5	0.04	0.2	<0.01	20	17,000
Encapuslated Solids	<0.01	0.03	24	<0.01	<0.01	<0.01	<0.01	0.03	1,800

Analytical and batch leaching results for pelletization of the FGD waste solids are shown in Table 2. The samples and leachate were analyzed for arsenic, selenium, mercury and chloride. Both pellet types showed no arsenic, mercury and selenium leaching, but essentially all of the chlorides were leached by both the TCLP and the 1-day and 30-day DI water leach.

Table 2: Results for pellets with ZLD solids and fly ash

Sample/ Parameter	FGD Waste Solids	2-Layer Pellet with binder	Homogeneous Pellet
Description	Dried high chloride FGD waste solids	PRB/Binder outer, FGD solids core	PRB/FGD Solids pre-mixed
FGD Waste Solids (% dry)	100	48	48
Class C Fly Ash (% dry)	0	48	48
Liquid (% of dry mix)	0	25.3	25.7
Concentration in Solids (ug/g)			
As	341	156	170
Hg	1.66	0.69	0.89
Se	24.7	11.5	14.3
Chlorides	142,000	46,700	57,400
TCLP Leach (mg/L)			
As	1.68	<0.2	<0.2
Hg	<0.05	--	--
Se	0.37	<0.05	<0.05
Chlorides	4,360	1,490	1,060
SGLP Leach (24 Hour, mg/L)			
As	--	<0.05	<0.05
Hg	--	<0.005	<0.005
Se	--	<0.05	<0.05
Chlorides	--	1,750	1,630
SGLP Leach (30 day, mg/L)			
As	--	<0.05	<0.05
Hg	--	<0.005	<0.005
Se	--	<0.05	<0.05
Chlorides	--	1,930	2,650

Permeability (Hydraulic Conductivity)

Samples were tested for hydraulic conductivity (permeability) via ASTM D 5084, Method C (falling head, rising tailwater)[6]. Solid mortar specimens were prepared from Class C fly ash mixed with 22% water and a proprietary waterproofing additive, formed into 2” diameter by 4” height (5.1 cm by 10.2 cm) brass cylinder molds and allowed to harden at room temperature. A photograph taken during sample preparation is shown in Figure 1.

Figure 1: Permeability Cell and Test Cylinders

Solid mortar specimens from 100% Class C fly ash mixed with 22% water and a proprietary waterproofing additive had average coefficient of permeability, k, of 3.7 x 10^{-7} cm/sec. A further test specimen prepared with Class C fly ash, 5% Portland cement and waterproofing additive had average coefficient of permeability, k, of 7.8 x 10^{-7} cm/sec with the same water ratio. The hydraulic conductivity standard for flexible geomembrane liners used in new CCR landfills is 1 x 10^{-7} cm/sec. Although the new standard was not achieved with the current additive recipe, results indicate that the permeability of the current fly ash and additive mixture is nearly as impermeable as a geomembrane liner, which supports continued development of ash slurry mixtures for use as landfill liners.

CONCLUSIONS

The characteristics of fly ash are changing as plants respond to increasingly stringent air pollution regulations. Traditional uses of fly ash, such as replacing a portion of cement in concrete, may be compromised by the addition of air pollution control chemicals, such as activated carbon and high solubility chemicals such as sodium-based sorbents, and may require different handling. Alternate uses such as in non-concrete building products may be an option, but are not expected to replace the quantity of ash currently used as an admixture in concrete.

Future fly ash could also be utilized as a solidification matrix material for wastes with high concentrations of metals, such as FGD wastewater brine. This could reduce long-term risk of leaching and/or groundwater contamination. Results from ADA testing of fly ash for stabilization indicated the following:

- Encapsulation of high chloride FGD waste solids in mortar samples with fly ash at 1:5 mass ratio immobilized the RCRA metals by TCLP and DI water leach. However, chlorides were entirely leached out.
- Pellets formed with 1:1 FGD waste solids and Class C fly ash retained arsenic, mercury and selenium but leached the chlorides.
- Preliminary permeability tests show that a fly ash solid layer formed by slurry placement could create an intermediate barrier to moisture penetration with a permeability coefficient comparable to the landfill liner itself (10^{-7} cm/sec).

Results from testing indicate that encapsulation minimized or eliminated leaching of the metals tested, but did not prevent leaching of high solubility chlorides. Although the batch leaching results presented provide valuable insights, they should be viewed as a relative comparison between materials and not a predictor of landfill leaching behavior because the leaching tests are conducted by completely immersing crushed samples. Landfill management techniques in conjunction with higher permeability encapsulation techniques are expected to reduce the overall volume of leachate that will be produced from a landfill to the extent they prevent or minimize water from reaching the chlorides.

ADA continues to evaluate options to utilize fly ash for products, to manage CCRs including those containing air pollution control chemicals, and to use ash as a component to solidify and stabilize scrubber effluents to support ZLD practices to support the ongoing reliable operation of coal plants.

REFERENCES

[1] Tingzhi Su, Honglan Shi, and Jianmin Wang, “Impact of Trona-Based SO2 Control on the Elemental Leaching Behavior of Fly Ash”, Energy and Fuels 2011, 25, 3514–3521.

[2] Ladwig,K. et. al. “Impacts of Sodium-based Reagents on Coal Combustion Product Characteristics and Performance”, EPRI Report 1017577, Nov. 2010.

[3] Muntingh, Y., Mahlaba J.S. and Pretorius C., “Utilising Fly Ash as a Salt Sinking Media Through Pasting with Industrial Brine”, Proceedings of the World Congress on Engineering 2009 Vol I, WCE 2009, July 1 - 3, 2009, London, U.K.

[4] EPA Method 1311, “Toxicity Characteristic Leaching Procedure”, Rev. 0, June 1992.

[5] Hassett, David et. al., “Leaching of CCBs: Observations from Over 25 Years of Research”, 2003 International Ash Utilization Symposium, University of Kentucky Center For Applied Energy Research.

[6] ASTM D5084-10, “Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter “.