ABSTRACT

Electric utilities that elect to scrub for control of SO2 emissions face solid byproduct volumes about 4 times greater than unscrubbed stations. Costs of handling these materials can amount to a surcharge of about $1.50 to $5.00/ton of coal. A cooperative project has been undertaken with an Illinois utility having a scrubbed power station to develop more economically handlable and potentially beneficial paste fill mixes from their fly ash and scrubber residue. Mixes have been developed with mild soil like strengths to enhance potential for revegetation. The mixes are pumpable as a paste without expensive dewatering system additions at the power plant. The pastes do not have problems with bleed water and inhibit the leaching of boron. Equipment for producing and handling the pastes have been identified and the components tested. Configurations have been developed that should reduce materials rehandling at the power plant and consequently save money.
EXECUTIVE SUMMARY

The primary intent of the present proposal is to produce a fast setting variable strength paste fill from a combination of sulfite rich FGD sludge, and ponded F type fly ash from the combustion of Illinois coal, in order to provide electric utilities with more cost effective methods of using and storing the larger volumes of byproduct material that result for flue gas desulfurization. The project will aid the economy of Illinois by helping utility companies to lower the bus bar cost of electricity while using Illinois coal and employing Illinois coal miners. When utilities can store or utilize the scrubber and fly ash products of Illinois coal consumption onsite, the cost amounts to $1.50/ton of coal. When off-site landfilling is used that cost becomes $5/ton or more.

Scrubber byproduct and fly ash from Duck Creek Station of CILCO were mixed in various ratios and with various activators in order to produce structural materials that could be pumped and placed to provide rolling topographic features that blend with and can be revegetated to match the surrounding landscape. Pumpable pastes should be more economic to handle than the current system of excavation, trucking, stacking, and compacting. The blended pastes should also inhibit the leachability of boron reducing build-up in ponds and potential release into the surrounding ground and surface waters.

Mix ranges found suitable would allow CILCO to operate extracting material from previous years from pond #2 and pump them to topographic reclamation features on pond #1 as part of the pond #1 closure program. Other mixes were developed that are compatible with addition of a dry fly ash handling system that would market a portion of the current ash production. Marketing of all the fly ash production is likely to be problematic in handling only scrubber byproduct.

Mixes were also developed for handling by truck or belt conveyor. These mixes were intended to have significantly greater strength and durability against the action of weather. Such mixes would have additives and would require deviations in materials ratio from the production ratio.

Tests have been conducted to determine the type of feeding, mixing and pumping equipment that would be needed to handle the CILCO material on a large scale. A likely equipment configuration was determined and components were tested. The equipment can be coupled to 4 or 5 different materials handling scenarios for removal of the byproducts from the power plant. The configurations should significantly reduce rehandling and consequential costs over the present system.

The remainder of this report contains proprietary information.
OBJECTIVES

The primary intent of the project was to produce a fast setting variable strength paste fill from a combination of sulfite rich FGD sludge, ponded F type fly ash from the combustion of Illinois coal and possibly clays and byproduct calcium rich solids from the combustion of Illinois coal (i.e. such things as FBC ash and industrial venturi scrubber sludge). The paste fill was to have the following virtues

1- The fill should be fast setting so as to minimize the need for construction of confining structures.
2- The fill should be either pumpable or a paste of sufficient thickness for belt or truck transport.
3- The fill should exhibit high shear strength such that slopes of at least 25% and 70 feet of height can be safely sustained even under adverse conditions of moisture and seismic load.
4- The fill should have bearing strength and rigidity sufficient for the support of heavy haulage vehicles to maximize freedom in selection of haulage routes onsite and to open potential for offsite sub-base sales.
5- The fill should have a matrix that retards or prevents the release of boron.
6- At least one fill mix with low permeability should be developed to minimize infiltration for reduction of boron leaching and to open opportunities for preparation of liner material.
7- At least one mix should be amenable to the establishment of vegetative cover and a root mass capable of preventing erosion.

The specific objectives of this project were to

1- Develop paste mixtures having the virtues described above
2- Assess the durability of the mixtures developed
3- In cooperation with CILCO to design a system for mixing and placing the developed mixes on a large scale at the Duck Creek demonstration site.
4- To set-up and operate a mixing and placing system and use it to prepare a 1,000 ton demonstration fill.

INTRODUCTION AND BACKGROUND

The project will aid the economy of Illinois by helping utility companies to lower the bus bar cost of electricity while using Illinois coal and employing Illinois coal miners. Under the new Clean Air Act, Illinois coal is assessed a cost penalty when it is burned due to SO₂ emissions. When credits are used, the dollar value of that penalty is variable with market conditions controlled by the EPA auction. At $120/ton credits that penalty can be $8/ton. Clearly there are prices for SO₂ credits at which no high sulfur fuel could compete. In all likelihood the price of SO₂ credits will go up significantly. Utilities using scrubbing have a fixed cost of SO₂ control and provide a market for Illinois coal where the product can definitely compete against western coal. Scrubbed units produce
almost 4 lbs of scrubber residue for every pound of SO₂ they scrub. When utilities can store or utilize the scrubber and fly ash products of Illinois coal consumption onsite, the cost amounts to $1.50/ton of coal. When off-site landfilling is used that cost becomes $5/ton or more. This project will work directly with a utility company in making a usable construction material out of ponded fly ash and scrubber residue that would normally have no outlet.

The major solid byproducts of coal combustion in a scrubbed pulverized coal combustion boiler are fly ash and scrubber residue. Usually fly ash comes to about 8% of the weight of the coal burned. Scrubber residue comes to about 3 times the amount of fly ash. Electric utilities must either find markets for this material or incur costs for disposal. Fly ash can, under some conditions, be marketed, but power plants must collect and store the fly ash dry. CILCO does not have the equipment to do this. Nationally, only a few percent of the scrubber residue is utilized and this is almost all scrubber residue that has been utilized has been force oxidized to synthetic gypsum. CILCO has a sulfite rich scrubber residue that cannot be used as gypsum.

When utilities do not market their byproducts the most common mode of storage and disposal is to slurry the solids into a pond and decant the water back. The solids settle to the bottom and fill the pond over time. This type of facility is permitted in Illinois as a water treatment works until the pond fills. At that point the utility must either clean the residue out of the pond and transport it to a monofill or repermit the pond as a monofill to make it the final resting place of the residue.

Ponds can provide environmental problems for the utilities operating them. Boron becomes concentrated in readily soluble form on the fly ash and upon contact with water is released. Many of the states power producers suffer major problems with Boron. Illinois Power shut down one of its power plants burning Illinois coal in large part because of boron rich drainages from F type fly ash. Other producers report concerns with monitoring wells or drainages into creeks. These problems are not unique to specific power plants and are widespread throughout the industry. Many power plants are operating with significant variances on boron and when this variance was denied in the Illinois Power case, a plant was shut down and a market for Illinois coal was lost.

The CILCO Duck Creek system runs an almost continuous vacuum on the fly ash hoppers below the electrostatic precipitators. The fly ash is drawn several hundred feet into a separator where water is injected to carry the fly ash to a large tank. This is a very dilute phase transport. The large tank is maintained by a demand-based system that pumps the settling solids adding water if necessary when the level of the tank rises. The discharge is pumped through a 10 inch line to pond #2 about ½ mile from the plant. The solids in the pipe run at about 5%.

The wet scrubber system uses a large recirculation tank of slurry. The scrubber residue is removed as a bleed stream which is sent to two sumps by the main pump house. From there the material is slurried through a separate 10 inch line, again using a demand based
The discharge lines for the fly ash and scrubber sludge are side by side but physically separate.

The Duck Creek Station was originally set-up for three ponds. The power station is in a rural open area with few theoretical land constraints. The farm land is good and would be expected to bring over $2,000/acre. In practice Duck Creek may face land constraints that are not readily apparent. On the east the station is bordered by the Illinois River. To the west are old abandoned strip pits. The land belongs to Freeman and has many final strip pit lakes that could be used for disposal purposes, but relations are not good with Freeman right now and the price of accessing the final strip pit lengths could be prohibitive. Duck Creek is itself, together with its ponds, located on old strip mined lands. Storage capacity for the station is running out in the clay lined ponds at the same time that the threat of deregulation and the potential to merge into a larger system is making capital expenditures harder to justify. Pond #1 is full and pond #2 is rapidly nearing capacity. Pond #3 was sited in an area since reclassified as a wetland and faces some permitting difficulties. CILCO is currently dredging material from Pond #2 with a backhoe, drying it on the surface, and trucking it for piling on pond #1. These operations were based on the Harco project funded by ICCI. The cost of the CILCO rehandle operation alone is $6/ton. The rehandle operation is probably keeping CILCO 1 to 2 years away from filling pond #2 and being left with no onsite storage capacity.

Pond #1 will not be permitable as a water treatment facility in the upcoming permit renewal and will have to be permitted as a waste storage facility. Boron is building in the ponds and starting to get into surrounding waters. It will be an issue in the new permit. While the project is a cooperative effort with CILCO, directed at solving CILCO problems, the issues faced at Duck Creek are not unique and methodologies developed here have cost saving potential for many Illinois utilities.

**EXPERIMENTAL PROCEDURES**

**Component Materials**

The coal combustion byproducts (CCBs) and additives to be used in the test program were identified in consultation with CILCO. The major byproducts to be managed were unoxidized sulfite rich scrubber byproduct and F type fly ash from a pulverized coal combustion (PCC) boiler at the Duck Creek Station. Within a 20 mile radius, F-fly ash is also available from the Edwards power plant and C fly ash from the Powerton plant. Fluidized bed combustion (FBC) fly ash from the ADM plant was ruled out as an additive byproduct for stabilization early in the project since transportation cost from Decatur, Illinois to Duck Creek would be high. Instead, lime was considered as an additive because of its potency relative to its weight and because of its similarity to some lime and cement dusts that might become available.

Because the intention of the demonstration was to ready plans, materials compositions and experience for full scale commercial use at the plant, it was critical that materials tested be in a form and representative of what would be available at the plant on the scale
of its full byproduct generation. During the month of December, a trip was coordinated to both of CILCO’s generating stations. At the Edwards power station, F type fly ash from unit #3 was collected. The fly ash is produced from mid sulfur Illinois coal and some spot purchases from the east. Little if any western coal was being burned at the time. The Edwards station uses a vacuum system to evacuate ash from 20 ESP hoppers. The vacuum system runs only a short distance to a separator where the ash is sluiced. Edwards is actively pursuing a dry handle system with most of the output being used for byproduct management rather than being actively marketed. One of the hoppers had plugged resulting in a full hopper and the need to disconnect the hopper from the vacuum system so that the bottom of the valve could be opened and rodded out. The ash from the freshly rodded hopper was collected. The area below the hoppers is a long enclosed bay with concrete floors and garage style doors. The rodded ash had just fallen into a giant heap on the floor. The sample was collected using a steel shovel, scooping from the top and sides of the pile. None of the ash taken had been in contact with the floor and both the drum and shovel were clean. The sample would be considered a grab sample but it was taken from a pile of ash collected over several shifts and cycles of the plant giving it a better average composition relative the load on the boiler. One 55 gallon drum with a bolted on lid was collected.

Duck Creek power station was also visited. Here also a 55 gallon drum of F type fly ash was collected. The F type fly ash comes entirely from the burning of coal from the Freeman United Crown mine complex. Duck Creek, like Edwards, uses a short vacuum line to a separator. A bleed line for sampling is available off of the vacuum line. The bleed line is not really intended for such large quantities of ash and it took over 1.5 hours to fill a 55 gallon drum. Because the sample was taken from the vacuum line it represented material from all ESP hoppers being drawn. The sample was taken starting about 11:30 am over the noon peak. The time interval represented was smaller than at Edwards, however a wide part of the hopper array was represented. The drum was sealed with a bolt on lid.

Scrubber byproduct was also collected. This is a sulfite rich material produced from the scrubbing of a high sulfur Illinois coal. The scrubber operates well above the stoichiometric ratio required and is not particularly efficient. Duck Creek does not “over-scrub” and runs the scrubber basically as designed. Limestone - sulfite slurry is recycled through the scrubber. To keep sufficient fresh reagent in the slurry the recycle tank is continually bled. The bleed slurry flows to sump. When the water level reaches a critical point the pumps activate discharging slurry through a 10 inch line to the pond area. Since this is a wet scrubber there is no dry handle point. The samples were taken from the sump on the west side of the pump house. The sample was collected using a backhoe with the bucket forced into the settled solids in the sump. The bucket was then tilted back and forth to drain as much water as possible from the load. Steel shovels were used to scoop solids from the bucket picking up as little decant water as possible. Extra material was forced into the drums to force water to over flow and further increase the solids in the drums. Bolt-on lids were placed on the 3 drums collected. The samples were taken to the high bay area at Carterville without attempt to further decant. The CCBs were characterized for moisture and particle size distribution.
All of the fly ashes and the lime can be considered dry effectively since the moisture content was well below 1%. Several methods of measuring the moisture content of scrubber sludge mixed with water in the container were tried since the scrubber sludge and water tends to separate. It was found that a consistent mix could not be developed and the moisture content varied more than 30%. The moisture content of the settled scrubber sludge was approximately 80%.

A sample of scrubber sludge was dried at 90°F for about 48 hours prior to running a screen particle size analysis. The sieve screen test for the Duck Creek scrubber sludge was inadequate as nearly 40% of the material passed a 400-mesh screen (.0015 inch opening). Hydrometer or Microtrack testing were required to perform fine particle size distribution analysis. A hydrometer grain size analysis was performed on Duck Creek fly ash, Duck Creek scrubber sludge, and a mixed sample of the mixtures that are under investigation. The hydrometer test was discounted as the measured specific gravities were less than the range (2.45 –2.95) of values given in the correction table for the test performed. The measured values are given below in Table 1.

<table>
<thead>
<tr>
<th>Table 1 Measured specific gravity</th>
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</thead>
<tbody>
<tr>
<td>Duck Creek Scrubber Sludge</td>
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<tr>
<td>Duck Creek Fly Ash</td>
</tr>
<tr>
<td>3:1 Mix Scrubber Sludge to Fly Ash</td>
</tr>
</tbody>
</table>

The Microtrack test was performed for Duck Creek CCBs and the results are summarized in Figure 1, Appendix A. The Microtrack test assumes uniform density for the particles.

**Mix Studies**

Test mixes were prepared from the Duck Creek fly ash and scrubber byproduct, variously amended with activators. The F type fly ash was considered to provide pozzolan. Activators consisted of calcium oxide rich additives such as lime and C type fly ash that attack the pozzolan and produce cement reactions. One of the first considerations was of what ratio to use for the Duck Creek fly ash and scrubber byproduct. One factor to be considered was the production ratio, since the byproducts must currently come to use and rest on the site. The production ratio is 3.25 parts of scrubber byproduct to 1 part fly ash. Pond #2 at Duck Creek is filling up. Since the fly ash and scrubber byproduct have been sluiced into the pond almost entirely from one end, the ratio of the ingredients in the pond change from the near to far side. Near the discharge there is about 0.5 units of fly ash to 1 of scrubber byproduct, while at the other end the ratio is about 0.25 units of fly ash to one of scrubber sludge. This then became the study range for the mix. The range provides for some of the fly ash to be diverted to market in a case where fresh products
were being used. Since the principal product is sulfite rich scrubber byproduct it was decided to measure other ingredients relative to 1 unit of scrubber byproduct.

In developing the mixes, one of the practical problems was to identify the amount of scrubber byproduct and water, since the two ingredients are hard to prevent from separating in storage. The most consistent method of developing a mix containing scrubber sludge was to pick up some of the settled material from the bottom of the container while minimizing the agitation of this material. It is known that such a material contains about 80% moisture. A split of this material is taken for drying to get an accurate measure of the dry weight and moisture content, however, this data is not available at the time the mix is prepared. (Obviously the slow low temperature drying procedure for a material with water of hydration would allow some change in moisture content in the study material). This remaining scrubber sludge not used for the moisture sample is weighed in the mixing bowl and an appropriate amount of fly ash and any other additive are added. This combination of materials is then mixed and more water is added to obtain the desired slump.

The possibility of drying scrubber sludge and then accurately measuring it for the precise weight or ratio control was considered. This could be easily done in the laboratory, but would be expensive and unnecessary for use on a commercial scale. Exposure to oxygen in the air on drying would allow some of the sulfite to oxidize to sulfate thereby, changing the chemical make up of the scrubber sludge. The change in chemical make-up could have more of an effect on the mix than the small change in ratio, due to the variation in the moisture content of the scrubber sludge. Therefore, the procedure above involving somewhat variable composition was considered appropriate for commercial practice.

A 325-watt KitchenAid Heavy Duty household mixer was used to mix the scrubber byproduct, fly ash and additives. The mixer had an approximate capacity of 4.5 liters. The scrubber sludge was weighed in the mixing bowl and an appropriate amount of fly ash and other additives were added. On average about a two kilogram sample was prepared for each test. This combination of materials was then placed in the mixer and mixed for two to three minutes while adding more water to obtain the desired slump. This action produced a uniformly mixed sample. Before the water could settle out of the mixture, the sample was tested for slump using a half-sized cone. The cone was placed on a clean glass sheet and the sample was added to the cone. The sample in the cone was then further homogenized using a 1/8" glass stirring rod. The sample would slump when the cone was vertically raised. The difference between the height of the cone and the slumped sample, in inches, was multiplied by a factor of 2 to obtain the slump of the sample. The use of cones half the size of the ASTM standard slump cone was studied in previous work done by Dr. Chugh for U.S.D.O.E. and I.C.C.I. and found to be valid for pumping design purposes. Since not all the material from the mixer was needed for the slump test, more water could be added to the remaining material to get a higher slump.

Following the slump test, the material that had been in the cone was split into two parts. One part was placed in a drying tray and the other was used to fill a plastic cube
measuring 2 inches on each side. For each sample at a given ratio, slump and additive dosage, three cubes were filled. The drying tray was 6.5" long, 3.5" wide and 2.5" deep. Both the tray and the cubes were then subjected to curing. The weight of the empty plastic tray and the weight of the tray with the sample to be cured in it, were noted.

The curing chamber was a container about five feet long, three feet wide and two feet high with an adjustable top. Water was always maintained to about six inches from the bottom of the container. The samples were kept above the water level. A small fan in conjunction with the adjustable top was used to maintain the humidity in the chamber at about 50%. The temperature in the curing chamber was at room temperature level, around 25°C.

The sample in the tray was periodically tested for strength by a pocket penetrometer. The penetrometer is forced into the sample to a certain marked depth and the observed reading is multiplied by a constant factor to get the compressive strength. It was ensured that only the un-cracked (if at all) area of the sample was being tested and that there was sufficient clearance, recommended by the procedure around the testing spot. The penetrometer was capable of measuring strengths up to 60 PSI. At the same time the weight of the tray was taken so that the moisture content of the sample could be estimated. When it was not possible to conduct any more penetrometer strength tests or when the desired strength was achieved, the sample in the tray was oven dried till there was no weight loss and the moisture content was determined. On the other hand, the sample in the cubes was left intact till tested for uni-axial compressive strength.

At the end of each week, one sample cube was taken out, weighed and subjected to uni-axial compressive strength testing. After the test, the sample was crushed manually and subjected to the ASTM Shake Test (ASTM D-3987) to determine leaching characteristics. In this test, suggested by the American Society for Testing and Materials, 100 grams of the sample is weighed and mixed with 2000 ml of distilled water. The mixture is then placed in a bottle and rotated in an end-on fashion for a period of 18 hours. After the agitation the sample is filtered and the desired parameters are quantified.

The filtered leachate from the ASTM shake test procedure was analyzed for parameters of interest. These included the pH and dissolved anions and cations. pH of the sample was measured to determine if the capture, or release of boron, was dependent on the pH. Sulfate was analyzed using a Dionex DC-10 Liquid Ion Chromatograph while a Perkin Elmer Plasma-400 Inductively Coupled Plasma Spectrophotometer was used to determine the cations, of which calcium and boron were of utmost interest. Boron was measured because the development of environmentally benign mixes that control the boron release was an objective of this project. Calcium was important in determining if the boron capture, if present, was due to the formation of cement compounds in the mix. Both boron and calcium were analyzed at multiple wavelengths to minimize interference from other elements.

One question that kept recurring throughout the project duration was if the mixes were drying or curing or, both. To help understand the phenomenon an experiment was set up.
After the sample was measured for slump, three sample cubes were made. One cube was placed in the curing chamber as before. The second cube was placed in an oven for drying while the third sample was placed in a plastic bag and placed in the oven. It was expected that the plastic bag would prevent the loss of moisture from the sample. Later, all the three samples were tested for strength.

Experiments were also performed to determine the rate at which the mixes bled. Six samples were prepared three of which used straight scrubber byproduct while the other three were made from a three to one ration of scrubber byproduct to fly ash with no additives. All the six samples were prepared to be in the pumpable range of 8 to 11 inches of slump. The samples were placed in graduated one-liter plastic cylinders and the water level readings were taken at regular intervals. This enabled the monitoring of bleed with respect to time.

To find the durability of the samples in the presence of excessive moisture, some of the sample cubes were immersed under water for a few weeks. Only limited practical qualitative data was generated.

Efforts were also made to determine the ease with which vegetation could be established on the ground reclaimed with pumpable pastes. Sample material left over from the slump tests was used to partially fill a plastic container that measured 18 in. long, 9 in. wide and 9 in. deep. A fresh mix was prepared and Fescue and oat seeds were thoroughly mixed in it. This sample was then spread over the mix in the container. The required light for photosynthesis was provided by two three feet long fluorescent tubes. The seeds were occasionally fed, about once every three weeks, initially with Foliar feed and after about three months with Miracle Grow for tomatoes. Miracle Grow was chosen because it was one of the few fertilizers that did not contain boron and the mixes used in the test faced the risk of boron leaching.

It was observed that the amount of germination was roughly one fourth to one fifth of what would be usually observed. After about six months of vegetative efforts most of oats had died while a majority of the Fescue plants were still alive. One first conclusion that was drawn was that the poor performance of the plants could be due to excessive pH, over 9.0, and not boron.

The statistical ANOVA was performed on the results to determine cross dependency, if any, on the strength and boron release of the mixes. The effect of the ‘independent’ variables in the mix, namely slump, ratio of scrubber byproduct to fly ash, the dosage of C-fly ash or lime and the curing or drying time was studied with respect to the ‘dependent variables’ mix strength and the boron concentration in the ASTM Shake Test. Interdependent variables like the products of ratio and slump, ratio and additives, slump and additives, time and additives, ratio and slump were also considered.

ANalysis Of VAriance software package initially determines the variance of the measurements with respect to the observed results considering all the independent variables at once. After that, the analysis is further refined using multiple regression. In
the Forward Selection procedure the software picks the most significant parameter from the initial ANOVA analysis and successively adding the next significant parameter, tries to find an equation that describes the dependent variable in terms of the independent variables. In the process the software calculates F values that indicate the probability P that the observed events could be due to random chance. The iteration stops when all the variables have been accounted for, or the probability exceeds some user-specified value.

In the Backward Selection procedure the analysis works the other way around. All the variables identified by the initial ANOVA are included and the least significant variables (identified by low F and high probability) are successively dropped. The Stepwise procedure combines the Forward Selection and Backward Elimination procedures. This procedure starts with the most significant parameters and keeps adding more parameters. Whenever the significance of a parameter, in combination with others, goes down below a certain value, it is taken out of the regression.

RESULTS AND DISCUSSION

The primary mix of interest is a pumpable paste capable of handling the bulk of the unmarketed coal combustion byproducts with a minimum of additives and additional costs. Two characteristics are key in achieving this

1- The strength of the set material
2- The slump of the mix

The data for identification of usable mixes come from three test procedures discussed in the procedures section. These data come from penetrometer tests on material poured into curing trays, unconfined compressive strength tests done on cubes of dimension 2 inch by 2 inch by 2 inch, and slump tests.

Since the mixes being prepared are to be a low strength concrete, curing reactions are expected to take place through time giving rise to an increase in strength. One natural question then becomes, at what point should strength be measured? Under ASTM procedures common strength measurements are taken at 7, 14, and 28 days. In this study, penetrometer tests done on initial mixes serve as a guide to when representative strengths may be achieved. Figure 2, Appendix A shows penetrometer strength as a function of time for a three to one ratio of scrubber byproduct to fly ash with lime, class C fly ash, and nothing as additives. It is interesting to note that it is several days before any strength develops. Class C fly ash produces the fastest set. Lime produces the highest strength but slowest set. The untreated case is intermediate. Mixes without lime appear to slow in strength gain after about 7 days, while for lime it would appear that 14 days is more a point of change. Based on this data and ASTM convention the set time for the strength cubes and full uniaxial compression tests were set at 7, 14, and 21 or 28 days.

The desired setting strength for the material is a minimum of 50 to 75 PSI. For ordinary pumped pastes, setting strengths above 400 PSI may result in difficult digging conditions should the material ever be handled later. Data from the ANOVA test matrix described
under procedures is used to identify mixes with a usable range. The ANOVA matrix considered that the strength achieved could be a function of the ratio of scrubber byproduct to fly ash, the slump of the mix (a practical engineering control on needed moisture level), the activator used, and the cure time. Figure 3, Appendix A shows that at 7 days mixes with a fly ash to scrubber byproduct ratio of 0.33 to 1 and no additives achieved the strength minimums without exceeding the strength maximums. As would be guessed from the figure, ANOVA analysis indicates that higher additions of pozzolan (fly ash) tend to produce higher strength. It is worth mentioning here that all the mixes tested had strengths in excess of the required minimums while not exceeding the maximums. This includes mixes with fly ash to scrubber byproduct ratios of 0.5 to 1 and 0.25 to 1 also. This would imply that in future, if some of the fly ash or scrubber byproduct were to be marketed or otherwise utilized, it would have no impact on the range of mixes that could be handled, at least to the limits of the test data.

The second key characteristic is slump. At each level of ratio indicated in Figure 3 there are three characters. These characters represent mixes at three different slumps. Mixes prepared with a zero slump where intended to be relatively rigid and lack bleed water. They were considered for batch handling in trucks. They would not be pumpable. Mixes were prepared at 7, which is the minimum level for handling over modest haul lengths using the heaviest concrete pumps. These low water pastes often have the least problem with bleed water. Mixes at 10 slump were prepared since the mixes could be more easily be pumped and might not need positive displacement pumps. In order to be handled as a pumpable paste a slump of 9 to 10 inches is recommended. This is somewhat higher than would typically be a minimal slump for paste, but as can be seen, mixes of all slump and ratio tested exhibited the required strength minimums in a pumpable range. ANOVA and subsequent regression analysis indicates slump by itself does not directly effect the strength of the mixes but may influence the strength in combination with the activator dosage or the ratio of fly ash to scrubber byproduct. The type of effect tends to be loss of strength with increased water addition and slump, as would be expected for a basic cement chemistry.

When additives are entered into the mix, the effect is to increase the strength of the mix. Figures 4a, b, and c, Appendix A, show the maximum strength achieved at different fly ash to scrubber byproduct ratios with nothing, C-fly ash, and lime as additives. The different figures cover different slumps. The ANOVA analysis found in appendix A, indicates that both lime and lime with time have strong effects, but when regression is applied, both lime and its interaction with fly ash were terms removed by the backwards and stepwise procedures. Indeed, in the Forward procedure the impact of lime addition is negative. Remembering the earlier figure which showed that lime delayed curing, the report is not surprising. The interaction of lime with fly ash was not surprisingly positive. Looking at Figures 4a, b, and c the impact of additives is clear. At low fly ash ratios the pozzolan concentration is insufficient to achieve maximum strength. As the pozzolan concentration becomes adequate, there is a sharp rise in strength at 0.5 ratio. When the ultimate strength achieved is considered, as in the figures, then lime always enhances strength, however, here too there is a sharp increase when adequate pozzolan is supplied. At low fly ash ratios, C-fly ash is a more effective additive than lime because it
also adds pozzolan. The pattern is the same at all slumps but, as previously discussed, too much water addition reduces strength. The negative impact of high slump is more pronounced on mixes with stronger concrete behavior than those mixes that were very weak. It is interesting to note that with 0 slump, high fly ash ratio and lime that the mix exceeds the 400 PSI strength limit set for an easily dug mix. Since this mix would not be pumpable anyway, it would be placed by trucks in lifts. Such a construction sequence would be most attractive economically for building the dikes and other structures around the edge of the capped pond. In this case, the higher strength mix would be desired and is worthy of note. Unless higher strength is needed, the minimums can be achieved without additives, and the expense of additives would probably be best avoided.

Based on the above discussion, it is felt that even without any additives, the scrubber byproduct and fly ash mixes can be pumped across the distances encountered at the Duck Creek station. All the mixes, even without any additives have the necessary strength to sustain themselves. Both the additives tested increase the strength of the mix, if desired, but lime causes bleed water above 10% at a slump of inches required for pumpability and as such is not recommended as an additive.

In identification of useful mix ratio intervals time effects must be considered too. Figure 5, Appendix A, shows that in general the effect of time is negative on strength. This loss of strength with time is in sharp contrast to the expected strength gain or even the continuously increasing strength identified above in the penetrometer test data. Even after the loss of strength, all the mixes continue to be within the suggested strength ranges.

The unexpected drop in strength with time raises issues with mix durability. One explanation of the unexpected result is shrinkage cracking, since scrubber byproduct by nature tends to be a very wet material. Figure 6, Appendix A, shows the variation of the mix strength with increasing moisture content for mixes with no additives. Not surprisingly after seeing the last figure, there is a decline in strength that occurs simultaneously with the weight loss. Direct measurements of strength relative to density are not available, as a specimen volume is required to go with the weight data and volumes different than the original measure are usually made by some sort of fluid displacement. In view of the ability of the material to absorb liquids such as water, fluid displacement tests not requiring special equipment were not practical. The shrinkage cracks were, however, very visible in experiments and the very low strength low moisture samples at the left of the figure were specimens already broken in two by shrinkage cracks before they were ever placed in the machine.

This leaves the issue of the contradiction between the drying trays and penetrometer tests and that observed in the cube tests. One experiment indicates a strength gain in time, while the other indicates a strength loss. When one remembers that the penetrometer test involves placing the point of the penetrometer on a small area away from previous holes and other defects and pressing down, while the uni-axial compression test involves placing the entire cube in the testing machine the dilemma disappears. The penetrometer measures very localized point strength chosen to avoid interference from macro scale
defects. As one would expect with a curing mix, the strength increases. The uni-axial compression test strength is governed by the weakest fracture plane, which includes all macro defects in the cube itself. Naturally the strength falls in the presence of major continuous shrinkage cracks.

One way to reduce the impact of shrinkage cracking on strength appears to be activator addition. In ANOVA analysis the lime and time interaction term is the only one which is significant, and backward and stepwise regression both identified the interaction term as having a positive affect significant at alpha values less than 1%. The cross term of time and activator was similarly identified as significant and having a positive impact on strength determined by regression. Figures 7 a through f, Appendix A, show a generally beneficial effect of activator, though with C fly ash it is more obvious for 3% addition than for 7%. This then suggests that the fundamental benefit of activator addition is in decreasing strength loss due to shrinkage cracking. One would thus, probably avoid the use of activators where simply falling within the strength interval is important, and add them when issues of cracking and degradation become more important.

Shrinkage cracking would of course lower the bulk strength of a material, but it also opens new areas to the influence of weathering. One type of testing done on materials was the soaking of partially cured cubes in water. Two cubes, one made with the c-type fly ash as the additive and the other with lime as the additive were soaked in water for a period of three weeks. The samples containing the lime as additive could be manually handled without breakage after a period of two weeks, though they did not appear to have developed any strength. On the other hand, samples containing the C-fly ash additive would disintegrate after only one week. The conclusions that can be drawn are only qualitative, but it appears that at least early in the curing process that the material behaves more like a weakly cemented soil than a concrete when exposed to water and weathering. Lime is more effective in reducing this behavior than C type fly ash.

Since the pumpable paste will be stacked and cured outdoors, it important to temper strength expectations with respect to slope and stacking height against the tendency of the material to soften in the presence of water just as would be the case with a natural soil. The handling plans discussed later under economics recognize this reality by keeping modest 10% slopes and limiting stacking height at any one time to about 25 feet. The cost of lime may find some offset in increased storage capacity or in producing materials that are less vulnerable to weathering and degradation.

While slump is an engineering property that indicates the ease with which a particular paste can be moved, it must be recognized that slump is controlled primarily by mineral grain size and shape and by the moisture of the paste. Figure 8, Appendix A, shows the relationship of moisture content to slump for a wide range of mixes. The data are consistent with the view that appropriate slumps will be achieved when the moisture content of the mix is about 55 to 72% depending on the presence of additives. It is noteworthy that additives in the concentration that best controlled strength loss with time (about 1% lime and 3% C fly ash) increase the moisture required to achieve a particular
slump. This may be because of the moisture consumed in the pozzolanic reactions between the additives and the fly ash in the mix.

The present handling system slurries fly ash and bottom ash out of one line into a pond at about 5 to 10% solids, and scrubber byproduct out another line at about 10% solids. The practical question from the standpoint of evaluating the economics of a paste pumping and stacking system is how materials currently delivered in this fashion can be brought into the moisture content range needed for the target slumps. Material is currently dredged from pond #2 and stacked in winrows (rehandle step #1). Dryer material that does not erode back into the pond for additional rehandle is then loaded into trucks and batch hauled to pond one for dumping (rehandle step#2) grading (rehandle step#3) and compacting (rehandle step #4). The process is both expensive and vulnerable to bad weather. Options available to get the lower moisture content include pile curing as is now done. Obtaining a representative field sample from piles of variable composition stacked along the serpentine system in the pond for various lengths of time at various elevations above pond water level would be difficult. It is known that well settled scrubber byproduct with water ponded above it contains about 80% moisture. It is also known that fly ash tends to dewater well and below the pumpable range when setting in field piles. It is also known that the un-eroded portions of the pile a couple feet above the pond level show no visible bleed and stand at fairly high angles of repose. This would suggest that most of the field stacked material is pumpable in its present condition and that water or activator additions may be the best way to make slump adjustments either up or down on an operating observation basis. The system does not allow good control on scrubber byproduct to fly ash ratio since fly ash is coarser and less platey and settles out closer to the discharge. Since the trial mixes in this study roughly bracketed the range present in the pond, one would expect to achieve strength in the suitable range for material removed directly from the pond.

Another similar approach would be to take material out of the pond directly to a paste pumping system. Some limited decanting of water off the top would be possible. Since this is the manner in which samples were taken for mix preparation and the scrubber byproduct had around 80% moisture, one would expect considerable problems controlling bleed and keeping a stable paste. In experimental work, dry fly ash additions were made. Such an action in combination with activator addition would likely bring the material from the pond into a pumpable condition with less rehandle and eroding.

The current materials handling system has created a serpentine system near the discharge outlets into pond #2 to try to stimulate the settlement of as much material as possible near areas where access ways have been built into the pond to allow equipment to dig and pile material for drying. Modification of the discharge points could allow fly ash and scrubber byproduct to settle out somewhat separately. This may be an alternative to needing a dry fly ash system and would limit the material requiring stacking and curing to the fly ash only.

Mechanical modifications may reduce the dewatering problems. Fly ash is collected dry from the ESP hoppers, however the vacuum system has only limited conveying capability
sufficient to bring the ash to the digestors. JTM is looking at the possibility of installing dry fly ash hoppers. One impetus to this is the ability to market the fly ash. This would further increase the scrubber byproduct to fly ash ratio. Only limited data for scrubber byproduct to fly ash ratios above 4 to 1 was prepared. Based on this information, if half the fly ash were marketed and the ratio shifted to 6 to 1, the mix would still possess the required strength and be pumpable. A dry fly ash system would provide a basically dry fly ash product. Mixing fly ash with scrubber byproduct of about 80% moisture at ratios in the 2:1 to 5:1 range, would still yield products with the required strength and pumpability.

The scrubber byproduct is produced in a wet system and bleeds to begin with have only about 10% solids. Thickeners could increase the solids to at least 40%. Cyclones could reach close to the same solids with much less space, but more complicated piping. The scrubber byproduct is probably too fine to respond well to sieve bends. Screen bowl centrifuges could get solids up to 60% which should be pumpable in the presence of additives.

Mixed systems could be based on mechanical dewatering of scrubber byproduct together with decant drying of fly ash. They could be based on dry handling of fly ash with decant handling of scrubber byproduct. They could be based on decanting of both materials, or they could be based on mechanical dewatering of both materials.

Other issues of mix preparation arise. Sulfite rich scrubber byproduct is thixotropic and platey. It behaves in a rather gummy fashion. Once the slump of a material is appropriately adjusted and the size consist resists phase separation and the material is in a positive displacement pump such as a concrete pump, there is little doubt that it can be moved over the likely required distance spans at Duck Creek. The size consist and slump of all the materials suggested so far are such that phase separation should not create settlement and plugging of the paste flow lines. Feeding and mixing sulfite rich scrubber sludge remains a more mechanically challenging aspect.

A trial run was made for mixing the Duck Creek scrubber sludge with the Duck Creek fly ash at the Illinois Coal development Park in Carterville. The objective of this run was to determine if scrubber byproduct and fly ash would effectively feed through augers and make a suitable mix for pumping. The auger mixer is shown in Figure 9, Appendix A. It has two bins with different feed rate augers. These feed into a central auger, which is about 8 inches in diameter. Water was added to the mix by a spray bar located above the central auger shown in Figure 10, Appendix A. The volume of water can be controlled through a flow meter. Scrubber byproduct was removed from the barrels at approximate moisture content of 80% and placed in the adjustable feed rate bin (shown in the bottom of Figure 9), and the dry fly ash was placed in the other bin (top of Figure 9).

The auger mixer had limited success in mixing scrubber sludge and fly ash and adding enough water to get a pumpable mixture. The scrubber sludge did not feed uniformly into the mixing auger at a sufficient rate, even with the controlling gate opened all the way, to achieve anything like a three to one ratio of scrubber sludge to fly ash. Better
results were obtained switching the feed hoppers so that the scrubber sludge would go in the fixed opening hopper and the dry fly ash in the regulated hopper. The dry fly ash could be nicely regulated as it flowed though the auger in the feed hopper. The 80% moisture content scrubber sludge with thixotropic behavior did not feed well despite, the auger in the bottom of the feed hopper. Water was introduced directly into the scrubber sludge feed hopper. This was, however, not very successful. The auger mixer may be successful in providing the necessary mixing if the scrubber sludge can be delivered to the mixer in pumpable slurry at a controlled rate and the dry fly ash is added to it. In a small scale laboratory experiment conducted to address this problem, it was observed that vibrating the scrubber feeder greatly increased the ease with which the scrubber byproduct drains into the auger. The feed rate of the fly ash can be controlled and the mixing auger should provide adequate mixing of the fly ash into the controlled stream of scrubber sludge slurry.

A final problem with obtaining a stable and handlable pumpable paste is the issue of bleed water. On quietly setting, even a relatively stable paste can have some water separation. In a slurry, such as is used with backfilling sand in some underground mining operations, the separating water can be a flow that requires a water discharge and handling system. In a paste the bleed water is supposed to be very minimal. Remembering the soil like behavior of many of the mixes, it is clear that significant bleed water could be source of erosion and even stack destabilization. Based on experience on field projects done within the Department of Mining Engineering, a bleed of up to 5% would usually be in line with evaporation and should not produce flows or erosion. Figure 11, Appendix A, shows the relationship of bleed to slump for various mixes.

One obvious observation is that lime additive increases the amount of water that is needed to achieve a given slump, but it also increases the bleed. The C- type fly ash additive increases the water needed for a slump, but does not increase the bleed the way lime does. If 5% is taken as a limit for bleed the following mixes which seemed feasible from other considerations will experience problems.

1. All Mixes using 1% lime in a pumpable paste for slump adjustment relative to moisture or for degradation control.
2. All Mixtures based almost entirely on scrubber byproduct.

Figure 12, Appendix A, shows how fast the bleed water separates from the mix for two different slumps of a no additive mix and two different slumps of scrubber sludge. The slope of the scrubber sludge is very steep initially, indicating that scrubber sludge settles out of a pumpable paste quickly. When fly ash is mixed with scrubber sludge this behavior change as indicated by the lower two lines of the no additive mix. All experiments showed that a mix of scrubber sludge and water alone is not appropriate since scrubber sludge separate quickly from water. Fly ash must be added to develop a stable mix with acceptable bleed.

Another criterion in mix development is the leachability of boron. Boron is an ancient plant nutrient and was concentrated by the organic material from which the coal was
formed. When the coal is burned, boron is easily volatilized and patricians to the fly ash or is captured in the scrubber. ASTM shake tests indicate leachate with 22 ppm boron from fly ash and 4 to 6 ppm from scrubber byproduct. Concentrations of boron are building in the Cilco ponds, in part because of closed loop recycle of water. Seepage or overflow of boron rich waters into the surrounding streams or aquifers can be an environmental issue. Mixes were evaluated for leachability of boron. For the State’s beneficial use law on coal combustion byproducts to apply, the mix must produce less than 2 ppm of boron in the leachate from an ASTM shake test. None of the mixes tried in this procedure met this criterion, though several came rather close.

The mixes noticeably sequestered boron, which should reduce boron build-up in pond waters and limit boron in run-off from the artificial topographic features set up to blend and reclaim the area. Figures 13, a thorough I, Appendix A, refer to boron leaching in the ASTM shake test. The dependent variable on the Y axis is the boron concentration measured in ppm in the leachate from an ASTM shake test. The data along the X axis is grouped into 3 parts, representing the 3 ratios at which fly ash was added to scrubber byproduct. Within each group is a bar representing mixes where no activator was added, and 3 additional bars representing different doses of two different activators. There are a total of 9 figures in the appendix. The appendix contains 3 sets of 3 graphs for 9 total. The three graphs in each set represent three different slumps, 0 to represent truck handled mixes, and 7 to 10 to represent the limits of the stable and pumpable range. The three sets measure leaching performance after 1, 2 and 3 or 4 weeks of cure time.

When ANOVA and regression analysis was run on the data, it was found that boron concentration in the leachate decreased in response to fly ash addition and the addition of the activator, increased with longer cure times, increased with high additions of both fly ash and activator, and increased in response to greater slump when lime is the activator. The results are visually confirmed on examination of the figures. Boron is better sequestered in mixes with good pozzolanic cementing than in poorly cemented mixes. One effective way to reduce the boron is to add fly ash to make a more stable and well cemented and reacted mix. Cementitious reactions apparently either directly sequester boron, or create a matrix which limits access of the leachate solutions to the boron. Simply adding a half part of fly ash to each part of scrubber byproduct brings the boron into the 6 to 10 ppm range, which is lower than either component separately.

Another very powerful effect comes from a lime activator. The mixes that were only parts per billion over the 2 ppm limit were all dosed with lime activator. Regression analysis indicates that lime is probably the single most important variable in reducing boron leaching. There are limits, however, to the benefits of lime. Regression indicates that the interaction of high lime with high fly ash addition increases boron. The figures appear to show the best mixes are well cemented with lime activated pozzolans. The positive value in the regression means that the benefits of lime and fly ash addition are not additive over the study range and the combined benefit of lime and fly ash is less than would be predicted simply by summing the benefits from each ingredient individually, i.e. there is a point of diminishing returns. The activator effect of C fly ash is even more interesting. In pozzolan deficient mixes like the 0.25 to 1 mixes, C type fly ash is as
effective as lime in getting boron leaching into the around 4 ppm range. Even though C type ash is not as powerful an activator as lime, it adds the pozzolan the mix needs to provide maximum stabilization. In the 0.33 to 1 mixes the C type ash is distinctly less effective than lime and distinctly better than nothing. For the regression analysis on ratio and activator interaction with C type fly ash activator, high values promote higher boron levels. The figures show that when adequate pozzolan is provided that adding additional boron from the C type ash is worse than adding no activator at all. This occurs at the 0.5 to 1 ratio.

There are several factors that limit the benefits that can be gained from a lime activator. Since lime and pozzolan both appear to reduce boron by creating a matrix that inhibits leaching action, the two effects are not independent and doing one lessens the improvement available from the other. Boron mixes that have cured a longer time also appear to leach more boron. This would appear at first to contradict the idea that a stable cement matrix reduces leaching, but probably actually results from another inhibition mechanism. Coal combustion byproducts with a high sulfur component can form entringite as a product of weathering. Boron is easily taken up by the entringite mineral structure. At higher pH values characterized by water and calcium oxide reactions entringite can form and sequester boron. As mixes cure, the unreacted calcium oxide reduces and that which is not consumed goes through hydrolysis and begins to recarbonate back to calcium carbonate. The usually seen drop in high pH values changes the most stable sulfur bearing minerals away from those which capture boron and thus boron which is leached is not likely to be recaptured by the matrix. The result is that a boron sequestering mix with high pH will leach around 2.5 to 3 ppm of boron, while a better cured mix with lower pH values will leach about 4 to 5.5 ppm boron. The C fly ash activated mixes with surplus pozzolan and more quickly depleted calcium oxide more than double boron leaching with time reaching close to 12 ppm.

Lastly, high slump limits the boron inhibiting impact of lime particularly raising leachable boron concentrations about 2 ppm. This is consistent with the view that a strong cement matrix limits boron leaching since high slump reduces the setting strength of conventional pozolanic concrete.

**SUMMARY AND CONCLUSIONS**

Characteristics of an ideal mix depend somewhat on the intended use. In this project three types of uses were intended, (1)- a durable high strength mix that could be trucked or belted for placement for roads and berms (2)- low cost pumpable mixes that utilize mostly surplus byproducts, provide moderate strength, and inhibit boron leaching (3)- mixes amenable to revegitation. The bulk of the material was to be the low cost pumpable mixes. Based on the work conducted the following conclusions are possible

(1)- Mixes with suitable strength and pumping characteristics can be prepared from the ratios of fly ash and scrubber byproduct located in the pond and within the range of ratios over which the two byproducts are now produced at the power plant.
(2) It is likely that if a dry handling system for fly ash is installed and half of the ash is marketed, that mixes of suitable strength and pumping characteristics can be prepared from the remaining materials.

(3) Adjustments for too little moisture and slump in mixes can be made by water addition and adjustments for too much moisture can be made by activator additions ranging from 1 to 3%. Such adjustments should make any of the proposed materials handling sequences workable within the range of ash and scrubber byproduct ratios specified. Some activators may allow excess water to bleed after the mix is placed.

(4) Mixtures prepared without activators or with a C fly ash activator soften on intense exposure to water which will limit slope angles but provide suitable rooting conditions for plants. Lime mixes retain a more concrete like form and could sustain greater slopes, but would be more difficult to revegitate.

(5) Mixtures prepared from the production ratio of fly ash to scrubber byproduct, either before or after marketing of some of the fly ash are unlikely to significantly inhibit boron leaching from what would be expected for the component materials. The present production ratio without other additives appears to be one of the worst combinations for boron leaching. Increasing the fly ash ratio to 0.5 parts to 1 could reduce boron leaching into the 8 ppm range, but this would require significant quantities of fly to be hauled in and would probably not be acceptable unless Duck Creek became the final site for fly ash from the Edwards Station, a situation not currently in any plans.

(6) Boron can be sequestered or limited most effectively by preparing mixes with 1% lime activator. Boron concentrations in the ASTM shake test in the 4 to 6 ppm range or less can be expected. Such mixes, however, produce bleed water volumes that may not be acceptable.

(7) Boron leaching can also be reduced into the 5 ppm range by marketing enough of the current fly ash production to bring the ratio to 0.25 to 1 and adding a C fly ash activator. A lime activator will also work but may produce unacceptable bleeds.

(8) Scrubber byproduct is difficult to meter effectively into mixing mechanisms. Vibratory feeders appear to fluidize the material for acceptable flow and metering. Screw augers appear to be capable of mixing the byproducts providing clump flow of the scrubber byproduct can be avoided. Mixes that should handle well through a concrete pump without separating can be prepared and will not have bleed water problems upon discharge providing there is close to 0.2 parts fly ash to scrubber byproduct, a moisture content under 70% and lime is not used.

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