The Carbonation of FBC Ashes

By E.J. Anthony[1] and Lufei Jia
Research Scientists
CETC, Natural Resources Canada
1 Haanel Drive, Nepean, Ontario, Canada, K1A 1 M1
[1]banthony@nrcan.gc.ca

ABSTRACT
FBC ashes from firing high-sulphur fuels display exothermic behavior on wetting, cause deleterious expansion in the landfill, and produce high-pH leachate that must be treated. Currently, the ashes are slaked in a relatively ineffective and potentially hazardous two-stage wetting procedure. Sonic energy, in its low- and high frequency forms, is a highly effective method of hydrating these ashes. However, even upon hydration, FBC ashes still create expansion in the landfill site, and a high pH leachate. Carbonation would be a better route, but direct attempts at carbonating these ashes have been unsuccessful. By contrast sonic energy is effective in carbonating FBC ashes. If CO_2 from flue gases is injected into the chamber where the FBC ashes are being sonically hydrated, then near-quantitative carbonation of FBC ashes in minutes is possible.

1.   INTRODUCTION

Circulating fluidized bed combustion (CFBC) boilers burning high-sulphur coal discharge an ash which can contain up to 20-30% free lime, $CaSO_4$ and other fuel ash-derived products. Typically, the solids are first conditioned with water in a pug mill, in order to hydrate unreacted quicklime in the residue, and then treated with water at the disposal site to complete the hydration process and achieve the optimum density (EC 1992). This is accompanied with an unconfined powerful exothermic reaction which can, in principle, pose a safety hazard (materials reach temperatures in excess of 100ºC) (Anthony 1999). The hydration reaction is also inherently slow, continuing in the landfill. Water losses due to steam of the order of 27% have been noted, for instance, with the Nova Scotia Power Inc. (NSPI) Point Aconi plant ashes.

An improved hydration method is highly desirable, and while there are alternatives such as the CERCHAR process (Khan 1994; Anthony 1997a), no commercially effective technology appears to exist. In an effort to develop an alternative technology, CETC investigated the use of power ultrasound and found that it was potentially highly effective as a hydration technology (Anthony 1996). Further, a commercially available grinding technology owned by Arc Sonics Inc. using low frequency sound (1-500 Hz), was demonstrated as being equally or more effective (Anthony 1998). This technology exists at a scale suitable for dealing with the very large quantity of ashes produced by plants such as NSPI's 165 MWe CFBC (e.g., 1000 t/day).

In the process of investigating the use of sonic energy to enhance hydration it was recognized that it might also be used to carbonate FBC ashes. Carbonation would eliminate the secondary reactions that lead to deleterious expansion in the landfill, the high pH of leachate and the exothermicity of the ashes.

1.1   FBC Ash Chemistry

Direct carbonation of FBC ashes is not possible below about 400ºC, unless the CaO first reacts with H_2O (Anthony 2000). Further, dry $Ca(OH)_2$ reacts more slowly with CO_2 than does "wet" $Ca(OH)_2$. It is also apparent that, when liquid water is present, Ca silicates, ferrites and aluminates (other calcium compounds or OCCs) which are also formed in a FBC may carbonate too. In the case of NSPI ashes, this may provide up to about 40% more "CaO" to the system. Ultimately, FBC ashes in the landfill carbonate, albeit over extended periods (months to years) (Anthony 1997b; Anthony 1997c). Therefore, short of performing the carbonation step at very high pressure, direct reaction of FBC ashes in water appears to be the most promising low-cost strategy for carbonating FBC ashes. A successful carbonation strategy would also reduce overall CO_2 production by a few percent and produce a material with minimal leaching problems.

2.   EXPERIMENTAL

This work has been carried out with ashes from the two 100 MWe CFBCs owned by the Nelson Industrial Steam Company (NISCO) in Louisiana and the Point Aconi 165 MWe CFBC owned and operated by NSPI. The NISCO boilers burn petroleum coke and the NSPI boiler burns a high-sulphur bituminous coal (Devco Prince.). These two ashes will henceforth be designated as NISCO and NSPI for convenience. Particles were sieved to maintain a size of <1.4 mm. and analysis results indicated that they contained 20.9 and 14.2% CaO content respectively.

For the ultrasonic work done here, the ash-liquid slurry is subjected to sonic energy (sonification) via an ultrasonic probe (Sonics and Materials, VCX 6000, frequency 20 kHz) immersed in the slurry. Carbon dioxide is bubbled through the slurry during the sonification tests. A more complete description of the apparatus can be found elsewhere (Anthony 1996). The low-frequency sonification experiments presented are also described elsewhere (Anthony 1998), but since the results are crucial to this paper, brief descriptions of the test apparatus and protocol are given here. The tests were done with a 75 kW horizontal sonicator on which was mounted a 3 dm^3 reaction chamber. The cylindrical stainless steel chamber is about 150 mm in diameter, and 190 mm in length. On the chamber faceplate there are gas inlet and outlet connections, a sampling valve and a thermocouple adapter. The chamber is also fitted with a jacket for throughput of a cooling or heating fluid, which is used to control the reaction temperature if required. The operational frequency for these tests was 105 Hz, and the apparatus is capable of operating over a range of 100-500 Hz (for comparison typical ultrasound frequencies are in the range of 20-40 kHz).

3.   RESULTS

Earlier work showed that ultrasonic energy could enhance the hydration rate of FBC bed ash, with conversions of up to 80% of the CaO to $Ca(OH)_2$ in periods as short as 20

minutes, which is equivalent to the level of conversion that might be produced by boiling water for a similar period of time (Anthony 1996). Unfortunately, it did not appear to be possible to provide equipment suitable for dealing with 600 to 1000 t/d of ash, necessary for an industrial scale CFBC boiler.

Initial carbonation tests were carried out at ambient temperature using slurries of about 20 g in 100 mL of water. These were subjected to carbonation with and without sonification. These preliminary results (Table 1) showed that, although sonification does enhance the rate of carbonation with natural CO_2 in air, it is still extremely slow. Also, sonification enhances the rate of conversion over direct carbonation of bed ash, when CO_2 is bubbled through the reactor. Finally, it is clear that NISCO ash carbonates more easily than NSPI ash, but with high enough amplitude[1] (i.e., sonic energy level), it is possible to quantitatively convert the CaO in NSPI ash to $CaCO_3$.

3.1   The Use of Low-Frequency Sound Energy

The problem with scale-up appeared to be resolved by technology, owned by Arc Sonics Ltd., which used low frequency sound energy (100-500 Hz) to grind and/or to react solids in a liquid phase. The equipment was already available at a size that would allow several hundred t/day of ash to be processed. A series of trials was carried out by CETC to determine whether this technology could be used to hydrate and carbonate, and the key results are given below. Initially, six tests were carried out. Two tests had 1 dm^3 of 3/8" Al balls added to the test chamber to promote grinding during the reaction process, and for a few tests CO_2 was added at a nominal 14 dm^3/min rate and the samples were subjected to a nominal 1 min reaction time.

These results are presented in Tables 2-4. The results demonstrate that low-frequency sound can enhance hydration, as well as, or better than ultrasound. It is also clear that, at least for short residence times, the conversion of bed ash to $CaCO_3$ is low unless a grinding medium is present. This suggests that the carbonation occurs as a result of the natural or autogenous grinding due to the sonic energy.

Further tests were carried out for longer periods, up to 10 minutes (Table 3). For bed ash, even at 5 minutes, there is relatively little conversion of CaO to $CaCO_3$, although there is a high conversion to $Ca(OH)_2$. However, in the case where grinding media have been added there is an almost linear relationship between the degree of reaction and reaction time (Fig. 1). As grinding is approximately linear with time, it appears that the degree of conversion of bed material over short times is due to the degree of grinding produced by the Arc Sonics equipment. Fly ash by contrast reacts more readily with CO_2 (Table 4). By 5 minutes almost quantitative conversion of the CaO occurs with NSPI fly ash.

However, the results for 1 to 4 minutes, are somewhat surprising, as they seem to show a jump in the carbonation at 5 minutes. One possibility is that the amount of CO_2 is defining the carbonation rate, since calculations show that at 14 dm^3/min, only 20% of

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[1] It should be noted that amplitude corresponds to the amount of sonic energy, and higher amplitude is equivalent to using more sonic energy.

the free lime in the fly ash could be carbonated in a one-minute test. It is evident that the sample is seeing more CO_2 than indicated by the information on CO_2 flow rates from these tests. However, the fact that there is no regular change in the degree of conversion for tests done from 1 to 4 minutes, does not fit with the idea of insufficient access to CO_2 and, instead, suggests an induction period.

It was decided to investigate this effect in more detail, but because of the expense of "large-scale" tests with Arc Sonics equipment, no further low frequency work was carried out. Instead, the tests were done with ultrasound, which also conferred the advantage that the samples were collected and analyzed within a day or less of the tests. For these tests, NSPI fly ash collected on June 11, 1996, was used. The tests were carried out in a 250 mL beaker with 30 g fly ash in 130 g water, except for those tests which were only 1 min in duration, for which only 10 g of fly ash was used in 130 g of water. Tests were done both with and without ultrasound to allow comparison of the rate of carbonation, but only one amplitude was used (50%). The complete fly ash test results are shown in Table 5. The minimum flow rate of 2.5 dm^3/min is sufficient to provide the stoichiometric CO_2 requirement to completely carbonate the ash within one minute.

These results demonstrate that a very high degree of conversion can be achieved by carbonation, especially at longer times. It is also clear that other factors are important, such as, for instance, the solid/water ratio, which influences the conversion strongly. It appears that the degree of conversion at 1 minute with a water-to-solid ratio of 13 is comparable to the results of sonification at 5 minutes. The most likely explanation of this observation is that the water/solids ratio influences the pH. It should be noted here that the solubilities of $Ca(OH)_2$ and $CaSO_4$ are of the order of 0.2 g/100 mL of water, and fall off with temperature, so that the solubility of these species is unlikely to determine the degree of conversion

A comparison of carbonation with and without sonification is interesting (i.e., at 50% and 0% amplitude respectively). At long reaction times for fly ash, high degrees of carbonation can be achieved by direct carbonation. At shorter times (3-4 minutes), there is an effect of sonic energy. Evidently, variations in CO_2 availability do not make a large difference in the degree of carbonation, as seen from the data for 3 and 4 minutes. This work indicates that, at longer periods of time (>5 min), the degree of conversion with and without power ultrasound is almost identical. However, at shorter times it seems clear there are differences between carbonation with and without ultrasound. The overall conclusion is, therefore, that both ultrasound and low-frequency sound promote carbonation of larger particles (greater than 100 μm) by promoting size reduction either by autogenous or self-grinding, or, as in the case of Arc Sonics equipment, by using grinding media. In the case of fine particles like fly ash, the rate of carbonation is very fast and depends on factors such as the solid/water ratio and, by inference, pH.

A final set of tests was carried out (Table 6) with NSPI bed ash (<1.0 mm size fraction). For this test series, 30 g of ash was added to 130 g of water in all but the 1 minute run which used 10 g of ash in 130 g of water. The CO_2 flow rate was about 3 dm^3/min. One test was carried out with cooling since, without cooling, ultrasound will heat the

water/ash mixture to about 65ºC in 10 minutes. During the test (BA-3), temperature of the ash/water mix was maintained at 18-21ºC at all times. BA-0 is not a test but represents the original composition of the bed ash used in this test. Test BA-1 was run without sonification and shows that without the effect of sonic energy, the degree of conversion to $CaCO_3$ is essentially negligible in the presence of a stream of CO_2.

These results clearly show that fly ash behaves quite differently from bed ash, and this is further evidence that the grinding action of sonic energy on bed ash is a key factor in converting CaO to $CaCO_3$. By thirty minutes effectively complete conversion has been achieved for bed ash with the use of ultrasound, and a visual inspection of the samples also shows that the ash has been reduced to a fine powder[2]. Although the conversions are higher, these results are essentially the same as those shown in Table 3. Cooling should both enhance the degree of sonification (by reducing the vapor pressure of water), and increase the solubility of CO_2 in water, but it will reduce the chemical reaction rate. The fact that there is such a large difference between the two results (BA-3 and BA-4) indicates that the chemical rate is the dominating factor. This is a positive feature for the development of any industrial process, as it indicates that less effort needs to be devoted to removing the heat produced by sonification, and the heat generated in the processes of hydration and carbonation reactions.

4.   CONCLUSIONS

This work has shown that both power ultrasound and low-frequency sound energy can be used to significantly enhance the rate of hydration. While carbonation must be preceded by hydration, the situation is somewhat more complicated. The major conclusions of this work can be listed as follows:

Natural carbonation such as produced by the interaction of CO_2 in the air with FBC ashes in the presence of water, is relatively slow, and is not an important factor here. For larger particles (greater than 100 µm) such as those typical of the bed material, both low-frequency sound energy and ultrasound can promote carbonation in the presence of a stream of CO_2. However, it seems that it does this by grinding, either self-grinding promoted due to the direct effect of the action of the sonic energy, or as in the case of the Arc Sonics equipment, by the addition of grinding media.

For small particles (less than 100 µm), the natural carbonation rate in the presence of a stream of CO_2 is very fast, and influenced by factors such as water/solids ratio. Nonetheless, there is an effect of sonic energy at shorter times. This work also seems to rule out any initiation period, as was initially suggested by data from the work done for CETC by Arc Sonics, that might be a barrier to achieving high conversions at short periods of time. These results clearly indicate that sonic energy (both high- and low-frequency) promotes carbonation of the whole particle size range of FBC ash and this approach has been patented by CETC for both hydration and carbonation.

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[2] A size analysis of this material has not been performed because it tends to adhere and clump, presumably in part due to the cementitious reactions associated with FBC ash.

5.   ACKNOWLEDGMENTS

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Table 1 - Carbonation of NISCO and NSPI bed ashes with ultrasonic energy.

Sample	Experiment	Time (min)	CO_2 flow rate (dm^3/min)	Amplitude (%)	% CaO converted to $CaCO_3$
NISCO 1	Carbonation	60	0.8	0	77.4
NISCO 2	Carbonation & sonification	60	0.8	70	95.6
NSPI 1	Carbonation & sonification	20	0.3	80	47.8
NSPI 2	Sonification	40	0	80	4.8
NSPI 3	Carbonation & sonification	60	0.8	100	90.3
NSPI 4	Carbonation & sonification	40	0.8	70	53.2

Table 2 - Test results for 1-min sonification trials on NSPI ash using low-frequency sound.

Test No	Ash	CO_2 added	Grinding	% Conversion to $Ca(OH)_2$	% Conversion to $CaCO_3$
CMA1	Bed	No	No	87.9	5.8
CMA2	Bed	No	Yes	86.8	6.3
CMA3	Fly ash	No	No	67	23
CMA4	Bed	Yes	No	88.5	8.0
CMA5	Bed	Yes	Yes	58.5	34.4
CMA6	Fly ash	Yes	No	46.5	41.8

Table 3 - Test results for sonification with NSPI bed ash using low-frequency sound.

Test No	Time (min)	CO_2 added	Grinding	% Conversion to $Ca(OH)_2$	% Conversion to $CaCO_3$
CMA7	5	No	No	89.8	4.1
CMA8	1	Yes	No	88.4	5.8
CMA9	5	Yes	No	87.9	6.6
CMA17	5	Yes	No	69.4	10.4
CMA18	5	Yes	Yes	37.6	59.8
CMA19	10	Yes	Yes	0.0	96.9
CMA20	5	Yes	No	75.7	10.4

Table 4 - % Conversion of fly ash CaO to $Ca(OH)_2$ and $CaCO_3$ using CO_2 with low-frequency sound.

Test No.	Time (min)	% $Ca(OH)_2$	% $CaCO_3$
CMA6	1	46.5	41.8
CMA10	1	42.5	37.8
CMA11	5	5.2	82.5
CMA12	1	47.0	45.9
CMA13	2	55.9	36.7
CMA14	3	50.5	42.3
CMA15	4	48.3	47.5
CMA16	5	11.6	89.0

Table 5 - The effect of ultrasound and carbonation on NSPI fly ash.

No.	Time, min	Power, %	CO_2, L/min	$Ca(OH)_2$ as CaO,%	$CaCO_3$ as CaO, %	FL, %	CaO, %	Total CaO, %
USF1	15	50	2.5	0	17.5	0.9	0.9	18.4
USF2	5	50	2.5	2	14.4	3.1	1.1	17.5
USF3	15	0	2.5	0	17	1.8	1.8	18.8
USF4	4	50	2.5	1.8	15.5	2.9	1.1	18.4
USF5	4	50	2.5	0	16.6	1.6	1.6	18.2
USF6	3	50	3	2.2	15.3	3.6	1.4	18.9
USF8	4	0	3.5	3.4	13.4	5.4	2	18.8
USF9	3	0	3.5	4	12.8	6.3	2.3	19.1
USF10-1	4	50	2.5	0	15.4	1.6	1.6	17
USF10-2	4	50	2.5	0	15.8	2.8	2.8	18.6
USF11-1	5	50	2.5	0	16.3	2.2	2.2	18.5
USF11-2	5	50	2.5	0	16.9	2	2	18.9
USF12-1	3	50	3.5	2.8	14.7	5.4	2.6	20.1
USF12-2	3	50	3.5	3.1	15.1	4.3	1.2	19.4
USF13-1	1	50	3.5	0	16.9	1.5	1.5	18.4
USF13-2	1	50	3.5	1.5	16.4	2.5	1	18.9
USF14-1	5	0	2.5	0	16.5	2.4	2.4	18.9
							Average	18.64
							Std. Dev.	0.69

Table 6 - NSPI bed ash conversion to $Ca(OH)_2$ and $CaCO_3$ expressed as wt.% CaO.

Test No.	time, min	Amplitude, %	CaO	$Ca(OH)_2$	$CaCO_3$	Total
BA-0	0	0	17.1	4.2	0.5	21.8
BA-1	15	0	6.6	10.2	2.2	19.0
BA-2	30	50	0.7	1.1	17.4	19.2
BA-3	15	50	8.7	6.8	3.2	18.7
BA-4	15	50	3.6	8.4	9.3	21.3
BA-5	5	50	6.2	7.4	5.6	19.2
BA-6	5	50	8.0	6.7	4.3	19.0
BA-7	3	50	6.1	8.7	1.7	16.5
BA-8	3	50	5.6	8.0	3.6	16.2
BA-9	1	50	8.4	5.8	1.3	15.5
BA-10	30	0	6.2	10.5	2.0	18.7
BA-11	15	50	3.8	10.9	4.2	18.9

Fig. 1 Conversion of CaO to $Ca(OH)_2$ and $CaCO_3$