

CFBC Ash Hydration Studies

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1. ABSTRACT

Hydration studies on CFBC ashes have shown that the acetone technique to prevent hydration in stored samples is relatively effective, only allowing some slight degree of hydration over days, in the presence of excess water. In the presence of large excesses of water sufficient to control temperature increases, the degree of bulk mixing has no effect on the degree of hydration, which is shown to be relatively slow at ambient conditions, taking hours to complete. Finally, the effect of salt addition on hydration has been shown to negligible at the low levels typical of wastewater, but there may be effects at ion concentrations typical of seawater. This work suggests that experience gained from lime hydration should be applied with caution to studies on hydration of CFBC ashes.

Keywords: FBC Ash, Quenching Hydration, Lime, Salt addition

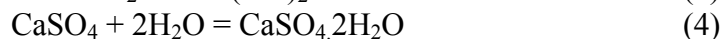
2. INTRODUCTION

Circulating Fluidized Bed Combustion (CFBC) is a very effective technology for burning high sulfur fuels with low SO₂ emissions [1]. SO₂ is capture by limestone added insitu, which reacts via the following two-step process:



The limestone particles calcine from a low porosity solid to a porous matrix of CaO, with about 50% porosity, and then sulfates. However, the CaSO₄ product blocks the pores of the calcined sorbent, and overall, utilization is typically from 20-40%, leaving a solid which contains significant CaO content in addition to CaSO₄, and fuel derived ash components [1].

The hydration process is dominated by direct hydration of the CaO component; whereas significant CaSO₄ hydration takes days to occur and can normally be ignored in hydration experiment lasting hours [2].



The standard treatment is to hydrate the ash prior to disposal to eliminate the exothermic properties of the discharged ash [3].

Unfortunately, CFBC ash hydration has received relatively little systematic attention, and many of the studies performed to date have involved the use of synthetic ashes prepared in a differential reactor by direct sulfation of calcined limestone, or materials that have come from small pilot plant. Moreover a number of those studies focus on reactivation of those ashes, rather than understanding the basic chemistry of the hydration process, e.g. Couturier, and others, [4] and Canadian Electric Association, [5]. However, recent work has shown that

CFBC ashes produced from some industrial-scale FBC can have substantially different properties from synthetic sorbents [6,7] due to the presence of other calcium compounds (OCC), namely calcium silicates, aluminates and ferrites [8], and also due to interactions with the fuel ash derived portion of the bed and fly ash.

This paper looks at the hydration process, both in terms of preventing hydration, in order to allow hydrated samples to be preserved at a particular extent of conversion, and also at efforts to enhance the rate of hydration, either by means of chemical additives or temperature and compares the hydration behaviour of CFBC ashes with that of industrial lime.

3. EXPERIMENTAL

The majority of this work has been done using bed ashes from the Point Aconi 165 MWe CFBC boiler firing Devco Prince coal (a bituminous coal with a high sulfur content of about 3-5%), and a local calcitic limestone (90% CaCO_3). Here $\text{Ca}(\text{OH})_2$, and CaCO_3 contents are determined using a Cahn 1100 thermo gravimetric analyzer (TGA).

Initial investigations were carried out with Point Aconi ash. Typically a 5 g sample of bed ash was covered with a 30ml/40 ml mixture of acetone/water and left for 18 hours in a covered flask. The weight loss of the filtered and air dried sample was then determined by TGA, as was an unhydrated sample and an acetone washed unhydrated sample to determine the reference levels of $\text{Ca}(\text{OH})_2$ and CaCO_3 in the parent sample. Finally, a sample was left in water for 5 days and agitated once daily since the ash tends to clump and solidify when left in water without agitation. A second set of samples of fine ash size fraction 75-150 μm) were then first ashed to destroy all of the $\text{Ca}(\text{OH})_2$ in an oven, and TGA was then used to confirm that portlandite was absent. Following this six 2 g samples were then covered with a 5 ml H_2O + 20 ml acetone mixture, and shaken and then two samples were exposed for 1, 2 and 5 days in the acetone mix, after which they were washed with deionized (D.I.) water, and separated by filtration and then transferred to a drying oven (105°C) and a vacuum oven (50°C), and dried for 6 hours, and then examined for $\text{Ca}(\text{OH})_2$ content.

For the direct hydration experiments 5 g of bed ash was used with a 100 g of water. On completion the samples were then filtered, and rinsed with acetone to stop further reaction. The sample was then dried in a vacuum oven and subject to TGA analysis. Here no stirring was employed for the bulk of the experiments, but as a check some stirring experiments were also done to see if this made a significant difference to the results. The relatively large amount of water was chosen to ensure that no significant bulk temperature rise was associated with the hydration process.

Further experiments were also carried out with additions of various concentrated salt solutions. Again the sample was Point Aconi Bed Ash with a size fraction of 150-300 μm , and the ash sample was ~1.5 g, with 15 ml of water added. The hydration was done at a temperature of 40°C, and after hydration the samples were rinsed for 1 to 2 minutes by deionized (D.I.) water under suction (to eliminate the salt solution). The residues were then transferred to a vacuum oven and dried at 45-50°C for 3 h.

4. QUENCHING HYDRATION REACTIONS

A technique that has been developed to quench hydration reactions is the use of acetone addition [9]. This technique, which involves immersing, samples of CFBC ash acetone which is then supposed to stop any further reaction of CaO component in the ash with water,

and thus preserve the samples CaO/Ca(OH)₂ content as it was at the point of treatment. This technique originates from cement chemistry where acetone has been used to stop curing reactions in C-S-H pastes (using cement chemistry notation), and to prevent carbonation [10]. However, it has not been systematically examined for CFBC ashes.

5. RESULTS

5.1 ACETONE QUENCHING EXPERIMENTS

The results of the initial experiments are given in Table 1, and apparently show that little or none of the CaO is hydrated in the presence of acetone. The tests were then repeated with a finer size fraction. Here the bracketed results are the oven-dried sample, the 0.5-1% differences in hydration levels is small enough that they might be due to experimental error, although the fact that the oven dried samples always indicated a lower concentration argues against that explanation. The difference may lie in the presence of small amounts of solid solutions, of C_xA_yS_zH_n or similar compounds (using cement notation), whose decomposition depends on the type of drying technique used, and Taylor mentions this issue (p. 161) (10).

Table 1: Extent of reaction of Point Aconi bed ash (wt%)

Composition	Untreated ash	Acetone washed Ash	Acetone/Water treated ash	5 d water treated ash
Whole ash				
Ca(OH) ₂ as CaO	2.5	2.8	3.5	9.1
CaCO ₃ as CaO	0.5	0.6	0.8	2.1
75-105 μm size fraction				
Hydration time	Untreated ash	1 d	2 d	5 d
Ca(OH) ₂ as CaO	4.4	5.0 (4.0)	5.3 (4.3)	5.4 (4.9)

For comparison it should be noted that the parent ash has a nominal CaO of about 15% CaO content, as determined by TGA, so that at 5 days either all the ash has not hydrated, or more likely some of it has reacted with the coal ash fraction to form other compound besides portlandite. However, what is clear is that the acetone does a relatively good job at stopping the hydration for the bed ash, although there may be some reaction. In the case of the fine ash fraction, there appears to have been some hydration. Interestingly, the fine ash has hydrated back to similar levels of the parent ash prior to heat treatment at 600°C. Thereafter it appears that the degree of reaction is very small indeed, assuming that the differences between the 3 samples are real and not simply due to experimental error. A possible explanation for the initial rapid hydration might be that the dehydrated ashes fragments and becomes particularly reactive and there is support for this view in that ground ash has been shown to hydrate more rapidly [11]. The conclusion of this work is therefore that for reasonable storage periods, acetone is effective albeit not perfect in slowing subsequent hydration even in the presence of significant quantities of water (i.e. with excess water over the stoichiometric required amounts of 300-500% or more).

5.2 Rate of Hydration

Hydration experiments were then carried out to assess the extent of reaction over longer periods of time. Table 2 gives the results for those experiments, together with data on the

amount of CaO converted to carbonate. Here no attempt has been made to look for ettringite or any other species that might form in this period and the TGA will show Ca(OH)₂ decomposition or decomposition of any other hydrate in the temperature window tested (350°-450°C). It should also be noted that other work has shown that in fact complicated interactions with ash and OCC occur over periods of ashes and these can affect the absolute amount of Ca(OH)₂, which can either decrease or increase depending on the type of interaction, independent of the formation of compounds such as gypsum or ettringite [6,7]. Therefore these results should be looked on as providing comparative rather than absolute data on hydration level.

Table 2 The effect of hydration time (h), all conversions as CaO equivalent (wt%)

Bed ash				
	Without stirring		With stirring	
Time (h)	Ca(OH) ₂	CaCO ₃	Ca(OH) ₂	CaCO ₃
2	6.8	0.8	7.1	0.6
6	10.7	0.9	-	-
16	11	1.2	-	-
24	14.8	1.1	11.8	1.9
48	16.2	1.2	-	-
Fly ash				
	Without stirring		With stirring	
Time (h)	Ca(OH) ₂	CaCO ₃	Ca(OH) ₂	CaCO ₃
2	9.4	6.3	8.3	6.6
24	11.8	5.8	8.8	7.7

These results show a number of interesting things. First that after about 6 hours most of the hydration is completed, and secondly, this material carbonates only very slowly with CO₂ in the air, again suggesting that this sorbent is resistant to carbonation. Not surprisingly, there is very little evidence that stirring makes a significant difference in the rate of hydration, which agrees with the idea that the primary resistance to hydration is due to resistance to the water penetration into particles pores. The major difference produced by stirring is that there may be a slight increase in carbonation at 24 hours due presumably to enhanced transfer of CO₂ from the air to form carbonate. The CaO conversion seen by 24 hours is close to the maximum expected on the basis of the original quick lime content of the ashes, which is as noted around 15%, and the slightly greater amount at 48 hours could either be due to experimental variation or possibly the release of CaO from OCC. Whatever the true explanation is, it is clear for this CFBC ash that hydration is a relatively slow process, and carbonation an even slower one. In this respect, CFBC ash hydration is a far slower process than hydration of industrial lime, which normally takes place in a period of minutes [12].

In the case of the fly ash the limited amount of experiments make it difficult to draw strong conclusions, but it is clear that hydration does not increase rapidly after 2 hours, and given the difference between the two sets of results with and without stirring, it is evident that providing contact with sufficient water is achieved, no substantial improvement in the degree of hydration has been produced by the enhancing the bulk mixing of the sample. This is a good argument for gentle stirring, since visual observation suggests that vigorous stirring has a tendency to create fines, which indicates mechanical damage of the particles. Another point

that is worth making is that the similarity of the stirred and unstirred hydration argues against any equivalent to the “drowning phenomena” known with lime hydration, in which an unreactive lime is deactivated by the formation of a “skin of lime putty” which reduces the subsequent rate of reaction [12]. Finally, it is worth remarking that similar results have been reported earlier in preconditioning studies carried out by Ghafoori and Sami, [13], who found that preconditioning FBC ash with between 10 and 15% water for 24 hours in sealed containers was effective in quantitatively hydrating FBC ashes, and that reaction was still detectable, as measured by heat increase, for several hours.

A limited number of experiments were done at higher temperatures, and these results are given in Table 3, as is well known the degree of hydration increases with increasing temperature [4] and it has been shown to do so for these ashes [7]. Here the most dramatic changes occur between 40°C to 60°C, and there may also be a modest increase in carbonation at these higher temperatures, although in the absence of a more detailed study, the differences in carbonation may simply be due to experimental error. Here all temperatures were controlled within $\pm 2^\circ\text{C}$.

Table 3 The effect of hydration temperature ($^\circ\text{C}$), all conversion as CaO equivalent (wt%)

Hydration time of 2 hours, with stirring		
Temperature	Ca(OH) ₂	CaCO ₃
40	8.8	1.1
60	14.6	2.5
80	12.9	1.9

5.3 The effect of salt addition

There is substantial experience from the lime industry in slaking quicklime. Boynton, [12], for instance notes that 6 Mt of quicklime are slaked in the US annually. It is therefore instructive to determine what information can be taken from the experience with lime that is applicable to hydrating CFBC ashes. It is known from the lime industry that chloride anions can increase the hydration rate of lime, albeit at much higher concentrations compared with 55 mg/l of total dissolved solids typical of potable water. In order to test this hypothesis, a number of experiments were performed with CaCl₂ and NaHCO₃, which is supposed to retard the hydration process [14], by blocking the pores due to CaCO₃ formation.

Table 4 Conversion to Ca(OH)₂ and CaCO₃ for 2 h time, as CaO equivalent (wt%)

	mg/l of CaCl ₂	mg/L of NaHCO ₃	% Ca(OH) ₂	% CaCO ₃
Bed ash	2220	0	7.2	0.8
Bed ash	2950	300	5.3	4.0
Bed ash	0	300	5.0	4.6
Bed ash	1310	300	7.1	4.0
Fly ash	1986	0	9	6.8
Fly ash	0	300	6	10.5

There is very little evidence that hydration is dramatically effected by either material. This suggests that in a lime product is already substantially sulfated, such effects are relatively unimportant, and in this context it should be noted that sulfate ion is known to have a strong retarding effect on hydration for limes and this may simply prevent CaCl₂ from having any

effect at these levels. However, it is clear that the NaHCO_3 does enhance the degree of carbonation, since the carbonation levels are close to those equivalent to conversion of the entire HCO_3^- ion to CaCO_3 . Such an observation is not altogether surprising since the presence of NaCl , and NaHCO_3 has been shown to be an effective strategy for carbonating serpentine minerals for instance [15].

Table 5, gives the results for high-level additions of Na_2SO_4 and CaCl_2 . Interestingly, there appears to be an effect on hydration at these higher levels of addition. High levels of sulphate do slightly retard the degree of hydration. However, the effects are somewhat marginal, especially when compared with the experiences with industrial lime and more importantly the timescale of the process is also dramatically different from hydration of limes, which normally are complete within seconds to minutes [16] whereas the effects we see appear to occur only after 10 minutes hydration time. Baker and Jordan's recommendations that:

“Water used in the slaking compartments should contain no more than 500 mg/l of a combination of sulfite, sulfate or bisulfate ions. Normally any service, industrial or municipal supply with less than 1000 mg/l total dissolved solids will be satisfactory”, are clearly too stringent for this type of ash. The best agreement with Baker and Jordan's work comes from tests with CaCl_2 , which indicates a small but definite promotion effect in terms of hydration rate using high concentrations of Cl ion. Initially we speculated that hydration might be somewhat better with seawater, where total salt concentration may be at levels of 35,000-mg/l. A more rapid hydration might be used to explain higher strength development seen in cubes of CFBC ash conditioned with seawater [17]. However, these results suggest the reverse that seawater may actually be retarding hydration rates. If this actually improves the strength developments, there are obviously better ways of achieving this retardation such as the use of alcohol or other organic compounds as we have discussed above. Finally, the addition of salts showed no effect on the atmospheric carbonation rate.

These results also suggest that any chemical agent that enhances Ca ion concentrations will accelerate hydration at least at longer times (minutes to hours). The data in Table 5 fit with the view that the first stage of the hydration process involves a rapid penetration and cracking of the sulphate shell (at least for limestones which sulphate in the unreacted core manner), and at higher temperatures complete particle fragmentation [11]. However, a much slower process in which overall solution chemistry becomes important then follows this process. This can involve other calcium compounds as we have suggested in other work [7,11], or sulphate ion migration as discussed by Scala et al, 2001 [18], or as we suggest here changes in the concentration of the Ca ion due to the presence of salts or alternatively some type of blocking of the crystallites by alcohol or other organic materials.

6. CONCLUSIONS

Test work on acetone to quench the hydration of CaO in FBC ashes, has shown that it is quite effective in slowing the hydration rate for periods of days. However, there is evidence that a heated sample regained its original levels of hydration, but thereafter showed only negligible increases in hydration levels, even in the presence of substantial quantities of water.

Quantitative hydration is relatively slow at ambient conditions taking many hours to occur. Bulk mixing of the solids and water, in the presence of substantial excess quantities of water and ambient conditions, also appears to be relatively unimportant in affecting the rate of the hydration reaction. This is consistent with the idea that the primary resistance to hydration is provided at the intra-particle and pore level. Finally, attempts to use salts to affect the hydration rate in a manner similar to that, which can be achieved with limes, failed to show

significant effect on the degree of hydration at low levels, but there appeared to be effects at high levels of addition of various salt, both positive and negative, moreover those affects persisted over minutes to hours. A general conclusion of this work is that while FBC ashes show many of the phenomena seen with lime hydration, there are nonetheless significant differences between the two materials, and that experience gained with lime hydration should be used with caution when applied to FBC ash.

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Table 5. Hydration and Carbonation in the Presence of Dissolved Salts
 (% Ca(OH)₂ and % CaCO₃, as CaO equivalent, (wt. %))

Salt Solution	5 min		10 min		15 min		30 min hydration		1 h hydration		2 h hydration	
	Ca(OH) ₂	CaCO ₃	Ca(OH) ₂	CaCO ₃	Ca(OH) ₂	CaCO ₃	Ca(OH) ₂	CaCO ₃	Ca(OH) ₂	CaCO ₃	Ca(OH) ₂	CaCO ₃
D.I. water	5.1	0.19	5.8	0.32	6.7	0.61	7.2	0.70	9.8	0.63	12.0	0.58
			5.0	0.36					8.8	0.41		
			6.0	0.16					11.0	0.51		
			5.6	0.28					Ave: 9.9	Ave: 0.52		
Nova Scotia Sea Water	-	-	-	-	-	-	7.9	0.16	8.5	0.19	9.8	0.55
			-	-					9.2	0.30		
			-	-					8.8	0.34		
			-	-					8.8	0.28		
10g/L of CaCl ₂	5.2	0.13	6.5	0.28	7.2	0.32	10.5	0.47	12.5	0.51	12.6	0.55
			6.8	0.25					11.1	0.47		
			6.3	0.21					10.5	0.45		
			6.5	0.25					Ave: 11.4	Ave: 0.48		
10g/L of Na ₂ SO ₄	5.1	0.29	5.3	0.29	5.5	0.31	7.7	0.30	7.9	0.38	9.8	0.39
			6.3	0.22					8.2	0.34		
			6.7	0.31					8.5	0.36		
			Ave. 6.1	Ave. 0.27					Ave: 8.2	Ave: 0.36		