



A Root Cause Study to Determine the Source of High Gypsum Moisture

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ABSTRACT

A study was launched to identify the root cause of periodic episodes of high gypsum free moisture being produced by a newly commissioned multi-boiler WFGD system. The investigation revealed the sources of the high moisture were unusually flat gypsum crystals which were making dewatering difficult. Testing revealed that a series of flyash elements were acting as gypsum crystal modifiers. Results also indicated flyash from only one of the four boilers appeared to drive the high moisture events. Flyash leaching experiments were successful in replicating the full scale problem. It is hypothesized that the combination of low WFGD sulfur loading and the unique flyash chemistry introduced from one of the boilers were central in producing the unique gypsum shape.

INTRODUCTION

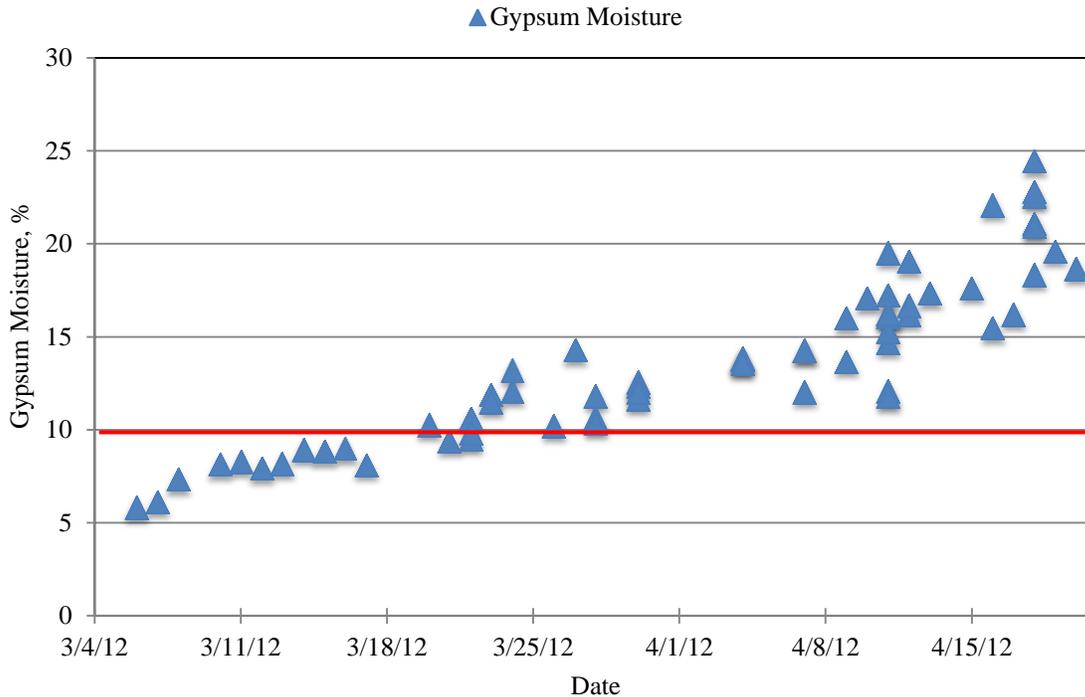
The study was conducted at a Midwestern utility (Plant A), which is a coal-fired generating station with a total net generating capacity of approximately 1,100 MW. Air pollution control equipment includes four ESP's, two SCR's and two WFGD's. The WFGD design is a Foster Wheeler (formerly Siemens Environmental Systems and Services / Wheelabrator Air Pollution Control) limestone forced oxidation system producing commercial grade gypsum. This WFGD system, commissioned in 2012, is an exact duplicate of the WFGD at a sister site (Plant B), which was commissioned several years earlier. The generating stations share an identical limestone supply and are fueled by similar low-sulfur PRB coal (0.5 wt.% maximum). The make-up water at both sites is from the same general source, but several differences exist in treatment and composition.

Two absorber modules were provided at both Plant A and Plant B. At Plant A, one module is dedicated to Boiler Units 5 and 6 and one is dedicated to Boiler Units 7 and 8. Each absorber consists of recycle pumps, a dual flow tray and a forced oxidation air blower. Limestone slurry is produced by horizontal wet grinding ball mills. The dewatering process begins with each absorber's dedicated primary hydroclone, where gypsum slurry is separated into a high solids underflow and a low solids overflow. The underflow streams from both of the primary hydroclones accumulate in the common filter feed tank before being sent to one of two

redundant vacuum filters for final dewatering. The overflow stream from the primary hydroclone is either recycled back to the absorber or processed through the secondary hydroclone system to purge chlorides and inerts. Gypsum quality parameters were defined as 10% maximum free moisture and 95% minimum calcium sulfate dihydrate (purity).

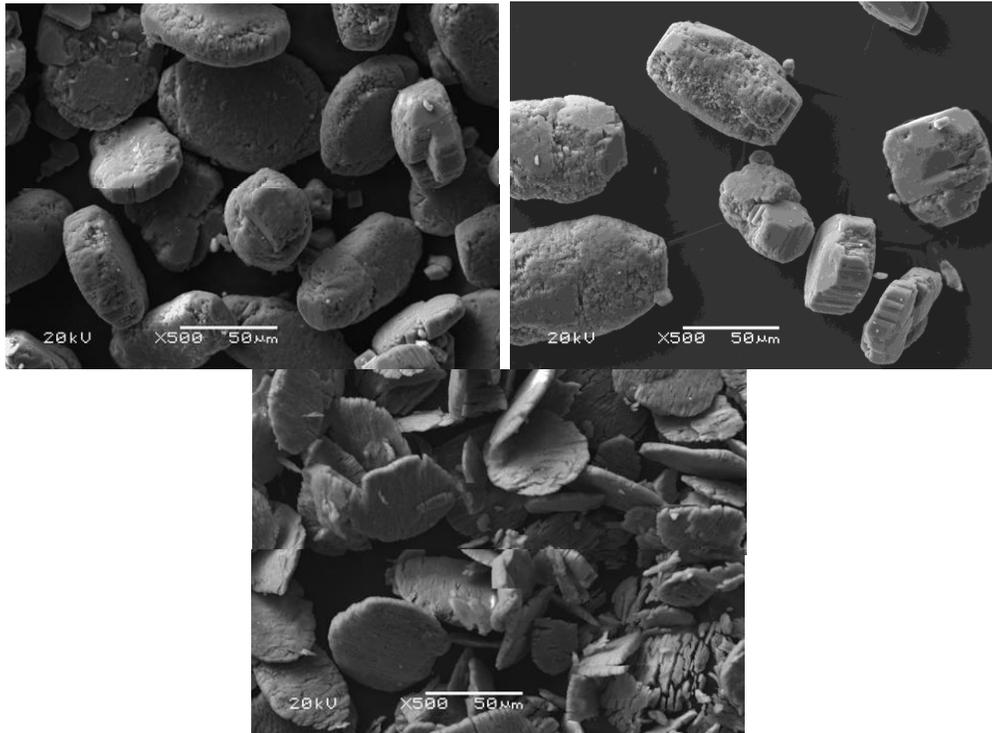
At Plant A, Unit 56 and Unit 78 Absorber startups were staggered by three months. During the initial Unit 56 start-up, the gypsum filter cake became increasingly difficult to dewater. Gypsum moisture values exceeded the 10% maximum specification after only two weeks of dewatering operation. By the seventh week, moisture had continued to increase and surpassed 20%. This is illustrated in Figure 1.

Figure 1. Unit 56 Initial Gypsum Moisture Excursion



Initial investigations focused on a number of equipment and process possibilities, including poor vacuum filter performance, improperly tuned hydroclones, absorber operating density, limestone quality and water quality. Pictures of the gypsum crystals taken by SEM (Scanning Electron Microscope) provided the first insight into the issue. Typical WFGD gypsum crystals appear block-like in shape and have a distinct structure, but the Plant A gypsum crystals appeared as flat, plate-like crystals with irregular edges. These flat crystals were exceptionally difficult to dewater because they created an impervious filter cake that prevented the extraction of moisture. Figure 2 compares typical FGD gypsum crystals with the irregular crystals from Plant A.

Figure 2. SEM Photographs of Gypsum Crystals
Typical Gypsum Crystals (Top), Plant A Gypsum Crystals (Bottom)



Plant B, which uses similar low sulfur PRB coal and identical limestone, had never experienced similar gypsum moisture issues in five years of operation. Additionally, Plant C, which shares the site with Plant A and also has a wet scrubber, had never experienced gypsum moisture issues. The limestone supplied to Plant C is identical to that of Plant A and Plant B. The quality of make-up water at Plant C is slightly different than that of Plant A due to differences in treatment, but both are supplied from the same general source. It is important to note that the Plant C system burns high sulfur eastern bituminous coal, which is distinctly different from coal burned at Plant A and Plant B. SEM photographs of gypsum from Plant B and Plant C gypsum confirmed typical crystal structure and low gypsum moisture content.

Upon discovery of the flat irregular crystals, it was hypothesized that the gypsum crystal morphology was being affected by a liquid-phase species within the absorber liquor. Operational data revealed that increasing the operating pH from 5.6 to 6.1 had a positive effect on reducing the gypsum moisture. Since metals often precipitate with increasing pH, it was suspected that a metal element(s) in the absorber liquor could be the species of interest. Additionally, it is known that certain transition metal elements can inhibit gypsum precipitation¹. Some of these elements are common and present in sufficient concentrations in WFGD liquor, including cadmium, copper, iron and chromium.

A root cause investigation was launched by Foster Wheeler to confirm or refute the hypothesis. A test program ensued.

METHODOLOGY

Stage 1

Foster Wheeler commenced Stage 1 of a root cause analysis program in early November 2012. Although the Unit 56 Absorber had experienced a greater number and higher degree of gypsum moisture excursions, it was entering an extended outage at the same time that the root cause test plan was developed. Due to the sensitivity and timeliness of the problem, the test program was therefore redirected to Unit 78 Absorber. It was believed that the Unit 78 Absorber would experience the same problem since it is of identical design and operation to the Unit 56 Absorber. The Stage 1 approach was to gradually reduce purge rates thereby allowing accumulation of chlorides and other dissolved species. The intent of this procedure was to induce the high gypsum moisture events and to determine the concentration at which the events occurred. Absorber slurry and gypsum samples were collected concurrently at pre-determined times to quantify levels of dissolved species and observe corresponding changes in gypsum morphology.

The chloride concentration in the absorber slurry served as the benchmark for sample collection. Chlorides were tested daily by the plant laboratory using EPRI Method O4. Baseline samples were collected at 3,000 ppm (mg/L) chlorides. Operation of the purge system was then limited to allow the chloride levels to increase in increments of approximately 500 ppm. The absorber was maintained at this level for one week before the next sample collection. To maintain consistency, absorber slurry and gypsum samples were collected during full load operation and at the start of a dewatering run. Sample collection continued in 500 ppm increments until a level of 5,500 ppm was reached. If gypsum moisture exceeded 10% consistently during the study, purging operation could resume until moisture was reduced to less than 10%.

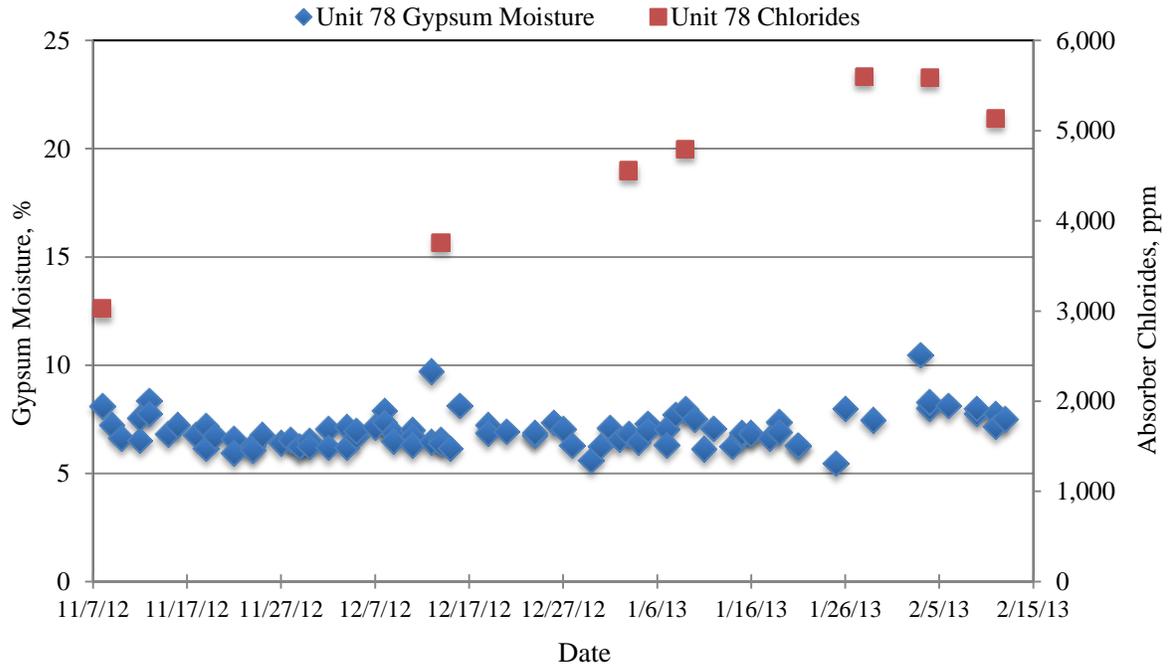
Absorber slurry samples were sent to the Siemens Water Enviroscan laboratory for full chemistry characterization including dissolved elements, ions and classical parameters. Gypsum samples were sent to RJ Lee Group for SEM analysis and photographs. The plant laboratory tested the gypsum samples for moisture using EPRI Method F1 and tested for purity and moisture using a thermo-gravimetric analyzer (TGA). On a routine basis, the plant laboratory also tested the absorber slurry for pH, specific gravity and percent solids. All of the test results, plus additional process highlights and observations, were compiled and recorded to support the root cause analysis.

RESULTS

Stage 1

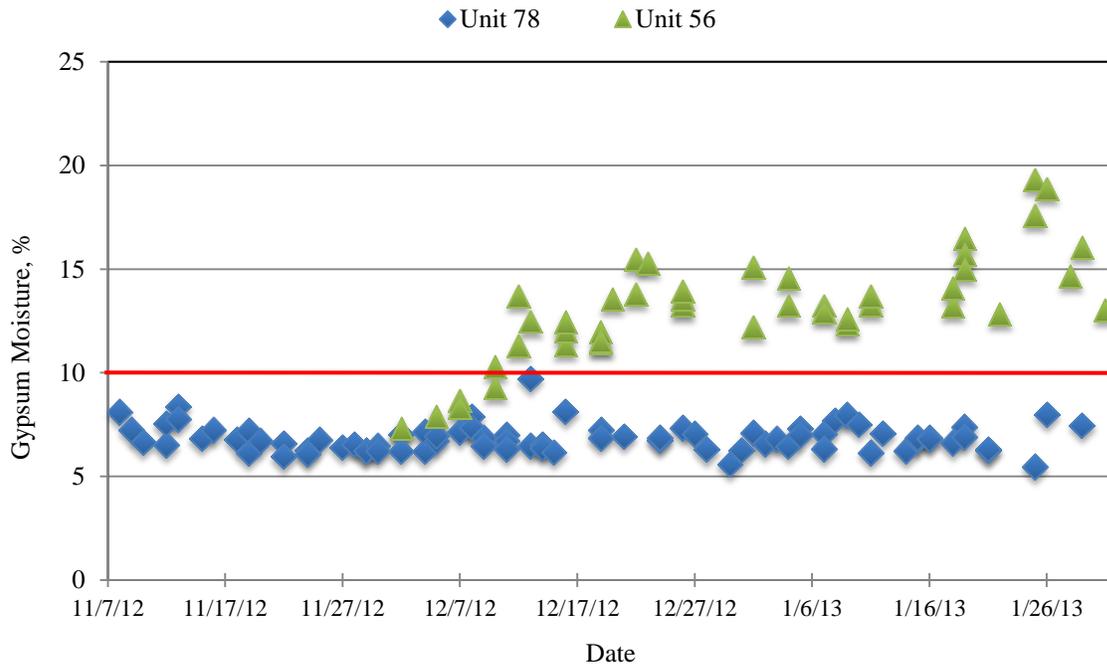
Surprisingly, the Unit 78 gypsum moisture values did not exceed the specification limits during the test plan even under the most concentrated conditions, as shown in Figure 3.

Figure 3. Results of Stage 1 Test



After the onset of the testing on Unit 78, Boiler Units 5 and 6 returned to service and resumed operation under normal AQCS conditions. Gypsum moisture excursions returned to the Unit 56 system but were absent on Unit 78, even though Unit 78 was operating with increased concentrations of dissolved species. See Figure 4.

Figure 4. Unit 56 & 78 Gypsum Moisture during Stage 1 Test



Although this was an unexpected development, the timing of events proved to be advantageous as they allowed Foster Wheeler to simultaneously analyze the differences between the systems and to determine why one absorber was producing poor gypsum crystals while the other was not. Of particular interest was the solution chemistry of each absorber, since Unit 78 was operating with much lower purge rates without any adverse effects on gypsum. The excursion indicated that the issue was unique to Unit 56, and therefore any system shared with Unit 78 could be eliminated as the root cause.

Thus began a more thorough investigation of upstream boiler operation, SCR operation, and ESP performance to determine what, if any, differences could be found. Upon investigation, it was noticed that the absorber inlet opacity on Unit 56 was generally higher than that of Unit 78. Performance test results agreed with the measurements of the installed opacity instruments, confirming a higher particulate loading to the Unit 56 Absorber and subsequent higher particulate capture as compared to the Unit 78 Absorber.

Stage 2 of the root cause analysis was then initiated to further explore the detailed differences in liquor-phase concentrations that may correspond to opacity and flyash elements.

METHODOLOGY

Stage 2

Based on the Stage 1 results, the test program for Stage 2 reflected a more focused program. Sample collection was closely coordinated with operational changes in the scrubber. Stage 2 highlights were as follows.

1. Several simultaneous absorber slurry and gypsum samples were collected from Unit 56 and Unit 78 using the same procedure and under similar operating conditions as described in Stage 1 methodology. Since the filter feed tank is common to both units, the slurry from each absorber was segregated to the extent possible.
2. The operating pH of the Unit 56 Absorber was increased from 5.7 to 6.0. The operating pH of Unit 78 remained unchanged. Absorber chloride concentrations were maintained.
3. Additional samples were collected from Unit 56 and Unit 78 after the pH change.
4. All samples were analyzed as described in Stage 1 methodology.
5. Monitoring of gypsum moisture values continued during Stage 2.

Flyash samples were collected from each of the four units at Plant A and also from the two units at Plant B. The samples were analyzed by RJ Lee Group for elemental composition, mineralogy, particle size and leaching properties. Two different leach tests were done. The first was the standard SPLP Leach Test (EPA Method 1312). The second leach test was a modified leaching procedure aimed at simulating FGD operating conditions. A brief summary of the modified procedure is as follows.

1. Mixed 100 ml DI water and 20 g flyash into a beaker and began to continuously stir.
2. Took initial pH and recorded.
3. pH was then adjusted to 5.7 with H₂SO₄.
4. Mixture was continuously stirred for 48 hours while trying to maintain a pH of 5.7.
5. After 48 hours, slurry was filtered, and the filtrate was analyzed for dissolved elements.

RESULTS

Stage 2

Analysis of the Unit 56 and Unit 78 Absorber chemistries revealed that significant differences existed between the absorbers regarding the concentrations of dissolved species. Because of the difference in purge rates between the absorbers, Unit 56 had three times less chlorides than Unit 78. It was therefore expected that the other dissolved components should be approximately three times less in Unit 56 as compared to Unit 78. This was the case for most of the species, but there were a few notable exceptions. Specifically, major elements associated with flyash, such as aluminum, iron, and silicon, were found at significantly elevated levels in Unit 56. Certain other elements were found in levels so close to detection limits that they were considered insignificant even though the ratio between absorbers was high.

After the pH increase on Unit 56, gypsum moisture began to improve. The samples taken after the change showed a significant decrease in the amount of aluminum in Unit 56 slurry. The data in Table 1 shows these ratios before and after the pH change.

Table 1. Ratio of Dissolved Elements, Unit 56 to Unit 78

	Unit 56 pH = 5.7			Unit 56 pH = 6.0		
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Chloride	0.4	0.3	0.3	0.2	0.2	0.4
Fluoride	0.4	0.4	0.4	0.3	0.4	0.4
Aluminum	2.8	2.3	3.5	1.2	0.5	0.2
Barium	0.8	0.8	0.9	1.1	1.0	0.9
Beryllium	1.6	0.9	0.8	ND	0.2	0.2
Boron	0.5	0.5	0.3	0.3	0.4	0.4
Cadmium	0.7	0.6	0.4	0.3	0.2	0.4
Calcium	1.0	1.1	1.1	1.0	1.0	1.0
Chromium	0.7	0.6	0.8	0.6	0.5	0.7
Cobalt	0.5	0.4	0.4	0.3	0.3	0.3
Copper	0.9	0.9	0.6	0.4	0.4	0.3
Iron	ND	0.4	2.8	2.6	1.1	1.1
Magnesium	0.4	0.4	0.3	0.3	0.3	0.3
Manganese	0.4	0.4	0.3	0.3	0.3	0.3
Molybdenum	0.8	0.7	0.5	0.4	0.4	0.4
Potassium	0.5	0.5	0.3	0.3	0.3	0.3
Nickel	0.4	0.3	0.3	0.3	0.3	0.3
Selenium	1.4	1.2	0.6	0.4	0.6	0.3
Silicon	1.6	1.8	1.6	1.6	1.4	1.5
Strontium	0.8	0.8	0.7	1.1	1.1	0.8
Sodium	0.5	0.5	0.3	0.3	0.3	0.4
Titanium	2.0	0.6	1.0	1.0	1.3	0.4
Vanadium	10.0	10.0	3.6	4.4	2.4	ND
Zinc	0.9	0.8	0.8	0.7	0.5	0.6

Flyash analysis showed that the mineralogy and elemental composition were fairly consistent among all four Plant A units. Samples from Plant B showed some minor differences in mineralogy and elemental composition as compared to Plant A. The particle size distribution of all Plant A samples was the same, but the Plant B samples had a larger average particle size distribution. However, major differences were observed in the leaching test results of Unit 5 flyash as compared to those of the other samples. Using the SPLP method, Unit 5 flyash leached significantly more elements, particularly aluminum, iron and silicon. Unit 5 flyash also leached significantly more aluminum using the simulated FGD conditions leach test. The results are shown in Table 2 and Table 3.

Table 2. SPLP Leach Test
All results reported in mg/L

	Plant A Unit 5	Plant A Unit 6	Plant A Unit 7	Plant A Unit 8	Plant B Unit 1	Plant B Unit 2
Aluminum	267	86.0	80.4	111	13.1	44.3
Barium	25.0	16.1	19.2	16.6	5.3	2.7
Beryllium	< 0.0080	< 0.0080	< 0.0080	< 0.0080	< 0.0080	< 0.0080
Boron	1.44	0.764	0.584	0.140	3.11	0.102
Cadmium	0.011	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Calcium	563	302	286	275	177	124
Chromium	0.285	< 0.020	< 0.020	< 0.020	0.079	0.301
Cobalt	0.050	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020
Iron	86.2	< 0.050	0.083	0.272	< 0.050	< 0.050
Magnesium	71.0	< 0.050	0.0802	0.293	< 0.100	< 0.100
Manganese	0.350	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020
Molybdenum	0.082	< 0.020	< 0.020	< 0.020	0.0098	0.168
Nickel	0.096	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Potassium	10.8	2.61	3.42	3.97	0.753	1.96
Selenium	< 0.0500	< 0.0500	< 0.0500	< 0.0500	< 0.0500	< 0.0500
Silicon	122	0.131	0.284	0.771	1.71	0.908
Sodium	57.0	22.0	33.3	24.8	21.2	31.9
Strontium	22.8	24.6	27.2	21.8	19.6	11.2
Titanium	15.5	< 0.070	< 0.070	< 0.070	< 0.070	< 0.070
Vanadium	0.475	< 0.010	< 0.010	< 0.010	0.014	0.034
Zinc	0.335	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
Mercury	0.0007	< 0.0002	< 0.0002	< 0.0002	0.0002	< 0.0002

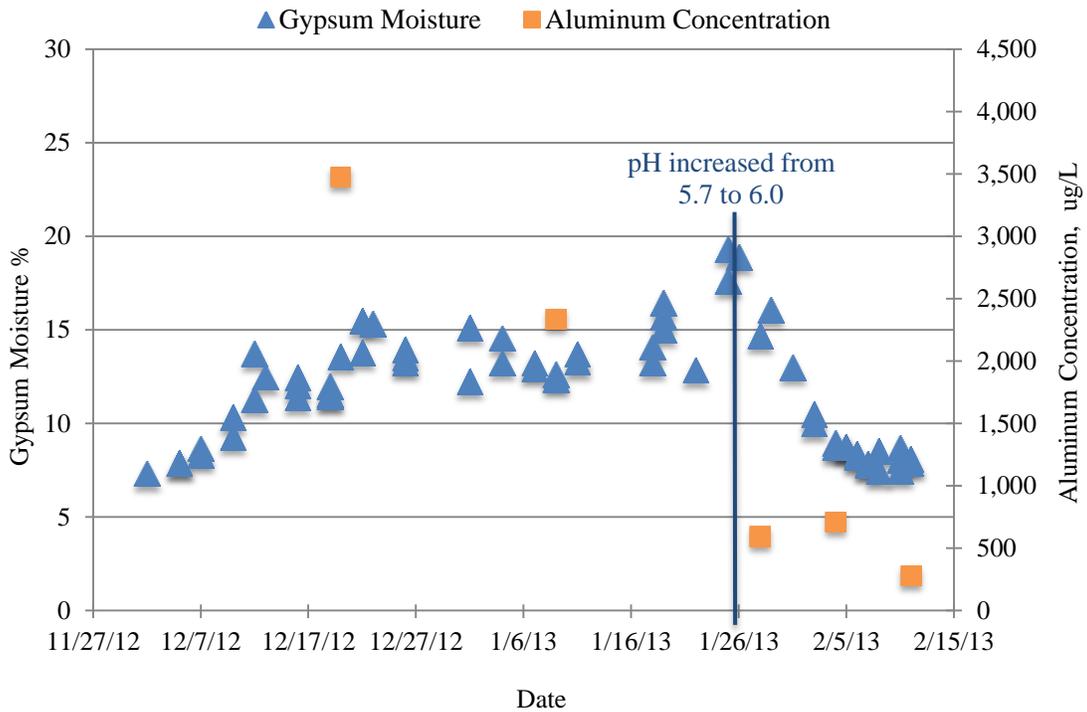
Table 3. Simulated FGD Conditions Leach Test
All results reported in mg/L

	Plant A Unit 5	Plant A Unit 6	Plant A Unit 7	Plant A Unit 8	Plant B Unit 1	Plant B Unit 2
Aluminum	2110	0.0784	3.20	0.347	0.249	0.197
Barium	0.256	0.172	0.193	0.181	0.200	0.0621
Beryllium	0.240	< 0.0080	< 0.0080	< 0.0080	< 0.0080	< 0.0080
Boron	71.0	36.6	49.2	39.0	59.8	50.7
Cadmium	0.086	< 0.010	0.036	0.019	< 0.010	0.075
Calcium	587	422	427	423	447	425
Chromium	1.92	0.557	0.148	0.416	2.02	0.062
Cobalt	2.19	0.297	0.965	0.514	0.024	1.22
Iron	44.0	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
Magnesium	3910	2100	3930	2540	1040	2320
Manganese	12.7	0.492	2.57	0.927	0.315	8.30
Molybdenum	0.035	0.129	0.027	0.084	0.188	< 0.020
Nickel	4.83	1.08	2.25	1.40	0.306	3.20
Potassium	63.6	8.54	36.6	16.5	5.30	19.9
Selenium	0.164	0.208	0.177	0.203	0.090	< 0.050
Silicon	325	33.8	57.7	42.5	24.6	24.8
Sodium	409	183	331	177	94.1	197
Strontium	19.2	11.1	9.18	10.4	16.3	10.9
Titanium	1.99	< 0.070	< 0.070	< 0.070	< 0.070	< 0.070
Vanadium	0.094	0.043	0.010	0.027	0.039	< 0.010
Zinc	15.8	< 0.050	2.35	0.596	< 0.050	4.53
Mercury	< 0.0002	< 0.0002	< 0.0002	< 0.0002	0.0003	< 0.0002
initial pH	11.26	11.32	11.71	11.68	11.2	11.1

The results of the leach tests correspond to the liquor-phase composition of the slurries. Elevated levels of elements such as aluminum, iron and silicon found in the Unit 56 slurry can be attributed to the unusual leaching behavior of the Unit 5 flyash. The leaching characteristics of Unit 7 and 8 flyash correlates to the lower levels of dissolved elements found in Unit 78 slurry. The leaching data also agrees with the presence of a problem on Unit 56 and the absence of a problem on Unit 78.

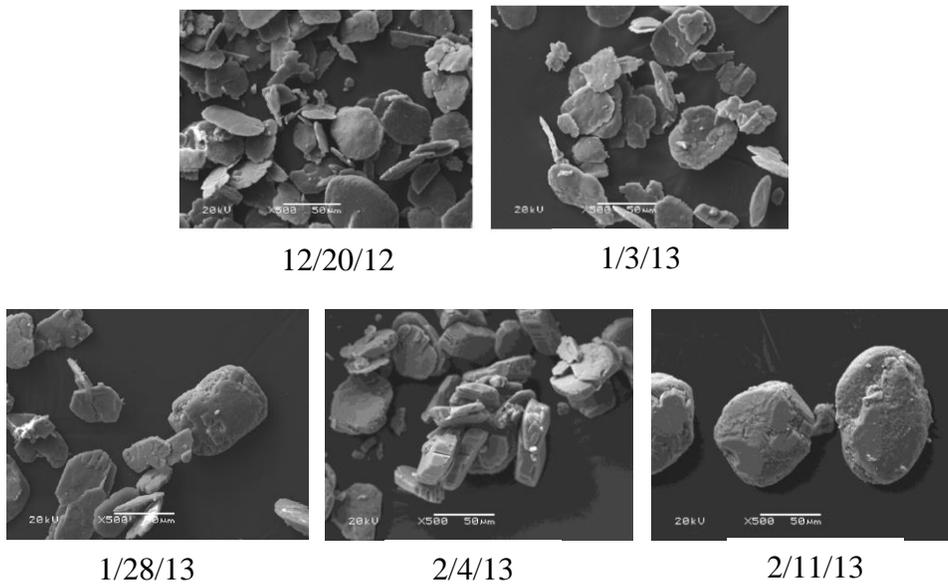
Test data showed that aluminum was an element that trended well with Unit 56 gypsum moisture. Figure 5 shows increased aluminum concentrations were observed during gypsum moisture excursions. It also shows that increases in pH reduced the liquid phase aluminum concentration, which subsequently improved gypsum moisture.

Figure 5. Unit 56 Gypsum Moisture and Aluminum Concentration in Relation to pH



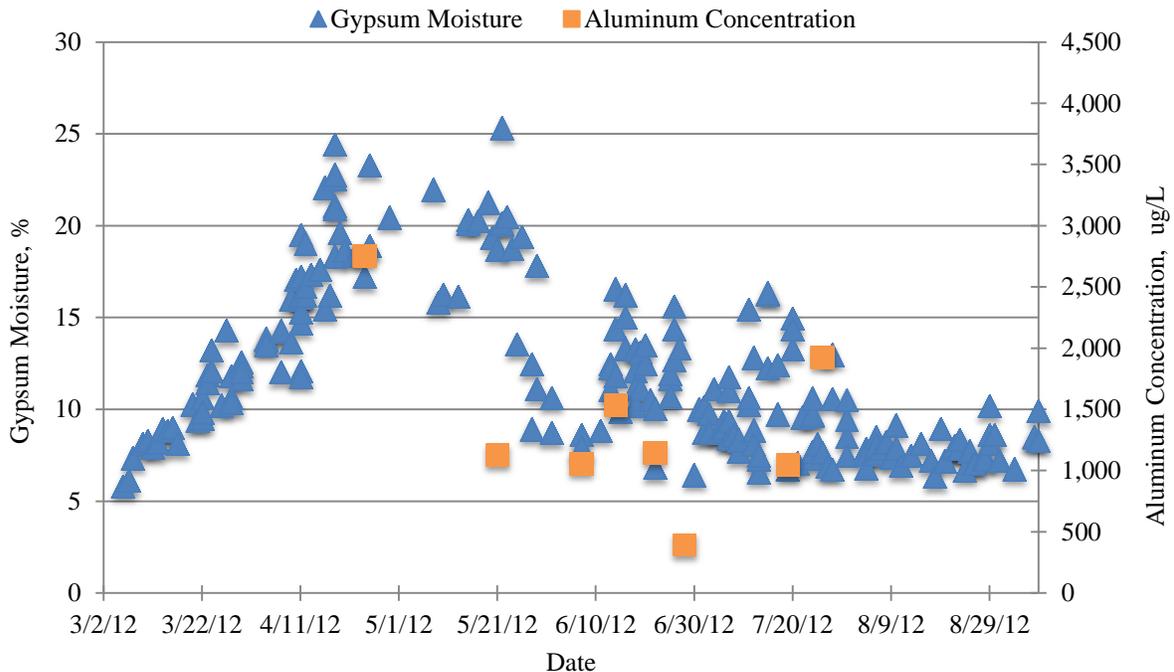
The improvement in gypsum moisture after the pH change corresponded to an improvement in gypsum crystal morphology. Initially plate-like crystals became thicker and more defined after the pH increase and subsequent drop in liquor phase aluminum concentrations. Figure 6 shows gypsum SEM photographs corresponding to the dates in Figure 5.

Figure 6. Unit 56 Gypsum SEM Photographs Corresponding to Figure 5



Review of all data collected from Unit 56 showed that the aluminum and gypsum moisture trend existed prior to the Stage 2 study, as seen in Figure 7. For clarity, pH changes were omitted from this chart.

Figure 7. Unit 56 Gypsum Moisture and Aluminum Concentration



Although aluminum appears to have a strong relationship with gypsum crystal deformation, it cannot be concluded definitively that aluminum is the problem. Aluminum could be a tracker for another element, or it may be a particular combination of elements that act together to inhibit or modify the growth of gypsum crystals. However, it can be concluded that these species leached from the Unit 5 flyash are modifying gypsum crystals and that a higher operating pH will reduce their concentration in the absorber liquor.

DISCUSSION

At least one other similar episode of a high gypsum moisture excursion has been reported². Amager Power Plant Unit 3 (APP3) in Denmark is fueled by a bituminous coal with 0.41-0.71 wt.% sulfur. The problem at this site began during a start-up period during which plugged pipes were limiting the purge capacity and the ESP was allowing increased amounts of flyash into the absorber. Foaming had interfered with the online density measurement, so the solids concentration had built beyond normal dewatering limits. As such, the solids residence time increased to greater than twice the normal amount. Additionally, the plant was operating at low load and burning lower-than-design sulfur content coal. Microscopy of the gypsum during the excursion showed the same thin, plate-like structure that was observed in Unit 56 Absorber at Plant A. The morphology change at APP3 was associated with high levels of dissolved aluminum, fluoride and iron in the scrubber liquor.

At Plant A, operating conditions similar to APP3 existed during the two most rapid excursions, both of which occurred during a start-up. Characteristics of start-up periods usually include low loads, longer solids residence time and increased carryover of flyash from the ESP. Ultimately APP3 identified two of the same elements – aluminum and iron – as being linked to the issue.

The fact that Plant A burns low sulfur coal is thought to be central to the problem. The low sulfur environment creates a slower gypsum growth rate that may cause dissolved impurities to affect the crystal structure to a much greater degree. At Foster Wheeler WFGD sites that burn higher sulfur coal, aluminum concentrations have been as high as 3 ppm without any gypsum issues. At Plant A however, concentrations above 1 ppm appeared to trigger gypsum problems. Therefore, it is hypothesized that the problem would subside as the ratio of sulfur to impurities was increased.

During the root cause study, the boilers of Unit 5 and 6 were operating with an oxidizing environment while Units 7 and 8 and the Plant B boilers were operating with a reducing environment. At the time, it was hypothesized that the oxidizing environment may play a role in creating unique flyash leaching properties. However, recent operational data may not fully support this theory. Although the ESP's on Units 5 and 6 perform less efficiently than Units 7 and 8, the chemical properties of the flyash should not be affected by the ESP.

Operational Remedy

To improve the gypsum quality, an operational remedy was implemented that required no changes to the inlet flue gas. It was shown that operation of the absorber at a pH of 6.0 or above would generally reduce gypsum moisture below 10%. However, this typically resulted in gypsum purity falling below the 95% minimum specification due to the presence of elevated residual limestone (CaCO_3). To find a balance between moisture and purity, the plant operated with modified pH control. The pH was set to 6.0 while the density of the absorber was low and the gypsum crystals were forming. The pH was then lowered to 5.7 several hours before dewatering commenced so that the unreacted limestone in the system could be consumed by system chemistry demands. After dewatering was completed, the pH was returned to 6.0. This operating method proved relatively successful in maintaining quality gypsum with acceptable free moisture.

SUMMARY

The high gypsum moisture problem at Plant A was a result of a change in gypsum crystal morphology. Testing concluded that a dissolved species or combination of species in the absorber liquor was acting as a crystal modifier(s) and causing formation of thin, flat gypsum crystals. This shape inhibited the dewatering the gypsum cake. Flyash leaching experiments simulated the behavior observed on Unit 56 by producing enrichment of the same flyash elements that were found in elevated levels in the absorber liquor. Furthermore, it was proved that Unit 5 flyash was the source of the higher concentration of elements introduced to the Unit 56 Absorber slurry. The most notable of these elements was aluminum, followed by iron and silica. Although elevated aluminum concentration appears to strongly correlate with high

moisture events at Plant A, it may be a combination of elements causing the crystal modification. Increasing the operating pH of the absorber lowered the concentration of aluminum and other elements in the absorber liquor, subsequently improving the gypsum crystal shape and dewatering abilities. Using this knowledge, an operating plan was implemented that fluctuated the operating pH, thus providing a reliable and effective solution to the problem.

It is believed that the low-sulfur nature of the plant contributes to the problem due to a low ratio of sulfur to impurities. More research is required to determine the cause of the unique leaching properties of Unit 5 flyash, although it is theorized that the boiler combustion process may play a role in altering the chemical properties of the flyash.

ACKNOWLEDGEMENTS

Foster Wheeler would like to thank RJ Lee Group for flyash testing and SEM analysis and Siemens Water Enviroscan for chemical characterization of slurry samples.

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KEYWORDS

Gypsum moisture, crystal modifier, flyash leaching, wet scrubber, WFGD