The Effects of Fly Ash Quality on Brine Encapsulation
Clark Harrison and Ben Clegg
Purestream Services
790 Komas Drive
Salt Lake City UT 84108

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ABSTRACT
To comply with wastewater discharge requirements, some power plant owners are considering if it is feasible to encapsulate wastewater or concentrated brine using fly ash and cementitious materials. Because lost revenue from fly ash sales is one of the cost factors that must be considered, process engineers are seeking to optimize use of fly ash while minimally impacting fly ash sales.

The markets and revenue potential from fly ash are directly related to ash quality (particle size, carbon content, etc.) and the quality of fly ash varies based on where it is collected in the flue gas path (ash source).

During 2018 Purestream Services sampled fly ash from various ash source hoppers (economizer, air heater, precipitator and baghouse) at a midwestern power plant that burns both bituminous and sub-bituminous coals (one unit all bituminous and the other unit a blend of bituminous and sub-bituminous). These fly ash samples were then combined with other cementitious materials and wastewater or brine to produce self-hardening grout. This grout would be placed for pond closure or landfilling. This paper presents the results (ash quality, grout characteristics and environmental considerations) for each ash source, and combinations of ash sources, and it includes an economics assessment of grout making based on fly ash quality and cost.

INTRODUCTION
Purestream conducted this investigation to complement an evaluation of thermal treatment of power plant wastewater at a midwestern power station. This part of the work focused on encapsulating the brine product from thermal processes so those thermal processes can be zero liquid discharge.

In December 2017, Purestream Services received 18,000 gallons of process wastewater from a pond that received bottom ash transport water, blowdown from flue gas desulfurization, and other miscellaneous coal-fired power plant wastewaters from time to time. The wastewater was to be evaluated at pilot scale as a candidate for evaporation and brine concentration using FLASH technology and samples of the brine were to be evaluated at lab scale for encapsulation. For the lab-scale encapsulation, the researchers tested various solidification media, including Portland cement, fly ash...
and quicklime in different proportions with the goal of finding a recipe that maximized the amount of brine in a solid matrix that would sequester trace metals and other potential pollutants. Fly ash used in the lab was the mixture that is typically sold from all hoppers of both units at the power plant. The success of the brine concentration and encapsulation work on the 18,000-gallon sample led to full-scale testing of 2 FLASH brine concentrators and pilot-scale brine encapsulation tests.

In August-November 2018 Purestream Services commissioned 2 FLASH brine concentrators to evaporate 3 million gallons of wastewater for the client. To confirm and supplement the lab-scale brine encapsulation work, Purestream conducted pilot-scale tests using fly ash from specific hoppers on each unit:

- Unit 1 Economizer
- Unit 1 Air Heater
- Unit 1 Precipitator
- Unit 1 Baghouse
- Unit 2 Economizer
- Unit 2 Air Heater
- Unit 2 Precipitator
- Unit 2 Baghouse

The remainder of this paper will present:

- Overview of the brine concentration and encapsulation process
- Description of lab-scale brine encapsulation tests
- Results of lab-scale brine encapsulation tests
- Description of pilot-scale brine encapsulation tests
- Results of pilot-scale brine encapsulation tests
- Economic Implications

BRINE CONCENTRATION AND ENCAPSULATION

Purestream Services offers 2 technologies for concentrating the metals and other non-volatile impurities in wastewater into brine. If the wastewater contains about 20,000 ppm TDS, it’s volume will be reduced by up to 95%, leaving 5% brine for use or disposal.

AVARA distills wastewater using electricity as the energy source in a technology referred to as mechanical vapor recompression. The clean distillate may be discharged or reused. The impurities in the wastewater are concentrated in the brine making them available for sequestration using encapsulation.

FLASH evaporates wastewater using natural gas or propane as the energy source. As the name implies, FLASH vents the clean steam to the atmosphere. In FLASH, the impurities in wastewater are also concentrated in brine.
Encapsulation sequesters impurities in a solid cementitious matrix that could be beneficially used or disposed. Whether the encapsulated material (grout) is used or disposed, it will likely be subject to a Toxic Chemical Leaching Procedure (TCLP test) to confirm sequestration. If the grout is designated for landfill, it must also pass a Paint Filter Test to confirm that all brine is part of the matrix and none will drain from the grout after it is in place.

Wastewater is evaporated and brine recycles until it is concentrated to a set point between 250,000 and 300,000 ppm TDS (sometimes higher). Then, brine begins to discharge into storage. FLASH uses natural gas or propane as its energy source and vents clean steam to atmosphere. AVARA uses electricity and condenses clean steam into reusable distillate.

There are several factors that should be addressed in encapsulation:

- **Objective** – immobilize pollutants and mitigate future environmental risk
- **Goal** – beneficially use if possible
- **Process** - simple and easy to execute using conventional equipment
- **Recipe** – maximize brine content and minimize expensive cementitious materials
- **Product** – strong enough for purpose with reasonable setting/curing times
- **Operations** – accommodate fluctuations in brine characteristics
- **Maintenance** – wear materials that last to control labor cost
LAB-SCALE BRINE ENCAPSULATION TEST

Paint Filter Tests were conducted on the mixtures at various intervals after production ranging from immediate to a few hours.

The 1/10th-scale pilot FLASH operated using propane (750,000 BTU/Hr) to produce about 900 gallons of brine at 3 different TDS levels – 150,000 ppm, 200,000 ppm and 250,000 ppm.

Brine was combined with various proportions of cementitious materials in a small mixer to make mixtures ranging in consistency from cream to yogurt. These mixtures were placed in 2-inch cube molds and allowed to cure in ambient air.
RESULTS FROM LAB-SCALE BRINE ENCAPSULATION

The cubes made with brine of 150,000 ppm TDS had a compressive strength of 2,690 psi. The cubes with brine of 200,000 ppm TDS had compressive strength of 3,120 and at 300,000 ppm TDS the strength was 3,440 psi. The conclusion from these tests is that concentrating this wastewater to higher TDS not only reduces the volume of brine that must be encapsulated but also increases the strength of the grout made from it.

After curing for 2-4 days, cubes with 40% brine and 60% Portland cement were sent to a third-party lab for TCLP testing. The results for pollutants of interest were analyzed to
be well below the required limits, as shown below (ND = Non-detectable). Moreover, the samples produced with higher TDS brine (300,000 ppm) do not indicate higher leaching potential. The implication is that higher volume reduction can be achieved by concentrating brine to higher TDS without environmental risks posed by re-liberating (leaching) pollutants after placement of the grout for beneficial use or disposal.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limit</th>
<th>150k</th>
<th>200k</th>
<th>300k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>5 mg/L</td>
<td>0.55</td>
<td>0.49</td>
<td>0.5</td>
</tr>
<tr>
<td>Barium</td>
<td>100 mg/L</td>
<td>0.99</td>
<td>1.05</td>
<td>1.07</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1 mg/L</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Chromium</td>
<td>5 mg/L</td>
<td>0.465</td>
<td>0.251</td>
<td>0.337</td>
</tr>
<tr>
<td>Lead</td>
<td>5 mg/L</td>
<td>0.07</td>
<td>0.09</td>
<td>0.07</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.2 mg/L</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Selenium</td>
<td>1 mg/L</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Silver</td>
<td>5 mg/L</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

From the dozens of recipes tested in the lab, several recipes were identified as good prospects based on the objectives of this wastewater study:
  - Use grout beneficially or pond closure
    - TCLP compliance is important
    - Because landfilling is not planned, the Paint Filter Test is interesting but not required
  - Minimize the cost for cementitious material and grout-making
    - Concentrate brine to 300,000 ppm TDS to reduce volume
    - Design a recipe to use a higher percentage of brine
    - Substitute fly ash for cement or lime, if possible.

These grouts made from the selected recipes set up to reasonable hardness, pass or come close to passing the Paint Filter Test within a reasonable amount of time and are potentially pumpable to remote locations. Other formulations are also likely to pass the Paint Filter and TCLP tests.
The recipe with 40% brine, 51% fly ash and 9% Portland cement seemed to be the most effective at meeting the goals of the project, so the detailed economics of integrated brine concentration and encapsulation were evaluated. As highlighted on the following figure, the recipe with 40% brine, 51% fly ash and 9% Portland cement is the best match for the objectives.

<table>
<thead>
<tr>
<th>Cementitious Material</th>
<th>Brine</th>
<th>Cementitious Material</th>
<th>Fly Ash</th>
<th>Paint Filter Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland Cement</td>
<td>40%</td>
<td>15%</td>
<td>45%</td>
<td>4-6 drops at 2hrs</td>
</tr>
<tr>
<td>Portland Cement</td>
<td>40%</td>
<td>9%</td>
<td>51%</td>
<td>1 drop at 2 hrs</td>
</tr>
<tr>
<td>Portland Cement</td>
<td>30%</td>
<td>17.5%</td>
<td>52.5%</td>
<td>NT*</td>
</tr>
<tr>
<td>Portland Cement</td>
<td>30%</td>
<td>10.5%</td>
<td>59.5%</td>
<td>NT*</td>
</tr>
<tr>
<td>Portland Cement</td>
<td>30%</td>
<td>3.5%</td>
<td>66.5%</td>
<td>Immediate Pass</td>
</tr>
<tr>
<td>Quicklime</td>
<td>30%</td>
<td>10.5%</td>
<td>59.5%</td>
<td>NT*</td>
</tr>
</tbody>
</table>

*NT = Not Tested

The bench-scale tests convincingly proved the concept and economics of encapsulation with brine levels up to 40% and various amounts of fly ash and Portland cement and encouraged the team to look into the details of fly ash sources, beneficial uses of grout and potential cost savings.

Because the station sells nearly all the fly ash from the power plant, additional work was completed in order to determine if the grout could be produced with fly ash with nominal market value and if the grout can be useful for pond closures or landfill operations.

PILOT-SCALE BRINE ENCAPSULATION TESTS
The encouraging results of pilot testing FLASH technology resulted in a decision to deploy 2 full-scale FLASHs for a 90-days to evaporate 3 million gallons from the power plant impoundment. Due to the site location and logistics, the 2 FLASHs (design capacity of 7.5 million BTU/HR) were fueled by propane during this deployment. Feed water storage tanks were repurposed from a previous project and temporary 480-volt electric service was installed.
The project plan anticipated evaporation of about 1 million gallons per month and corresponding brine production of 41,667 gallons with TDS or approximately 300,000 ppm. Operation of the 2 FLASHs over the 90-day period confirmed the performance expectations.

At 300,000 ppm TDS, some of the wastewater constituents reached their saturation point and formed suspended solids that exited the FLASHs in the brine. The brine used by Purestream for the pilot-scale encapsulation tests included these suspended solids so their potential pollutants would be sequestered along with the solids that remained dissolved in the brine.

This photo shows the white propane tank, blue frac tanks for brine storage and gray open-top tanks that were repurposed for feedwater, in addition to the 2 FLASHs.

The purposes of pilot-scale encapsulation testing were:

- Confirmation of lab-scale testing
- Larger batches of grout for field observation
- Investigation of more variables, including fly ash types and sources.
Fly ash used for lab-scale encapsulation testing was collected from a silo that stores a mixture of fly ash removed from all the hoppers on both units. It may have contained more fly ash from one unit or the other (one unit burns a blend of bituminous and subbituminous, or PRB, coals and one unit burns 100% bituminous coal). It may also have been biased toward a specific group of ash hoppers.

The subject power plant sells fly ash for beneficial uses so the use of salable fly ash for brine encapsulation penalizes ash sales and affects revenue. On the other hand, fly ash from certain the hoppers has no value and may compromise the value of “higher-quality” fly ash. Fly ash collected from precipitator hoppers meets the specifications of high-value markets but fly ash from other hoppers has less, if any, value. Pilot-scale encapsulation tests were designed to determine whether encapsulation could be effectively achieved with low-value fly ash.

As shown in the following sketch, the fly ash product stored in a silo and sold for beneficial use is a mixture of fly ash from 4 sources:

- Economizer
- Air heater
- Precipitator
- Baghouse

The dry fly ash handling system cycles through the various hoppers on a schedule that keeps each hop within the setpoint levels. As each hopper is being emptied, its fly ash is delivered to the bulk silo.
A 2-pound sample of the typical fly ash sold from the bulk silo (similar to the fly ash used in the lab-scale encapsulation tests) is shown in the photo below.

The pilot-scale encapsulation tests were conducted on fly ash from the silo and from the individual sources on each unit. Each of those sources of fly ash is different in terms of quantity, color, fineness, and chemical composition. The following photo shows the breakdown of the 2-pound sample in relative proportions of fly ash from each source and illustrates some of the differences in fly ash from each source.
In addition to evaluating the different sources of fly ash, the pilot-scale tests compared some of the potential deposition/placement alternatives for the grout:

- Continuous pours (slabs)
- Vertically-poured columns (piers)
- “Lava flow” along the side of the impoundment
- Underwater injection onto the impoundment floor

RESULTS FROM PILOT-SCALE BRINE ENCAPSULATION

Pilot-scale encapsulation with fly ash collected from the silo (mixed across all sources on both units) confirmed the lab-scale testing:

- The 2-inch cubes from the pilot test had the same strength as cubes from the lab-scale test.
- Setting and curing times were largely the same between lab and pilot.
- Feeding and mixing were the same between lab and pilot

Following the same encapsulation recipe (51% fly ash, 40% brine and 9% Portland cement, the fly ash from different sources gave different results.

1. As may be expected, bulk fly ash from the unit burning a blend of bituminous and subbituminous coal made grout with faster setting and curing and ultimate strength.
2. Fly ash from the economizers and air heaters produced grout with lower strength.
3. Fly ash from the precipitators closely resembled the encapsulation performance of the bulk samples.
4. Fly ash from the baghouse performed better than the bulk sample and was actually the best fly ash for brine encapsulation due to faster curing time and ultimate strength.

Economizer and Air Heater ash
- Only about 4% of the bulk quantity
- Not desirable for beneficial uses
- Coarser particles (like sand)
  - Less surface area to carry brine
  - Adds no strength to the grout
  - Bulk density makes it harder to mix well
- Economizer ash has low Loss on Ignition (<1)
- Air heater ash has higher Loss on Ignition (>5)

Precipitator Fly Ash
- Largest source (>75% of total fly ash)
- Highest market value
  - Meets specs for cement
  - Loss on Ignition <5
  - Quality is less variable than fly ash from other sources

Baghouse Fly Ash
- About 20% of total fly ash
- Very fine particle size
  - Harder to handle and feed during grout making
  - High surface area has higher brine carrying capacity
- Contains lime injected into flue gas (adds So4-enriched cementitious material)
- May contain mercury from Hg emissions controls system.
- LOI >5
- Not as valuable for other beneficial uses – buyers would like to exclude it.

These 6 containers shown in the following photo were stored outdoors in the weather for about a month. The weather conditions included nominal sunlight, lots of rain, and a couple freeze-thaw cycles.
- The 2 containers on the right were covered.
- The 2 containers on the left had “weep holes” drilled at the top of the grout to drain rainwater from the surface.
- The 2 containers in the center had drainage holes drilled below the grout to allow water to exit the containers AFTER is soaked through the grout.
- The grout in all 3 containers set up and hardened to about the same strength after a month.
- The uncovered samples showed surface spalling as shown.
- The grout that had water draining through to the holes along the bottom had the most spalling.
These columns shown in the following photo were poured into PVC pipes that had been buried vertically in bottom ash. As the PVC pipes were filling up with grout, they were withdrawn from the surrounding bottom ash, leaving the grout behind. These 3 columns of about 30 inches length cured to strong columns that did not break when weight was applied in compression, but they did break into 2 pieces when lateral force was applied. They broke into 2 pieces: they did not shatter.
ECONOMIC IMPLICATIONS

- **Method** – Regulated pollutants in wastewater can be concentrated in brine and encapsulated
  - Confirmed lab recipe and grout strength at pilot scale
  - Depending on their chemical composition, solids in the brine may improve encapsulation process.
  - Concrete process equipment can be used for encapsulation.
- **Material** - Fly ash with low market value may be used
  - Saves money without compromising encapsulation performance
  - Some ash types may improve encapsulation product strength
- **Placement** - Grout has beneficial use
  - Specialized equipment is not necessary for most placement methods
  - Underwater placement is feasible
  - Lime or Portland cement may be selected based on local prices

At the conclusion of the pilot-scale evaporation and lab-scale encapsulation tests, Purestream developed a conceptual cost estimate for the entire process from brine concentration through encapsulation, including capital, energy, consumables, labor and other O&M costs. The estimate was updated based on lessons learned from the full-scale evaporation and pilot-scale encapsulation tests and the result was a reduction of over 5% in total cost. If the sources of fly ash can be segregated to allow encapsulation to use the fly ash with no commercial value, the expected project costs can be reduced by an additional 5% or more.

CONCLUSIONS

- Evaporation and encapsulation turn wastewater into useful solids (grout).
- Fly ash types affect setting time and strength of grout.
- The recipe for grout can be controlled to achieve desired grout characteristics.
- Grout can be produced using conventional material handling equipment.
- The equipment and method for deposition/placement is site-specific.
- Evaporation and encapsulation are ready for full-scale deployment.