

# Hydration of Partially Sulphated CFBC Ash with Saturated Water Steam

*Y.H. Wu\**, *E.J. Anthony* and *L. Jia*

*CANMET Energy Technology Centre (CETC-O)*

*1 Haanel Drive, Ottawa, ON K1A 1M1, Canada*

## ABSTRACT

The hydration of partially sulphated fluidized bed combustion (FBC) ash with saturated steam was carried out in the laboratory. The ash samples were obtained from a commercial-scale 165 MWe circulating fluidized bed combustor (CFBC) firing a petroleum coke and coal blend. Both the bottom ash and fly ash were tested, and in addition the bottom ash was also separated into five size fractions and tested. These solid streams and the “as-received” fly ashes were hydrated by steam produced in a pressure bomb for different lengths of time at different saturated temperatures. Samples of the ashes were analyzed for free lime and calcium hydroxide content before and after the hydration process. Scanning electron microscopy (SEM) with an energy dispersive X-ray system (EDX) was employed to investigate the physical characteristics of the samples. X-ray diffractograms (XRD) were also used to determine the phase composition. These results show that after hydration treatment with saturated temperatures and elevated pressure, the unreacted CaO in the partially sulphated material can be quantitatively converted to Ca(OH)<sub>2</sub>. However, the free lime content is also observed to change throughout the hydration process, which indicates that the hydration of CaO is not the only reaction occurring in this system. It is also clear that for fines, i.e., fly ash and <75 μm bottom ash, the effectiveness of the hydration

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\* Corresponding author, e-mail: ywu@nrcan.gc.ca

depends much more strongly on hydration time and temperature than for coarser ashes and it is also clear that the behaviour of each particle size is different.

**Keywords:** hydration, reactivation, FBC ash, free lime, Ca(OH)<sub>2</sub>, saturated steam

## INTRODUCTION

A wide range of fuels can be fired in fluidized bed combustors (FBC), which is noted for its ability to control SO<sub>2</sub> emissions *in situ* by using calcium based sorbents (typically limestone or dolomite). In atmospheric FBC boilers, the fuel and limestone are fed together into a combustion chamber where the SO<sub>2</sub> is captured at a temperature of between 800-900°C. The process takes place in two steps, with the CaCO<sub>3</sub> in the limestone first calcining in the furnace.



The limestone is thus converted into a porous CaO matrix, which then sulphates via a process described by the overall reaction:



Theoretically, CaO and SO<sub>2</sub> should react on a 1:1 molar ratio; however, sorbent utilization is actually much lower (typically 20-45%) and it is common for Ca/S molar ratios of 2:1 or 2.5:1 to be used in industrial boilers to achieve a desirable degree of SO<sub>2</sub> removal (normally 90%). The phenomenon can be accounted for in terms of the “shrinking core” model. As the molar volume of CaSO<sub>4</sub> is much larger than that of CaO (46 vs. 17 cm<sup>3</sup>/mol), this model suggests that the

blockage of pores in limestone by the  $\text{CaSO}_4$  reaction product occurs during the progress of the sulphation reaction. In consequence, as pores are filled, a  $\text{CaSO}_4$  shell forms on the sorbent surface, which prevents  $\text{SO}_2$  from reaching the unreacted core of the limestone derived particles (Anthony and Granatstein, 2001).

Ash produced from the FBC process usually contains 20-30% unreacted CaO because of the use of such a large excess of sorbent. The high CaO content leads to many problems, ranging from exothermic behaviour on wetting, high pH leachates which require treatment before discharge, and expansion in the landfill, etc. (Anthony et al., 1999). Thus improvement in the utilization of limestone sorbents in FBC would bring benefits in terms of overall process economics, plant operation and ash disposal. Many methods have been proposed to increase the reactivity of the calcium sorbent, but by far the simplest is the reactivation of spent sorbent by hydration, either with water or steam (e.g., Canadian Electrical Association, 1994; Anthony and Granatstein, 2001; Laursen et al., 2000). The hydration reactions for the  $\text{CaO}/\text{CaSO}_4$  system are as follows:



However, the second of these reactions is slow and can actually be ignored from the point of view of sorbent reactivation (Couturier et al., 1994). During hydration of the partially sulphated material, water permeates the outer  $\text{CaSO}_4$  layer of the sorbent particles and reacts with CaO in the core. Since the reaction product,  $\text{Ca(OH)}_2$ , has a larger molar volume than the CaO (33 vs. 17  $\text{cm}^3/\text{mol}$ ), the core swells and cracks the sulphated shell. When the reactivated sorbent particles are re-injected into the fluidized bed, the  $\text{Ca(OH)}_2$  produced by hydration, decomposes and the

previously inaccessible CaO core becomes available for further sulphation (Laursen et al., 2000; Couturier et al., 1994; 1999).

Two kinds of FBC ashes have been previously tested by CETC, using liquid water and the effectiveness of the conversion of CaO to Ca(OH)<sub>2</sub> (Wu et al., 2002a; b) has been demonstrated for both of them. However, this study represents the first attempt by us to systematically examine the effects of steam hydration on one of those ashes.

## **EXPERIMENTAL**

### Materials

The partially sulphated material (including bottom ash and fly ash) used in this study was obtained from the 165 MWe CFBC boiler at Point Aconi, Nova Scotia, Canada, which currently fires petroleum coke and coal blends at a mass ratio of about 60:40. Proximate and ultimate analyses for the fuels, which were fired in a 50:50 blend during the production of the ash used here, are listed in Table 1. The CaCO<sub>3</sub> content in the limestone used for capturing SO<sub>2</sub> was between 90-92%. The bottom ash was sieved into several size fractions before hydration (Table 3) while the fly ash was hydrated “as-received”.

### Determination of Free Lime and Ca(OH)<sub>2</sub>

The free lime is defined as the sum of [CaO + Ca(OH)<sub>2</sub>] in the sample, and is expressed as CaO percent (Iribarne et al., 1994). This was determined by means of the sucrose method in this study, as described in ASTM C-25, lime index. Ca(OH)<sub>2</sub> was determined by a thermogravimetric

analyzer (TGA). The details of the method for determination of free lime and  $\text{Ca(OH)}_2$  have been described elsewhere (Wu et al., 2002b).

### Hydration with Steam

Hydration experiments were carried out in a pressure bomb (Parr 4522M Pressure Reactor) using tap water. The lower part of the bomb was a steel cylinder about 400 mm high with 100-mm i.d., which was sealed by bolts with a removable top. It can be heated externally up to 350°C when using water. A small amount of samples (~2 g) was put in a basket, which was suspended in the middle of the bomb and immersed in the steam during hydration. The hydration temperatures and pressures employed are listed in Table 2. The hydration time employed were 0.5 h, 1 h and 2 h for each temperature and pressure. The hydrated solids were then removed from the bomb and filtered off with D.I. water and transferred to a vacuum oven maintained at 45°C to dry for 3-4 hours. This low temperature should minimize any effect of heating on gypsum, if any is formed, and also ensure minimal subsequent reaction of the sample with surface moisture. The free lime and  $\text{Ca(OH)}_2$  contents of the dried samples were determined by the methods described above. Hydration tests and free lime and  $\text{Ca(OH)}_2$  analyses were repeated 2-3 times for many selected samples to obtain a mean result.

### SEM and XRD Analyses

Scanning electron microscopy (SEM) with an energy dispersive X-ray system (EDX) was employed to investigate the physical characteristics, such as surface structure or morphology, and calcium or sulphur distribution in the hydrated particles and one of the bottom ash fractions (300-600  $\mu\text{m}$ ) was analyzed in detail. The equipment used was Hitachi SEM Model S-750, provided

with Link AN 10/85S EDX system, at the University of Toronto. The chemical compositions for three samples--the fly ash and two fractions of bottom ash, <75  $\mu\text{m}$  and 75-150  $\mu\text{m}$ , --were examined by quantitative X-ray diffractograms (QXRD) at CETC.

## **RESULTS AND DISCUSSION**

### Sample Analyses before Hydration

The “as-received” bottom ash was sieved into 6 size fractions before hydration and Table 3 gives the particle size distributions. The medium size ranges (150-300 and 300-600  $\mu\text{m}$ ) accounted for most of the sample mass (i.e., 62% and 22.5% of the total mass respectively), while the remaining size fractions accounted for about 15% of the sample weight. Free lime determination indicated that most of the sample in the size range of >1400  $\mu\text{m}$  (equivalent to about 4% of the sample mass) consisted of fuel-derived ash, so this size fraction was discarded without further study.

The chemical analyses of the fly ash and divided bottom ash by X-ray fluorescence (XRF) are given in Table 4<sup>1</sup> and the carbonate analysis was provided in Table 5. The back-calculation results of the difference between the total CaO and the CaO required for  $\text{CaSO}_4$  and  $\text{CaCO}_3$  formation are shown in Table 6. The results were significantly higher than those determined by the sucrose method (Table 6). In the case of the bottom ash fraction this difference was much larger than is possible due to experimental errors. This indicates that some of the CaO must have combined with fuel ash components, the so-called other calcium compounds (OCC) (Anthony and Granatstein, 2001).

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<sup>1</sup> 600-1400  $\mu\text{m}$  was not subjected to this XRF test because it was rather heterogeneous although it had a relatively high free lime content.

For the bottom ashes, the unsieved sample has an average free lime content of 19.1%. Two major size fractions contained the highest and lowest free lime content respectively, 31.1% in the 300-600  $\mu\text{m}$  fraction and 15.4% in 150-300  $\mu\text{m}$ . The largest and smallest size fractions studied here contained relatively high free lime, 27.1% in 600-1400  $\mu\text{m}$  and 19.1% in  $<75$   $\mu\text{m}$ . The free lime content in “as-received” fly ash was determined to be 26.7%.

The results for  $\text{Ca}(\text{OH})_2$  content prior to hydration are also shown in Table 6. These results indicate that fractions  $>75$   $\mu\text{m}$  initially contained little  $\text{Ca}(\text{OH})_2$  but finer particles had a higher content, 4.55% in fly ash and 5.44% in  $<75$   $\mu\text{m}$  (expressed in  $\text{CaO}$ ). The most likely reason for this is that the finer particles have a stronger ability to absorb and react with the atmospheric water vapor during storage.

#### Effect of Hydration Temperatures and Pressures

The six diagrams in Figure 1 show changes of the free lime content in fly ash and the five size fractions of bottom ash after hydration at different temperatures (and pressures) as a function of time. In general, at a given hydration time, the free lime content was higher at a lower hydration temperature both for the fly ash and the fine fraction ( $<75$   $\mu\text{m}$ ). However, two distinct phenomena appeared for different size fractions: the free lime could either decrease or increase following the hydration process. For fly ash and three fractions of bottom ash,  $<75$ , 300-600 and 600-1400  $\mu\text{m}$ , the free lime content was significantly reduced after 30-minute hydration at all temperatures used. After longer hydration periods, the free lime usually decreased further, but the changes observed were less regular and showed considerable fluctuation. The contrary observation was: for the fraction of 150-300  $\mu\text{m}$ , the free lime appeared to increase to higher levels than seen prior to

hydration. This apparently paradoxical result has been previously observed by Bulewicz et al. (2000) and was recently confirmed during liquid water hydration experiments with two other ashes from the Point Aconi 165 MWe CFBC burning a local Nova Scotian coal and for the petroleum coke/coal mixtures described above (Wu et al., 2002a; b). This is regarded as clear evidence that during the hydration process free lime can be released from the OCC, i.e., Ca silicates, aluminates, etc. (Iribarne et al., 1994), as well as consumed by reactions with the coal ash components, such as silica. Free lime content was observed to fluctuate very slightly at the two higher temperatures of 200 and 250°C throughout the time scale of the hydration for the fraction of 75-150 µm. But at 150°C, the free lime reached a peak value of 20.3% at 1 h hydration and then reduced back to its initial level of ~18%. The free lime in this fraction was deemed to be quite stable under steam hydration.

The variation of  $\text{Ca(OH)}_2$  content as a function of time and hydration temperatures (or pressures) are shown in Figure 2. It can be seen that  $\text{Ca(OH)}_2$  always increased rapidly even after a short hydration period of 30 minutes and then stayed at a relatively stable level. Although the initial level of  $\text{Ca(OH)}_2$  was similar (~1-5% expressed in CaO), the behaviour of each fraction was different. For the two finer fractions (fly ash and <75 µm), which had higher  $\text{Ca(OH)}_2$  initially, the influence of temperature (or pressure) was obvious: at a lower temperature,  $\text{Ca(OH)}_2$  increased more quickly compared with other fractions. With longer hydration periods  $\text{Ca(OH)}_2$  increased only slowly or sometimes decreased slightly. The fact that the  $\text{Ca(OH)}_2$  content can decrease is also strong evidence that during the hydration process it can be consumed by reaction with other components present in the system. For the fractions of 75-150, 150-300 and 300-600 µm, there was no significant influence of temperature (or pressure) on  $\text{Ca(OH)}_2$  content, however, the highest increase (from ~2% to 27%) was observed for fraction of 300-600 µm, which had a highest initial free lime content (31%). Interestingly, the fraction of 600-1400 µm showed the



reverse tendency when compared with the finer fractions:  $\text{Ca(OH)}_2$  increased with increasing temperatures at a given hydration time.

It should be noted that the free lime and  $\text{Ca(OH)}_2$  for the two coarser fractions (300-600 and 600-1400  $\mu\text{m}$ ) showed irregular behaviour. This is almost certainly due to problems associated with sample size since only small samples (15-30 mg) can be loaded into the TGA for testing, and experimental errors are therefore greater for such larger sized particles.

### Effect of Hydration Time

It can be seen from Figures 1 and 2 that the free lime and  $\text{Ca(OH)}_2$  content continued to change with the hydration time, for all the size fractions and hydration temperatures. The most significant changes typically occurred after 30-minute hydration. However, in many cases there were only slight changes for both free lime and  $\text{Ca(OH)}_2$  contents after longer period of hydration. In some cases, the free lime and  $\text{Ca(OH)}_2$  contents after 1 h hydration were even lower at a given hydration temperature than for shorter time periods. This demonstrates that longer hydration times do not always increase the extent of hydration from the view of  $\text{Ca(OH)}_2$  production via hydration treatment.

### Apparent Conversion of CaO to $\text{Ca(OH)}_2$

Using a comparison of values of  $\text{Ca(OH)}_2$  before and after hydration and the initial CaO content in the ash prior to hydration, the apparent conversion of CaO to  $\text{Ca(OH)}_2$  for each fraction was obtained, as shown in Figure 3.

It is clear that, for the finer particles (fly ash and  $<75 \mu\text{m}$ ), temperature (or pressure) was an important factor in steam hydration. The higher the temperature, the lower the conversion. After 0.5 h, a conversion of 60% can be achieved at a hydration temperature of  $150^\circ\text{C}$  for both fractions, but this conversion dramatically diminished to only  $\sim 5\%$  after 0.5 h hydration at  $250^\circ\text{C}$  for fly ash. For the other three fractions (75-150, 150-300 and 300-600  $\mu\text{m}$ ), temperature had a less important role. All of these size fractions achieved 80% conversion for each hydration temperature and for the fraction of 150-300  $\mu\text{m}$ , the conversion was close to 100%. In the case of hydration at  $150^\circ\text{C}$  for 1 h, the degree of conversion of CaO even appears to exceed 100%. This can happen if free lime is produced by the hydrolysis of OCC, what is surprising here is that this can occur in the absence of liquid water. The coarsest particle (600-1400  $\mu\text{m}$ ), demonstrated a reverse trend with finer particles at 1 h hydration: when temperature rising, the conversion increasing. But the results at 2 h showed excessive variation probably due to its heterogeneous character of the sample, and large experimental error seem to be inevitable for this size fraction. In general, the most significant increase of the conversion always occurs within 30 minutes of hydration.

### SEM Analyses

SEM photographs of the unhydrated and hydrated bottom ash, fraction of 300-600  $\mu\text{m}$ , are presented in Figures 4-7. The left columns in these figures show typical fields, the right specific particles picked out from the fields with higher magnification.

Figures 4(a) and 4(c) illustrate two typical fields of particles in the unhydrated samples at a magnification of 50x. Two particles in field 4(a) (in the upper left quarter) are shown in 4(b),

magnified to 150x. Most of the particles in fields 4(a) and 4(c) appeared to have an outer shell. EDX results indicated that the shell was not fully sulphated; in general, it consisted of a mixture of  $[\text{CaO} + \text{CaSO}_4]^2$ . Around the lower particle in 4(b), a double shell can be clearly seen. The outer shell consisted mostly of  $\text{CaSO}_4$ , with some  $\text{CaO}$ ; the inner one was a mixture of  $[\text{CaO} + \text{CaSO}_4]$  in similar proportions. The core was pure  $\text{CaO}$ . With few exceptions, the particles remained whole, showing little sign of being fractured or having started to disintegrate.

With hydration at  $150^\circ\text{C}$  for 0.5 h, the disruption or disintegration of particles appeared to be quite advanced (Fig. 5(a)). The sulphate shells were broken and many fragments were lost and appeared as smaller isolated bright particles in the field. The cores were frequently broken open. Fig. 5(b) shows details of one particle in Fig. 5(a). The thick shell of  $\text{CaSO}_4$  was broken at the left and cracks were found in the core. Fig. 5(c) and (d) show two typical fields of hydration for 1 h. EDX revealed that the dark regions in the particles were either pure  $\text{Ca}(\text{OH})_2$  or  $\text{Ca}(\text{OH})_2$  with some  $\text{CaSO}_4$  and the brighter broken shells or rest of shells consisted of  $\text{CaSO}_4$  mixed with  $\text{Ca}(\text{OH})_2$ . The bright particle at the centre in Fig 5(c) showed on EDX predominant Si plus some Al and K, suggesting quartz with some silicate. It was surrounded by a thin shell of  $\text{CaSO}_4$  with some  $\text{Ca}(\text{OH})_2$ . Similar characteristics were observed after hydration of 2 h, as shown in Fig. 5(e) and (f). Most particles lost their shells and mixture of sulphate shell fragments and dark  $\text{Ca}(\text{OH})_2$  regions were found in the lower central particle.

After hydration at  $200^\circ\text{C}$ , fewer particles remained entire while the abundance of debris increased. The bright particle in Fig. 6(a) showed on EDX to be  $\text{CaSO}_4$  mixed with some  $\text{Ca}(\text{OH})_2$ , sometimes almost pure  $\text{CaSO}_4$ . Fig. 6(b) shows two particles at 130x: the upper one in frank disintegration, the lower one being a core of  $\text{Ca}(\text{OH})_2$  plus little sulphate which lost entirely

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<sup>2</sup> In locations where EDX gives only the elements S and Ca, pure or nearly pure  $\text{CaSO}_4$  is indicated when the heights of the S peak and the first Ca peak are about equal or S is slightly higher than the main Ca peak.

its shell. In Fig. 6(c) particles showed very advanced disintegration. Some showed the production of a large accumulation of  $\text{Ca}(\text{OH})_2$  crystals (Fig. 6(d)).

Fig. 7 shows hydration at  $250^\circ\text{C}$ . Almost all the sulphate shells in Fig. 7(a) disintegrated into loose particles. Fig. 7(b) showed a typical dark area of a particle core, taken from in Fig. 7(a) (at  $X=0.6$ ,  $Y=0.5$ ) at a high magnification of 2000x. The small grains of  $\text{Ca}(\text{OH})_2$  seemed to have attached to each other at various angles. It is surprising to see large particles in Fig. 7(c) in existence after hydration at  $250^\circ\text{C}$  for 2 h. However, their structure suggested that many of them were most likely formed by re-attachment of fragments rather than coming from the original particles of the samples.

### XRD Analyses

XRD results for three groups of samples, the fly ash and two size fractions of bottom ash,  $<75\ \mu\text{m}$  and  $75\text{-}150\ \mu\text{m}$ , are summarized in Table 7. For all of the unhydrated samples, the predominant phases were  $\text{CaO}$ ,  $\text{CaSO}_4$  and  $\text{SiO}_2$  prior to hydration and no  $\text{Ca}(\text{OH})_2$  was detected by XRD. This indicates that  $\text{CaO}$  in the samples had not reacted significantly with atmospheric water vapour. The  $\text{CaO}$  content decreased dramatically to undetectable level after hydration.  $\text{Ca}(\text{OH})_2$  increased markedly compared with unhydrated sample but it did not increase proportionally in the ash as the hydration conditions became more severe. For example, in the fly ash,  $\text{Ca}(\text{OH})_2$  dropped from 38.1% to 13.1% when the hydration temperature was increased from  $150^\circ\text{C}$  to  $250^\circ\text{C}$  which means that some  $\text{Ca}(\text{OH})_2$  must have been consumed. These results agreed with those obtained from TGA analysis previously. Anhydrite and quartz were both reduced slightly to different extent after hydration. Some amount of calcite was formed and it is assumed that this

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S peaks lower than the first Ca peak indicate that mixtures of  $\text{CaO}$  or  $\text{Ca}(\text{OH})_2$  and  $\text{CaSO}_4$  exist.

was produced from the reaction of  $\text{Ca}(\text{OH})_2$  with  $\text{CO}_2$  in the atmosphere during the treatment. It should be noted that for all these fractions, ettringite and hemihydrate or gypsum are not detectable after the hydration process.

## CONCLUSIONS

The hydration temperature (or pressure) plays a very important role in the hydration of FBC ash with saturated water steam. For the two finer fractions (fly ash and  $<75 \mu\text{m}$ ), the free lime and  $\text{Ca}(\text{OH})_2$  contents are higher with decreasing hydration temperature (or pressure) at a given hydration time.  $\text{Ca}(\text{OH})_2$  content always increases rapidly after hydration for all fractions, however, there is no significant influence of temperature (or pressure) on  $\text{Ca}(\text{OH})_2$  content for three bottom ash fractions: 75-150, 150-300 and 300-600  $\mu\text{m}$ . These results show that different hydration patterns exist for different particle size fractions.

While the unreacted CaO in the partially sulphated material can be converted quantitatively to  $\text{Ca}(\text{OH})_2$ , the most significant changes of free lime and  $\text{Ca}(\text{OH})_2$  typically take place after 30-minute hydration. In many cases there is little change for either the free lime or the  $\text{Ca}(\text{OH})_2$  contents after longer period of hydration.

Most remarkably, the free lime content is not constant during the hydration process. Instead, it can either decrease or increase during the hydration process, showing that it is both consumed by other reactions and produced by the hydrolysis of the OCC in the ash. This result is similar to results produced for the hydration with liquid water and is supported by the XRD analysis. It is viewed as clear proof that other reactions besides hydration affect the levels of free lime and

Ca(OH)<sub>2</sub> and, therefore, any attempt to determine the hydration behaviour of such ashes must take these reactions into account.

## ACKNOWLEDGEMENTS

The authors wish to thank Professor Julio Iribarne and Dr. Agripina Iribarne for their considerable assistance with various SEM analyses in this work. They would also like to thank Mr. William Richards of Nova Scotia Power Inc. for supplying the ashes used here and finally, the authors also acknowledge the financial support of PERD during the course of this work.

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**Table 1. Proximate and ultimate analyses of the fuels**

<b>Delayed Petroleum Coke</b>			
Proximate Analysis (as received, wt.%)		Ultimate Analysis (dry basis, wt.%)	
Moisture	5.89	Carbon	86.18
Ash	0.31	Sulphur	6.65
Volatile Matter	9.37	Hydrogen	3.56
Fixed Carbon	84.43	Nitrogen	1.45
		Oxygen (by difference)	1.83
		Ash	0.33
		Gross Calorific Value (MJ/kg)	35.3
<b>Colombian Steam Coal</b>			
Proximate Analysis (as received, wt.%)		Ultimate Analysis (as received, wt.%)	
Moisture	7.9	Carbon	68.44
Ash	6.94	Sulphur	0.73
Volatile Matter	35.88	Hydrogen	5.14
Fixed Carbon	49.28	Nitrogen	1.35
		Oxygen (by difference)	9.47
		Ash	6.94
		Chlorine	0.03
		Moisture	7.9
		Gross Calorific Value (MJ/kg)	28.6

**Table 2. Hydration temperatures and pressures**

Temp., °C	Pres., bar
150	4.79
200	15.6
250	39.9

**Table 3. Particle size distributions of the bottom ash**

Size Fractions, µm	Distribution, wt.%
>1400	4.16
600-1400	2.03
300-600	22.49
150-300	61.99
75-150	8.21
<75	1.13



**Table 4. Chemical analyses for NSPI ash (in oxide form, wt.%)**

	<b>Fly Ash</b>	<b>Bottom Ash &lt;75 μm</b>	<b>Bottom Ash 75-150 μm</b>	<b>Bottom Ash 150-300 μm</b>	<b>Bottom Ash 300-600 μm</b>
<b>SiO<sub>2</sub></b>	15.92	15.34	7.98	6.77	7.27
<b>Al<sub>2</sub>O<sub>3</sub></b>	4.72	3.57	2.24	2.23	2.30
<b>Fe<sub>2</sub>O<sub>3</sub></b>	1.57	1.39	0.71	0.67	0.63
<b>TiO<sub>2</sub></b>	0.20	0.15	0.11	0.11	0.10
<b>P<sub>2</sub>O<sub>5</sub></b>	0.052	0.029	0.024	0.032	0.032
<b>CaO</b>	46.44	43.55	51.08	52.59	59.11
<b>MgO</b>	0.78	0.68	0.59	0.61	0.67
<b>SO<sub>3</sub></b>	19.25	25.35	32.83	32.60	26.79
<b>Na<sub>2</sub>O</b>	0.20	< 0.20	< 0.20	< 0.20	< 0.20
<b>K<sub>2</sub>O</b>	0.86	0.46	0.21	0.18	0.27
<b>BaO</b>	0.213	0.875	0.093	0.043	< 0.030
<b>SrO</b>	0.039	0.061	0.037	0.037	0.040
<b>V<sub>2</sub>O<sub>5</sub></b>	0.368	0.602	0.639	0.784	0.356
<b>NiO</b>	0.071	0.093	0.097	0.115	0.051
<b>MnO</b>	0.177	0.135	0.163	0.156	0.185
<b>Cr<sub>2</sub>O<sub>3</sub></b>	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008
<b>LOF</b>	9.14	7.58	3.09	3.07	2.12
<b>Sum</b>	99.998	99.88	99.89	100.00	99.92

**Table 5. Carbonate analysis (wt.%)**

	<b>Fly Ash</b>	<b>Bottom Ash &lt;75 μm</b>	<b>Bottom Ash 75-150 μm</b>	<b>Bottom Ash 150-300 μm</b>	<b>Bottom Ash 300-600 μm</b>
<b>Total Carbon</b>	4.27	2.45	0.23	0.10	0.36
<b>Carbon Dioxide</b>	2.69	0.72	0.50	0.34	0.56

**Table 6. Free lime and Ca(OH)<sub>2</sub> content before hydration (expressed as CaO, wt.%)**

<b>Bottom Ash</b>	<b>Free Lime<sup>a</sup></b>	<b>Ca(OH)<sub>2</sub><sup>b</sup></b>
Unsieved sample (as-received)	19.1	-
<b>Size Fractions, μm</b>		
600-1400	27.1	2.23
300-600	31.1 (39.63 <sup>c</sup> )	1.31
150-300	15.4 (29.32 <sup>c</sup> )	0.89
75-150	18.2 (27.44 <sup>c</sup> )	1.32
<75	19.1 (24.87 <sup>c</sup> )	5.44
<b>Fly Ash (as-received)</b>	26.7 (29.53 <sup>c</sup> )	4.55

a: by sucrose method; b: by TGA; c: by back-calculation from chemical analysis

**Table 7. Phase analyses by XRD (wt.%)**

<b>Bottom Ash, &lt;75 µm</b>						
	<b>Unhydrated</b>	<b>Hydrated at 150°C</b>			<b>Hydrated at 200°C</b>	
		<b>30 min</b>	<b>1 h</b>	<b>2 h</b>	<b>30 min</b>	<b>1 h</b>
<b>Lime (CaO)</b>	11.1	-	-	-	-	-
<b>Portlandite (Ca(OH)<sub>2</sub>)</b>	-	29.0	28.5	32.7	24.8	27.7
<b>Anhydrite (CaSO<sub>4</sub>)</b>	74.8	60.2	57.4	61.1	64.9	58.4
<b>Quartz (SiO<sub>2</sub>)</b>	10.2	8.4	9.2	5.6	6.6	8.4
<b>Calcite (CaCO<sub>3</sub>)</b>	-	4.9	4.6	3.9	5.1	2.9
<b>Magnesite (MgCO<sub>3</sub>)</b>	-	-	-	-	1.9	2.4
<b>Bottom Ash, 75-150 µm</b>						
	<b>Unhydrated</b>	<b>Hydrated at 200°C, 2 h</b>		<b>Hydrated at 250°C, 2 h</b>		
<b>Lime (CaO)</b>	9.1	-		-		
<b>Portlandite (Ca(OH)<sub>2</sub>)</b>	-	27.8		27.4		
<b>Anhydrite (CaSO<sub>4</sub>)</b>	83.3	61.4		64.2		
<b>Quartz (SiO<sub>2</sub>)</b>	2.5	1.3		1.6		
<b>Calcite (CaCO<sub>3</sub>)</b>	-	3.4		3.7		
<b>Magnesite (MgCO<sub>3</sub>)</b>	-	3.5		2.5		
<b>Fly Ash</b>						
	<b>Unhydrated</b>	<b>Hydrated at 150°C, 1 h</b>		<b>Hydrated at 250°C, 1 h</b>		
<b>Lime (CaO)</b>	19.4	-		-		
<b>Portlandite (Ca(OH)<sub>2</sub>)</b>	-	38.1		13.1		
<b>Calcite (CaCO<sub>3</sub>)</b>	8.4	11.3		8.2		
<b>Anhydrite (CaSO<sub>4</sub>)</b>	61.9	43.8		31.6		
<b>Quartz (SiO<sub>2</sub>)</b>	9.0	5.5		3.2		
<b>Katoite (Ca<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)(OH)<sub>8</sub>)</b>	-	-		18.1		
<b>Fluorellestadite Ca<sub>10</sub>(SiO<sub>4</sub>)<sub>3</sub>(SO<sub>4</sub>)<sub>3</sub>F<sub>2</sub></b>	-	-		26.9		