ABSTRACT

Coal combustion generates a range of solid particulates including bottom ash and slag in the boiler; uncombusted coal fines and fly ash captured in baghouses and electrostatic precipitators; and calcium sulfates, sulfites, and carbonates from flue gas desulfurization that are generally referenced as coal combustion residuals (CCR). Water treatment for reuse or discharge during CCR excavations and other operations requires removing these particulates. The larger combustion particulates including bottom ash and boiler slag are less cumbersome because they settle very quickly, however, smaller particulates such as fly ash settle at a slower rate. These residual fines cause the water to be highly turbid for hours to days. Depending on the end use of the water, the turbid water may be reused without further solids removal. However, some uses require lower turbidity and the slow settling rate makes for impractically long retention times. In these cases, the application of commercial coagulants/flocculants was shown to be effective in removing suspended solids. In addition to affecting water disposal, fines may also foul the nonwoven geosynthetics frequently used in the construction of leachate collection systems for CCR storage cells. Underdrains constructed with sand and gravel had a longer functional life because they were less prone to flow reduction from fines accumulation compared with nonwoven geosynthetics. Our investigations illustrate the importance of characterizing the behavior of fines in the design of CCR handling and disposal systems.
INTRODUCTION

Coal combustion residuals (CCR) are generally noncombustible chemically complex particles of varying sizes. The physical behavior of CCR, especially the ash component, largely depends on particle size. Most of the ash has a diameter greater than 1 micrometer (µm), with a broad peak in the range of 3 to 50 µm in diameter. Ash particles that are entrained in combustion gases are called fly ash. Submicron sized ash particles typically make up to 2% of the total fly ash mass in the gases from pulverized coal combustion systems. Figure 1 shows a photomicrograph of fly ash.

Fine particles less than 10 µm in diameter present a potential human health risk because they can penetrate deeply into the lungs and may contain a variety of trace metals. Therefore, trapping small particles in a scrubber is important to avoid air pollution. Wet scrubbers produce wastewater containing ash particles. Achieving water of dischargeable quality often requires removal of ash fines as measured by the total suspended solids (TSS) concentration and turbidity, among other parameters. Particle removal techniques are less effective for small (submicron) particles than for larger particles. The CCR particles in wastewater are often regulated as total suspended solids (TSS) or turbidity because of their degradation of water quality. Therefore, managing, handling, and disposing of CCR microparticulates is important in wastewater treatment processes at coal fired power plants.

This paper presents case studies illustrating solutions to address CCR impacted water issues.

Figure 1. Microscopic Photo of Fly Ash (100x magnification)
CASE STUDIES

Particulates Settling during Dredging Operations

A coal fired power plant was performing CCR excavation and hydraulic dredging activities from a basin at a rate of approximately 160 tons of solids per hour. Settling and characterization tests on the dredged slurry samples informed wastewater treatment design for CCR removal. These tests, designed to quantify key design parameters for a hydraulic excavation and dewatering system, included slurry solids content, solids settling rates without added coagulant or flocculant, and ash grain size distributions. CCR slurries were collected periodically during dredging operations.

Three dredge slurry samples (Slurry #1, #2, and #3) were collected at three different times during normal operations. Settling test were performed on the Slurry #3 sample using a modified Standard Method 2710 E Zone Settling Rate test. This modification involved using clear glass one-liter graduated cylinders. Initial mixing was achieved by capping and inverting the cylinders to fully suspend solids. Five tests with Slurry #3 were performed in parallel to enable periodic sacrificial sampling for measurement of turbidity and TSS. TSS was measured after 24 hr, 48 hr, and 120 hr of settling. The fifth column was undisturbed for the duration of the five-day test. During the process of settling, the height of the (i) solids/liquid interface and (ii) the clear zone/cloudy zone interface were recorded in inches. In addition, the settling time was recorded using a stopwatch. The solid/liquid interface and the clear zone/cloudy zone interface are shown in Figure 2. Time series photographs were taken to document the settling process. The TSS of the 200 ml aliquots was measured by Standard Method 2540 D using solids collected on 0.7 µm glass fiber filters, dried at 105°C, and weighed with a 4-decimal place analytical balance.

Figure 2. Ash Slurry Settling Interfaces
The heights of the solid/liquid interface and the clear zone/cloudy zone interface were measured and plotted as a function of time to produce settling curves (Figures 3 and 4).
The initial settling rates were calculated from the slope of the best fit line through the linear portion of the settling curves where the rate of solids settling was not significantly influenced by the settled solids on the bottom of the cylinder. The calculated initial settling rate for the solids, based on the data from the first hour of settling, was about 9.8 inches per hour (in/h), equivalent to approximately 0.8 feet per hour (ft/h). The initial settling rate for the clear zone, based on data from the first eight hours of settling, was estimated at 0.5 in/h, or approximately 0.04 ft/h. The turbidity of the aliquots collected from the clear zone ranged from 31 to 35 Nephelometric Turbidity Units (NTU). TSS ranged from non-detect\(^1\) to 11 mg/l. These samples had very little TSS, which was in agreement with the observation of clear water following a long settling time without the aid of a flocculant. Additional calculations were performed based on settling velocity to estimate the size of a settling basin surface area (width x length) to achieve an adequate settling time to meet water quality criteria for discharge. Results indicated that the minimum surface area required for a settling basin is about 0.9 acres for the larger ash particles and 18 acres for fine ash which settled at a rate of about 20 times slower than the larger ash. In practice, phenomena including slowing of settling as particles approach the bottom of the basin, wind, temperature gradients, and disturbances due to pumping drop the efficiency of settling basins. Therefore, the above influences on solids settling should be accounted for in the design of a settling basin. The use of flocculants could increase the fine particles settling velocity and thus decrease the size of the settling basin required for finer ash. The use of flocculants to improve solids settling was evaluated in the next case study.

**Improved Solids Settling Rate and Removal for Wastewater using Flocculants**

A coal fired power plant stored their CCR wastewater in a holding/settling pond. Discharge criteria dictated that the water had to meet the TSS criteria of 30 mg/l (monthly average) and 50 mg/l (daily maximum). To support the design of a wastewater treatment system, bench scale tests were conducted: (i) to evaluate solids settling characteristics by gravity without adding any flocculant, (ii) to evaluate the effectiveness of adding a flocculant in solids removal in CCR wastewater, and (iii) to determine the dose of flocculant required.

Settling tests were performed on three FGD wastewater samples (Sample A, Sample B, and Sample C) without adding a flocculant. The volume of settled solids was recorded over time. Photographs were taken every 5 minutes up to 60 minutes; however, settling was so slow that a settling rate for Samples A and B could not be calculated from data collected over 60 minutes. The calculated settling rate for Sample C was 0.02 inch per minute (in/min). Although each sample was allowed to settle for up to 24 hours, fines remained suspended in Sample A and Sample B. The final settled volume in Sample C was too little to be quantified in a 1 liter graduated cylinder. Therefore, the test was repeated in Imhoff cones (Figures 5a and 5b). The total settled volume of fines was 0.7 ml for both Samples A and B, and 11 ml for Sample C; however, some of the fines adhered to the wall of the Imhoff cones and failed to settle to the bottom of the cones (Figure 5b).

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\(^1\) Non-detect occurred where weight of filter before and after passing 200 ml sample was within the sensitivity of the analytical balance of 0.1 mg.
Jar tests with Sample B and Sample C evaluated the effect of adding a flocculant to improve solids settling. Six Phipps and Bird beakers were filled with one liter of Sample B followed by dosing with a flocculant stock solution in increasing amounts to yield final working concentrations of 10, 25, 40, 50, 75 and 100 mg/l. The lowest flocculant dose (10 mg/l) visually yielded the clearest water with cloudiness increasing as the flocculant concentration increased (Figure 5c). The largest flocs were also observed in the 10 mg/l dosed sample and floc particle size decreased as the flocculant dosage increased. Based on these observations, 10 mg/l was considered the best dosage for Sample B among the concentrations tested. Settling tests with the flocculant treated samples were conducted in graduated cylinders. All the flocs settled within 3 minutes. The settling rates were calculated by measuring the average heights of the solids layer as it settled during a 1.5-minute period. The approximate settling rates, which were comparable for all 6 treatments, ranged from 6.8 to 8.8 in/min. The volume of settleable solids was determined in Imhoff cones. Samples dosed with 10 mg/l and 40 mg/l flocculant had settable solids of 1.5 ml and less than 1 ml, respectively, indicating that the 10 mg/l treatment produced a “fluffier” or less dense floc than the 40 mg/l treatment although water clarity was better with the lower flocculant dosage.

The same jar test procedure was repeated for Sample C with the same flocculant doses. Flocs formed quickly and settled to the bottom of the beakers while water between the particles became visually clear. The beaker dosed with 40 mg/l flocculant was the clearest by visual observation among the six treatments. Flocculant treated water was poured into graduated cylinders and settling tests were performed. Treatments were allowed to settle for 1 hour, and photographs were taken at intervals. A photograph of the final settled solids after 1 hr is presented in Figure 5d. The treatment dosed with 40 mg/l flocculant had a settling rate of 0.64 in/min, which was the fastest among the 6 concentrations tested. Treatment with 50 mg/l flocculant had a settling rate of 0.53 in/min. The other four treatments dosed with 10, 25, 75 and 100 mg/l flocculant had comparable settling rates, ranging from 0.11 to 0.24 in/min. These data confirmed that adding flocculant enhanced the solids settling with the settling rate improved by up to 30 times. The settling test was repeated in an Imhoff cone using the 40 mg/l flocculant-dosed Sample C. The settleable volume was measured to be 19 ml, which was an 8 ml increase from 11 ml with no flocculant added. Flocs settled with no adherence to the wall of the Imhoff cone.

In addition to affecting wastewater disposal options, ash fines present in storage cell leachate can accumulate in and clog leachate collection underdrains. The next case study investigates this problem with a study of the behavior of ash particles in leachate collection underdrain systems.
Evaluation of CCR Removal by Storage Unit Underdrain Materials

A coal fire power plant was in the process of designing a CCR storage unit. However, CCR with various grain sizes, gradations, and hydraulic conductivities in the same storage cell posed challenges in meeting conventional filter criteria and lead to concerns about clogging of the leachate collection system (LCS). Decreased permeability of the LCS can result in head build up on the liner with subsequent leachate seeps and outbreaks along side-slopes leading to potential slope instability. As part of a CCR storage cell design project, the filtering capability of a geotextile and a graded sand and gravel underdrain system was evaluated using a full-scale thickness, gravity drained, flow through CCR column study. Flow rate, suspended solids in the leachate, and leachate quality were measured to document the physical performance of the LCS designs.

The two LCS designs, evaluated during this investigation, were (i) a sand and gravel LCS that included, from bottom to top, one foot of coarse gravel (particle size of approximately 2 to 3 inches in diameter), one foot of fine gravel (approximate particle size of 0.5 to 1 inches in diameter) and one foot of sand (approximately particle size less than 1/8 of an inch) and (ii) a single layer of geotextile. Flow rate and leachate characteristics were analyzed for 22 days in 12-inch diameter flow-through columns prepared with each drain design, one foot of overlying ash or a mixture of ash, bottom ash, and gypsum and two feet of standing water above the top of the CCR solids.
The flow rate through the sand and gravel LCS was consistently higher than the geotextile LCS by a factor of three to five. The flow rate for each column is shown in Figures 6 and 7. The rates are normalized to one square foot of LCS with 3 feet of hydraulic head. Both LCSs retained fines; however, the sand and gravel system performed better based on lower turbidity and total suspended solids. Neither design clogged with fines during the testing period as indicated by consistent daily flow rates. The particular fly ash sample used for testing had an alkaline pH that was buffered to about pH 9.5 by the sand and gravel LCS whereas the geotextile did not alter leachate pH. Neither LCS was particularly effective at retaining dissolved anions, although the sand and gravel design seemed to retain carbonate while sulfate and chloride passed through.

Arsenic was not detected in leachate with only three exceptions in 12 samples where concentrations ranging from 0.0167 to 0.136 mg/l were observed. At the end of the study (22 days) arsenic was not detected in the leachate from any of the columns. Selenium was detected in every leachate sample with concentrations ranging from 0.045 to 0.158 mg/l. The leachate from the sand and gravel LCSs had measurably lower Selenium concentrations than leachate from the geotextile LCSs.

The conclusion was that the sand and gravel leachate collection system performed better than the geotextile based system. Based on our findings, the sand and gravel filter provided the desirable combination of more reliable leachate collection and improved leachate quality.

Figure 6. Flowrates through Ash Columns
CONCLUSIONS

Microparticulates provide challenges to water treatment regardless of whether the source is process water, runoff, or leachate. The proper selection of removal technologies can eliminate microparticulates from water to reduce the time required to treat water to permitted discharge or reuse criteria and to design systems that are less prone to fouling by microparticulate accumulation.

REFERENCES
