PERGAMON

Waste Management 20 (2000) 1–13

WASTE
MANAGEMENT

www.elsevier.nl/locate/wasman

Pacification of high calcic residues using carbon dioxide

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Accepted 22 September 1999

Abstract

The development of an alternative to hydration for the treatment and/or disposal of FBC ash was investigated. Carbonation (pacification) of the ashes was the option examined. The process is rapid at FBC operating conditions for dry ashes, but does not proceed below 400°C. Hydration of the ashes promotes the carbonation reaction below this temperature. Rapid carbonation of hydrated ashes occurs at 200–230°C. Carbonation will occur at ambient conditions for hydrated ashes, although the reaction is extremely slow. An unexpected finding in this research was that CaO, combined in the form of silicates, ferrites and aluminates (OCCs), also react with CO_2. Specifically, OCCs, which are formed by reaction of the CaO in the sorbent and the fuel ash components, react with CO_2 if the ashes are fully hydrated and liquid water is present. This has an impact on the disposal of FBC ash, as the reaction with CO_2 will continue after placement in a disposal area. Control of the reaction would be advantageous in stabilization of the FBC ash. An effective limit to conversion of the free lime to carbonate, in the range of 60–70% was observed for the ash. The work showed the type of limestone is an important factor in the success of the recarbonation. Dolomitic limestone, a more porous sorbent, should have greater conversion rates, making the process more economic. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Fluidized bed combustion (FBC) is an environmentally accepted method of controlling the release of sulphur from coal to the atmosphere. Limestone is injected into the FBC for in situ capture of SO_2. The limestone is converted to sulphate through a two-step process:

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H = +182.1\,\mathrm{kJ/mol} \tag{1}$$

and

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \quad \Delta H = -481.4\,\mathrm{kJ/mol} \tag{2}$$

Calcination of the limestone [reaction (1)] proceeds to completion, while sulphation of the lime [reaction (2)] is about 30–45% complete in FBC. The resulting ash thus contains significant quantities of CaO, sometimes up to 30%. Generally ash content and composition of the fuel limit this to 10–20%. The calcic nature of the ash has required extensive research into safe disposal practices.

Initial hydration of the ash raises health and safety issues if it is not properly managed. The high lime content of the ash results in highly exothermic behaviour when the ash is hydrated with water [1], and temperatures in excess of 100°C have been recorded when the ash is hydrated. The hydration process involves only the free lime portion of the ash:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad \Delta H = -65.27\,\mathrm{kJ/mole} \tag{3}$$

and not the anhydrite component:

$$CaSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \quad \Delta H = -17.20\,\mathrm{kJ/mol} \tag{4}$$

Landfill sites for FBC ashes have potential for high pH runoff or leachate (pH of 12–13) requiring treatment [2]. Changes at the site occur through excessive expansion, poor freeze/thaw characteristics of the ash and loss of compressive strength. An initial low permeability of 10^{-7} cm/s increases over months and years as the

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PII: S0956-053X(99)00305-0

materials expand and crack to 10^{-4} and 10^{-3} cm/s, more typical of a sandy soil. Unconfined compressive strengths decrease from 2–7 MPa to as low as 100 kPa in less than two years [3]. As these changes occur, expensive processing is required to keep swelling/cracking and other problems from leading either to penetration of the lining used in the landfill, or the production of excessive quantities of high pH leachates. Development of a treatment technique, which would minimize the troublesome characteristics of the FBC ash, was the goal of this work.

1.1. Hydration techniques

Currently Environment Canada recommends a two-step hydration method using a pug mill for the conditioning of FBC ash [4]. The ash is hydrated prior to discharge from the unit to reduce its exothermicity. After transportation to the landfill site, a second application of water aids in placement and compaction of the ash.

The CERCHAR process [5–7] was developed to address the exothermic nature of the hydration reaction. The spent solids are wetted at atmospheric pressure while being continuously mixed in a pressure vessel. Additional water is added to just over the stoichiometric amount required for the hydration of CaO and the pressure rises to just over 1 MPa. The conversion of CaO to $Ca(OH)_2$ occurs at temperatures in excess of 100°C, preventing the formation of ettringite. The hot solids are discharged dry. The benefits of this process include a reduction in expansion of the ash at the landfill site [5–6] and control of the exothermic reaction of the hydration of CaO. Unfortunately high pH leachate and freeze/thaw degradation [7] of the ash are still an issue.

1.2. Alternative pacification concept

Development of a technique for treating the ashes without using water or at least minimizing the amount consumed would be beneficial. The use of CO_2 contained in flue gases to convert the quicklime back to $CaCO_3$, the reverse of reaction 1, was proposed. This concept will be termed pacification.

A preliminary economic and technical feasibility study was carried out, indicating that, depending on the conditions necessary to ensure quantitative recarbonation, a pacification device for a 183 MWe circulating FBC (CFBC) unit burning high sulphur coal would be feasible. The key issue is the conditions required to make the recarbonation process rapid and effectively quantitative at near ambient conditions, since the higher the temperature/pressure or longer the reaction time, the less economically attractive any such process would become.

There is evidence that ashes from pressurized FBC (PFBC) have superior disposal characteristics [8–10]. In PFBC the fuel is burned at pressures varying from 1 to 2 MPa [8], and the partial pressure of the CO_2 is greater than that for calcination at typical combustion temperatures (800–950°C). As a result free lime is never formed and the sulphation process proceeds through the overall reaction:

$$CaCO_3 + SO_2 + \frac{1}{2}O_2 = CaSO_4 + CO_2 \tag{5}$$

The solids discharged consist primarily of fuel-derived ash, $CaCO_3$ and $CaSO_4$. Ca silicates, ferrites and aluminates formed during the FBC combustion process may also exist, although there is only limited evidence for the formation of these compounds in PFBC ashes at present [11]. The solids discharged from full-scale units appear to contain very little free lime ($<1\%$) and the pH of leachates from these solids is much less alkaline with values down to 9.5–10 [8–9].

It is possible that carbonation might be associated with the formation of thaumasite [$Ca_3Si(OH)_6(SO_4)(CO_3)\cdot 12H_2O$]; however, the authors did not detect evidence for its formation in any of the CFBC residues studied. It would have a decomposition peak at temperatures above 110°C [12]. This was not seen in any of the thermogravimetric analysis (TGA) work carried out on recarbonated samples.

When wetted, PFBC solids show self-hardening properties. This is presumably due primarily to the formation of gypsum. For the compacted residues the permeability has been reported as low as 10^{-7} cm/s, and strength developments over a year of up to 18 MPa can be achieved [8,9]. In principle, if circulating and bubbling FBC solid residues could be quantitatively recarbonated so as to mimic the chemical characteristics of PFBC ashes, a considerable improvement in disposal properties over either conventionally hydrated ashes or CERCHAR treated ashes would be achieved. The only possible disadvantage would be for applications where the free lime content was desirable.

1.3. Thermodynamics and kinetics of recarbonation

The recarbonation reaction must proceed fast enough to give quantitative or near quantitative conversions over short periods of time (<1 h), a practical condition for a commercial process. The partial pressure of CO_2 over limestone can be calculated, over the temperature range of 700–900°C, from an expression developed by Hill [13]:

$$\ln(P_{CO_2}) = -19680/T + 21.337 \tag{6}$$

where T is in K and P is in kPa. From this equation it can be seen for a typical partial pressure of CO_2 in flue gases (15 kPa), recarbonation is thermodynamically favoured at temperatures of 780°C or below.

A typical ash cooler will produce solids at a temperature of 160–200°C. However, if the reverse reaction goes to completion, a considerable amount of heat energy will be released (−182.1 kJ/mol compared with −65.27 kJ/mol for the hydration reaction, i.e. reaction (3)). This heat of reaction must be taken into account. Assuming a mean specific heat capacity of ash of 1000 J/kg/K, for ash containing 20% free CaO a maximum temperature up to 525°C could be reached if the recarbonation process occurs via reaction (7) and not (8). Therefore, on equilibrium grounds, the partial pressure of CO_2 in the flue gases will be more than sufficient to drive the recarbonation reaction at typical solids discharge temperatures.

$$CaO + CO_2 = CaCO_3 \tag{7}$$

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O \tag{8}$$

The limitations of the process are, therefore, mass transfer and kinetic and not thermodynamic. In a study on carbonate decomposition at atmospheric pressure and elevated temperatures, Hills showed the reaction was not chemically controlled. Instead the rate-limiting step was determined by both the heat transfer rate and mass transfer of CO_2 away from the interface at which limestone decomposition takes place upon calcination [14]. For the reverse reaction at or near ambient conditions, the major concerns are whether the chemical rate is fast enough to achieve quantitative recarbonation in a short period of time (< 1 h) and whether pore plugging will effectively terminate the transfer of CO_2 into the particles. This arises because $CaCO_3$ has a higher molar volume than does CaO (37 cm^3/gmol compared with 17 cm^3/gmol).

The recarbonation process at FBC temperatures is significantly faster than the sulphation process [15]. Under conditions of the simultaneous sulphation and recarbonation experiments, i.e. at 850°C and pressures of 0.8–2 MPa, 60% conversion of the CaO to $CaCO_3$ occurred within the first 5 min, compared with only 5% conversion to $CaSO_4$. Little or no research on carbonation or recarbonation at low temperatures has been performed. That the CERCHAR process can proceed quantitatively at temperatures below 200°C and pressures less than 1 MPa (albeit the molar volume of $Ca(OH)_2$ (33 cm^3/gmol) is less than that of $CaCO_3$), suggests a practical recarbonation process might be feasible. Researchers at Niigata University [16] have also been independently investigating the possibility of using the carbonation/recarbonation reactions as a method of removing CO_2 from power plant flue gases. The main difference from the present study is that their recarbonation process step was to be carried out at 600°C. As their primary aim is to remove and concentrate CO_2 for disposal, there is no need to achieve the quantitative recarbonation levels of the limestone sorbent which are essential to the development of an alternative to the hydration of FBC residues.

2. Ash sources

Three different ashes were used in this work. Ashes from the 183 MWe Point Aconi CFBC unit owned and operated by Nova Scotia Power Incorporated and from the CANMET 0.8 MWt CFBC pilot plant in Canada, were both produced from Devco Prince coal and Calpo limestone. Also used were ashes from the two 100 MWe CFBC boilers burning petroleum coke, owned and operated by the Nelson Industrial Steam Company Ltd (NISCO), Louisiana.

Chemical analysis of the Point Aconi, CANMET and NISCO ashes was performed in order to determine the Ca speciation of the samples. Free lime was determined directly rather than through back calculation. This also allowed the assessment of CaO combined in "other calcium compounds" (OCCs), i.e. ferrites, aluminates, silico-aluminates, etc. [17]. These data are given in Table 1.

The $Ca(OH)_2$ and $CaCO_3$ contents of both the Point Aconi and CANMET ashes were determined (Table 1). In all, three determinations were carried out for the Point Aconi bed ash and four for the CANMET bed ash. The results suggest that both ashes contain only a very small amount of portlandite and $CaCO_3$, with the CANMET bed ash containing more of both species. This is reasonable given it was approximately 4 years old compared with only a few months for the Point Aconi bed ash, during the period these trials were carried out. This also introduces a 1 or 2% potential error into the calculations unless the initial portlandite and carbonate concentrations in the ashes are taken into account.

3. Experimental procedures

There were three sets of apparatus used in the experiment. They have different operating conditions allowing

Table 1
Ca speciation of the FBC bed ashes (wt%)

	Point Aconi	CANMET PC2	NISCO
CaO	14.9	17.6	20.0
$CaSO_4$	38.6	18.0	59.3
$CaCO_3$	1.35 ± 0.05 0.4[a], 2.1[b]	2.00 ± 0.57 1.0[b]	2.2[b], 3.3[b]
$Ca(OH)_2$	1.56 ± 0.06; 2.0[a]	3.77 ± 0.23	
OCC[c]	6.6	2.0	8–9

[a] Determined by TGA.
[b] Determined by chemical analysis.
[c] Expressed as CaO.

coverage of the full range for a practical recarbonation process.

The glass autoclave (50 cm^3, constructed by Autoclave Engineers Ltd., UK) can operate at temperatures of up to 150°C and pressures of up to 1 MPa, Fig. 1. The Parr autoclave, also known as the Parr bomb, is a 2 dm^3 stainless steel autoclave. It can operate at temperatures of up to 300°C and pressures of up to 10 MPa. The pressurized Cahn 1100 Thermogravimetric Analyzer (PTGA) is able to operate at pressures of up to 2 MPa and temperatures of up to 1000°C.

Test work with the glass autoclave was initially done at two temperatures, 50 and 75°C and subsequently always at 75°C. The glass autoclave temperature was maintained to within 3°C by a Glas-Col 400 W heating mantle. Typically about 10 g of ash was weighed out and introduced into the autoclave. Then, if the sample was to be hydrated, about 2 cm^3 of water was added and mixed using a metallic scoop. The autoclave was sealed and placed in the heating mantle. Throughout the test series only unfiltered deionized water was used. The sample was then hydrated either for 3 h or for a longer period. In a number of cases tests were performed with dried hydrated samples, as the goal was to examine the influence of water in the liquid state. After hydration, the samples were dried at 110°C overnight. Initially the sample was dried to constant weight, followed by two or more drying periods. This procedure demonstrated that it was sufficient to dry the samples overnight.

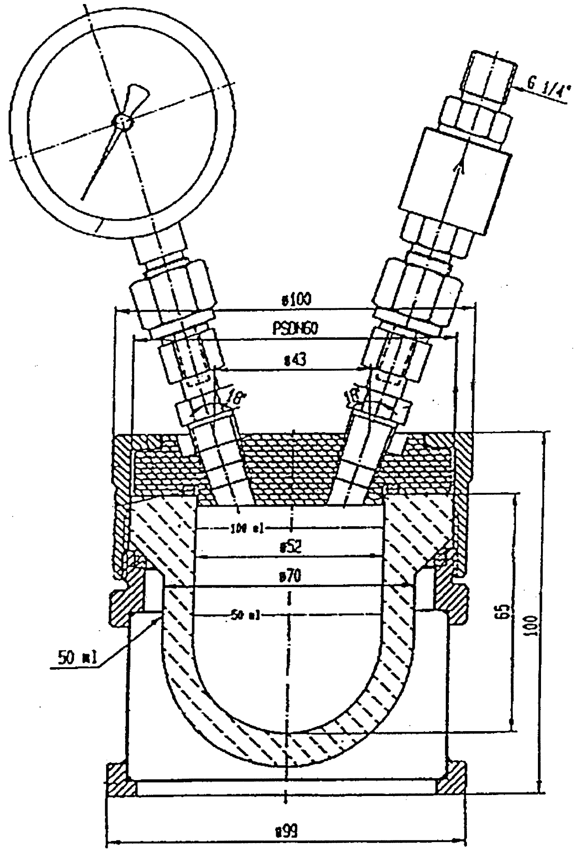

Fig. 1. Glass autoclave.

The choice of hydration temperature was made with two considerations in mind. It had to be high enough to ensure complete hydration of CaO and at the same time preventing the formation of hemihydrate ($CaSO_4.1/2H_2O$), gypsum ($CaSO_4.2H_2O$) and ettringite. A number of TGA results were examined for the formation of ettringite, thaumasite and $CaSO_4$ hydrates (i.e. hemihydrate and gypsum). These have decomposition temperatures of 50–100°C (ettringite), 110°C (thaumasite) [12] and about 140–160°C (hemihydrate and gypsum) [18]. On thermodynamic grounds both hemihydrate and gypsum should not be formed at temperatures above 50°C [19], and in fact no TGA evidence was found of the formation of any of these compounds during this study. A typical TGA measurement was shown in Fig. 2.

Both the hydration and drying procedures were verified using Point Aconi bed ash by performing a series of experiments in which 10 g of sample was added to a weighed crucible and weighed. Water (2 cm^3) was added and the crucibles were placed in an oven at 110°C. Seven samples were prepared and left in the oven for 1, 2, 4, 6, 8 and 24 h. After the drying period was complete they were removed and cooled in a desiccator for 15 min, and weighed. These samples were again placed in the oven for 24 h at 110°C, and subsequently cooled and weighed again. In all cases, after 2 h or more of drying the samples showed an effectively constant weight increase of $4.24 \pm 0.20\%$. This corresponds to a free lime content of 13.2%. When the $Ca(OH)_2$ originally present in the Point Aconi ash is taken into account, this gives a value of the free lime in these samples of 14.4%, which is very close to the chemical determination of CaO in

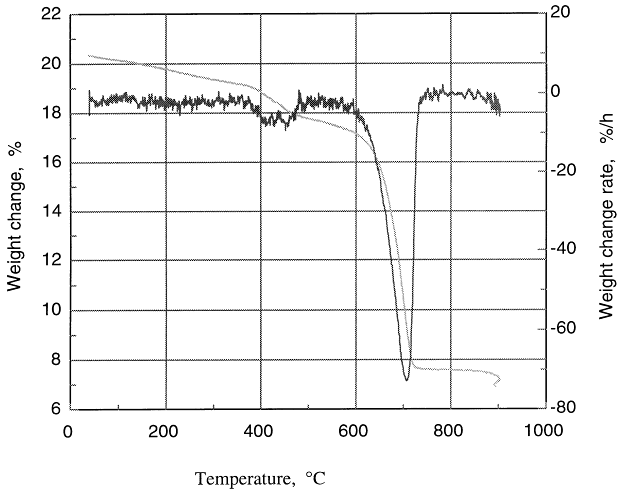

Fig. 2. Point Aconi bed ash, hydrated at 75°C for 3 h, pacified at 75°C for 2 weeks.

Point Aconi bed ash of 14.9%. Three tests were carried out in which samples were dried for 2 h and then 70 h at 110°C. Again there was no significant difference in weight between the samples.

Couturier et al. [19] suggested that micropores become closed due to the molar expansion caused by $Ca(OH)_2$, and may trap significant amounts of water in hydrated CFBC residues. Subsequent mercury and nitrogen porosimetric measurements have shown that, for Point Aconi bed ash at least, micropores are effectively absent in both the unhydrated and hydrated ashes. This was a concern initially because weight differences are critical to the determination of conversions to the chemical species of interest, $Ca(OH)_2$ and $CaCO_3$.

After hydration was complete, the autoclave was pressurized with CO_2. The flow of gas was adjusted to 0.11 dm^3/min for a minimum of 5 min to ensure the displacement of air in the glass autoclave. For longer runs where an appreciable amount of the CO_2 reacted with the sample, the vessel was periodically repressurized with CO_2 to maintain a pressure of 1 MPa. At the end of the pacification time the sample was removed and placed in a weighed crucible. It was dried in an oven at 110°C overnight, cooled in a desiccator for 30 min, and weighed. The sample was then placed in an oven at 550°C for 2.5 h in order to decompose the $Ca(OH)_2$. After being cooled in a desiccator for 30 min, and weighed, the sample was ashed at 800°C for 2.5 h to decompose the $CaCO_3$. A final cool down in a desiccator and weighing were performed.

A 500 g sample was used with the larger Parr autoclave. This was first placed in the autoclave, and 0.1 dm^3 of deionized water was added. The ash and water mix was stirred with a steel rod then the autoclave was sealed and placed in the heating unit. The temperature was set and the sample was heated for 3 h. Once the hydration period was over, the final temperature was set for the test, and CO_2 introduced into the autoclave. The pressure vessel was flushed at approximately 2 dm^3/min for at least 5 min, to ensure air in the Parr autoclave was eliminated. Initially the pressure was adjusted to one-half to three-quarters of the final desired pressure to allow for the appropriate expansion of the gases. The pressure was adjusted as the temperature reached its final level in order to obtain the desired value. At the end of the pacification period, the sample was removed and dried. As before, 10 g of sample was placed in a weighed crucible and ashed and weighed as described above. Triplicate samples were ashed and used for $Ca(OH)_2$ and $CaCO_3$ determinations.

Kinetic limits for both the unhydrated and hydrated FBC solids were studied using the PTGA. The samples were first screened to less than 1.4 mm. The residues were either tested "as is" or after hydration. For hydrated solids, the hydration step was carried out with excess water (approximately 5 times the stoichiometric requirement) at room temperature for 5 days and the samples were then dried at 110°C.

For the atmospheric pressure tests, the PTGA was flushed with pure CO_2 at 0.120 dm^3/min for 30 min before the test started. In pressurized tests, after first flushing the apparatus with CO_2, the PTGA was pressurized to 1.1 MPa before the heating furnace was turned on. The heating rate for all tests was 7°C/min. As high pressure affects TGA readings, a run was carried out with silica sand, as an "inert" under the same conditions as the tests with the CFBC residues. The recarbonation test results were then corrected following the procedures developed by Brown et al. [20].

The CaO content was determined for each batch of ash used. A 10–20 g sub-sample of the ash was placed in an Erlenmeyer flask with twice the weight of deionized water. The sample was boiled for 2–2.5 h, filtered and dried overnight at 110°C. The sample was ashed at 550°C for 2.5 h and the weight difference used to calculate the amount of CaO.

4. Results and discussion

4.1. Pore structure of Point Aconi bed ash

A Quantachrome Autosorb automated gas sorption system was used for determination of the pore structure of Point Aconi bed ash. Nitrogen was used in the tests. Unhydrated bed ash and samples hydrated for 2, 4, 6, 24 and 48 h were tested. Micropores are defined as pores with diameters < 2–3 nm [21,22]. Pore sizes were seen to be greater than 3.1 nm, which in effect shows an absence of micropores. As an example, accumulated adsorption surface area for Point Aconi bed ash hydrated for 6 h is shown in Fig. 3. The accuracy of BET analysis was about 2.5% determined by multiple analysis. Table 2

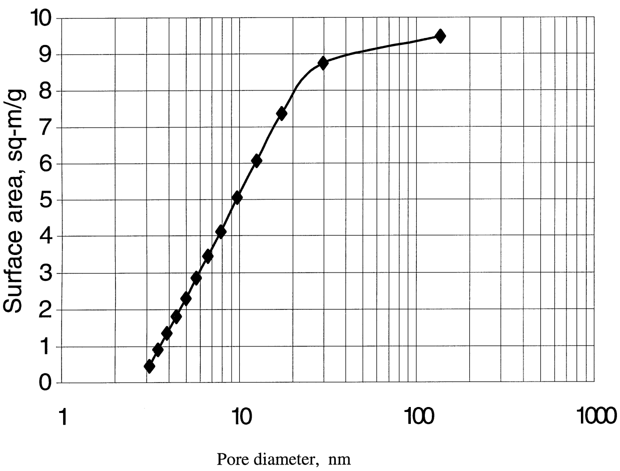

Fig. 3. Accumulated adsorption surface area for Point Aconi bed ash hydrated for 6 h at 75°C.

Table 2
Porosity measurements for unhydrated and hydrated Point Aconi ash

Hydration time (h)	0	2	4	6	24	48
Total pore volume (cm^3/g, d < 279.56 nm)	0.00537	0.0493	0.0515	0.0532	0.0560	0.0582
Average pore diameter (nm)	28.6	20.68	21.48	20.22	22.78	23.52
Multi-point BET m^2/g	0.751	9.54	9.60	10.52	9.84	9.91
Langmuir surface area m^2/g	6.539	73.17	77.88	85.72	78.71	79.29
Mesopore area, m^2/g	0.752	9.537	9.601	10.52	9.84	9.91

gives the results for the more important parameters. The data show a significant increase in the surface area associated with the hydrated over that of the unhydrated bed ash. It is interesting to note that the multi-point BET surface area for the unhydrated ash (0.751 m^2/g) is extremely close to that previously determined for CANMET ash (0.79 m^2/g). No significant differences exist between the samples hydrated for different times. There is a slight increase in the average pore diameter, which might aid the carbonation process, and at least on a priori basis, it might be expected that these samples carbonate to similar levels independent of hydration time. A mercury porosimetry measurement was carried out on Point Aconi bed ash, which gave a total pore area of 2.4 m^2/g and a median pore diameter of 15.7 nm. This is in reasonable agreement with the data in Table 2 given the differences in technique.

4.2. Hydration of bed ash

A number of tests were carried out using different hydration duration to determine the effect on recarbonation behaviour. Two TGA measurements were made of the $Ca(OH)_2$ contents of two Point Aconi bed ash samples hydrated for 3 and 16 h respectively in the glass autoclave. These indicated $Ca(OH)_2$ contents of 21.3 and 21.0% respectively, which correspond to CaO contents of 16.1 and 15.9% respectively. This suggests that hydration is effectively complete within approximately 3 h in the glass autoclave. This is contrary to the suggestion that micropores are trapping significant quantities of water in their structure or are preventing CaO crystallites from being hydrated by blocking access to the water molecules. If large numbers of micropores exist in the ash samples as some authors have suggested, the hydration process will be highly time dependent because water will have difficulty getting into these micropores.

4.3. Cahn PTGA tests

Initial experiments on the Point Aconi bed ash with the 50 cm^3 autoclave showed that no appreciable carbonation occurred with dry CFBC residues, even over periods of many days at temperatures of up to 150°C and pressures of up to 1 MPa of CO_2. This was confirmed by three determinations of conversion to $CaCO_3$ content from a 70 h test with the Parr autoclave at 300°C. This gave a mean conversion to $CaCO_3$ of $1.28 \pm 0.09\%$, compared with 1.35% in the original ash (as determined by TGA), indicating no recarbonation within the limits of experimental error. This suggests that, although hydrated FBC residues carbonate at ambient temperatures, albeit slowly, the kinetics of the reactions with the dry solids are exceedingly slow. In consequence, it was decided to study the kinetic limits for both unhydrated and hydrated Point Aconi and NISCO FBC solids using the PTGA.

The carbonation reaction for unhydrated Point Aconi bed ashes started at 370°C for the atmospheric test and at 380°C for the high pressure test. This indicates that pressure does not strongly affect the temperature at which carbonation starts. For the atmospheric pressure test, the weight gain stopped at about 550°C, and sample weight remained constant until 850°C. The maximum rate of weight gain was 5.15%/h, which occurred at 490°C. Based on the weight gain and an assumed 16.7% CaO in the sample, it was estimated that only 9% of the CaO was converted to $CaCO_3$. For the high pressure test the bed ash gained weight between 380–600°C and 660–900°C and, using the same criteria, it is estimated that 24.7% of the CaO was converted to $CaCO_3$. The overall conversions are given in Table 3. The high pressure may have promoted CO_2 to have access to the CaO that was not available for reaction at atmospheric pressure.

For the hydrated Point Aconi bed ash under atmospheric conditions, weight gain started at a considerably lower temperature, about 260°C, and stopped at a slightly higher temperature, 600°C, compared with the untreated ash. Thereafter, the weight remained constant to 850°C. The maximum rate of weight gain occurred at 545°C and had a value of 27%/h, which is five times that observed with the untreated ash. This equates to a

Table 3
Overall conversions of Point Aconi and NISCO bed ashes (wt%)

Pressure (MPa)	0.1	1.1
Point Aconi bed ash	9.0	24.7
Hydrated Point Aconi bed ash	51.7	60.0
NISCO bed ash	23.5	27.4
Hydrated NISCO bed ash	54.5	58.6

conversion of 51.7% of the CaO to $CaCO_3$, significantly higher than that for the unhydrated ash. For the high pressure test, the Point Aconi bed ash showed only one weight gain period between 310 and 620°C and achieved a conversion of 60% of the CaO to $CaCO_3$.

For the NISCO bed ash the results were roughly similar. The unhydrated ash in the atmospheric pressure test showed weight gains between 370 and 530°C and between 700 and 870°C. The maximum weight gain was about 15%/h and occurred at 450°C. Assuming a 22.75% CaO content in the ash, the weight gain is equivalent to conversion of 23.5% of the CaO to $CaCO_3$. For the hydrated ash, the weight gain started at a much lower temperature, 230°C, and stopped at 600°C, with the weight remaining constant thereafter, with no second weight gain period. The rate of weight gain had two maxima, at 360 and 540°C, and for both the rate of gain was about 15%/h. One possible explanation for the two maxima is the decomposition of $Ca(OH)_2$ and carbonation of CaO were happening at the same time. Overall, about 54.5% of the CaO was converted to $CaCO_3$.

In the pressure tests with untreated NISCO bed ash, there were two periods of weight increase between 400–600°C and 660–870°C, with an overall conversion rate of 27.4% of the CaO to $CaCO_3$. For the hydrated ash there was again only one weight gain period, occurring between 290 and 600°C, and again it had two maxima with values of about 12 and 15%/h. The overall conversion of CaO to $CaCO_3$ was 58.6%. The TGA test for hydrated NISCO bed ash pacified at 1.1 MPa is shown in Fig. 4.

It appears from these results that a practical recarbonation process would require elevated temperatures and pressures (i.e. over 600°C and partial pressures of CO_2 greater than 1 MPa), or hydrated ashes. As economic considerations seem to rule out ash treatment processes at elevated temperatures, all subsequent work in this study was done with prehydrated ashes.

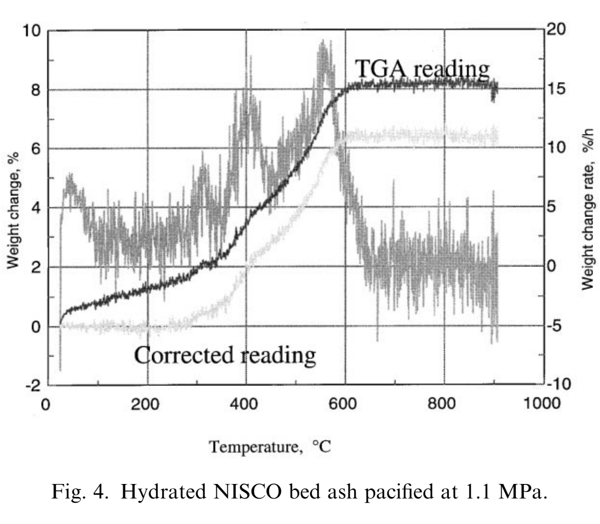

Fig. 4. Hydrated NISCO bed ash pacified at 1.1 MPa.

4.4. Carbonation behaviour of OCCs

As will be discussed later, one of the more interesting results from the pacification work was the apparently greater amounts of CaO converted to $Ca(OH)_2$ and $CaCO_3$ than were shown to be present by direct free lime determinations. Given that chemical determinations on the Point Aconi sample indicated it had about 30% of the free lime present as OCCs, the obvious explanation is that these compounds were carbonating. In order to verify this hypothesis, tests were carried out in which typical OCCs (synthetic) were hydrated for 3 h, carbonated at 1 MPa at 75°C, then subjected to TGA to determine whether they had hydrated or carbonated. As it was not known how easily such materials would carbonate, tests were carried out for over 100 h. Table 4 gives the details of the compound and carbonation time.

Apart from the gehlenite result, for which very low conversions are apparently achieved, so low in fact to suggest that this material has not reacted at all, it is evident that all other OCCs can carbonate. In the case of the tetracalciumaluminoferrite, TGA work indicated that water was released at about 150°C below the decomposition temperature of $Ca(OH)_2$, at about 300°C, and hence we have ascribed the hydrate to the species $Al_2O_3{\cdot}3H_2O$ and not portlandite formation. Nonetheless, it is apparent that, with the exception of gehlenite, which is known from other work to be very unreactive [18], these OCCs can carbonate, and hence there is a possible extra source of "CaO" available to the system, whether or not the OCCs hydrate.

4.5. Glass autoclave pacification tests

Results from trials with the glass autoclave and Point Aconi ash for short recarbonation times (up to 3 h) and different hydration times are given in Table 5 and Fig. 5. Initial experiments indicated that the hydration time seemed to have an effect, so test periods of 1, 3, 16 and 24 h were examined.

From these data it is apparent that absolute conversions of the CaO in the ashed samples vary from 27 to 46%, which is too low to represent a commercial level of recarbonation. It is also questionable, given the degree of experimental scatter in the data, whether variations in hydration times make a significant difference. The apparent equivalent CaO contents of these samples is also somewhat higher than the Point Aconi bed ash, with a mean of $19.0 \pm 1.5\%$. If the CaO content determined is corrected for the carbonate and shale content, a value of 16.7% is obtained for the equivalent CaO content of the ash, which is closer to the experimental values in Table 5, but the difference still seems rather large. This may not be an artifact of the experimental work, as phase separation of the Point Aconi bed ash [17] has shown that it contains about 6.6% of OCCs,

Table 4
Hydration and carbonation tests on selected OCC

Compound	Time (h)	Hydration levels		Carbonation levels	
		% $Ca(OH)_2$	% Conversion	% $CaCO_3$	% Conversion
Dicalcium ferrite $(CaO)_2Fe_2O_3$ or C2F	130	16.4	34.5	19.2	29.3
Gehlenite $(CaO)_2 \cdot Al_2O_3 \cdot SiO_2$ or C2AS	130	–	1.2	–	0.08
Larnite $(CaO)_2 \cdot SiO_2$ or C2S	130	20.5	27.7	20.5 (3.0, 15.3)	20.3
Tetracalciumaluminoferrite $(CaO)_4 \cdot Al_2O_3 \cdot Fe_2O_3$ or C4AF	130	6.4[a] (7.75%)[a]	20.8[a]	3.4 (0.7, 2.5)	4.3

[a] Calculated on the basis that Al_2O_3 was the species that was hydrolyzed to $Al_2O_3 \cdot 3H_2O$ and not CaO. ( ) Data represents TGA determination, and for data presented in the form (*x*,*y*) *x*, represents what was present in the sample before hydration and carbonation, and *y* what was present after.

Table 5
Hydration and carbonation levels of Point Aconi ash for short test periods

Test	1	2	3	4	5	6	7	8
Hydration time, temp. (h, °C)	1, 75	1, 75	1, 75	3, 75	3, 75	24, 75	16, 75	3, 75
Pacification time, temp. (h, °C)	3, 75	3, 75	3, 75	3, 75	3, 75	3, 75	3, 75	1, 50
% $Ca(OH)_2$	13.6	15.5	15.3 (15.0)[a]	15.2	16.5	15.0	13.5	14.8
% $CaCO_3$	13.8	9.0	7.8 (9.0)[a]	12.2	10.3	12.5	15.6	7.8
% CaO equivalent	18.0	16.8	15.9	18.3	18.2	18.3	18.9	15.6
% Corrected CaO equivalent	19.9	18.2	17.2	20.2	19.9	19.0	21.0	16.8
% Carbonate conversion	42.9	30.0	27.5	37.3	31.6	38.3	46.2	28.0

[a] ( ) TGA data. % Corrected CaO equivalent is the CaO content of the dry, calcined sample. i.e. corrected for removal of H_2O and CO_2.

displaying carbonation propensity similar to that described above (see Table 4). The corrected CaO appears to be increasing as a function of recarbonation time. The mean data for corrected CaO content are 21.0 ± 1.2% and 22.4 ± 1.4% for Tables 6 and 7, respectively. It is interesting to note that the run with 1 h pacification time has an overall conversion of only 16.8%, which is very close to the original CaO determination, suggesting that the exposure time to CO_2 in liquid water is critical in converting these compounds.

As indicated above, these conversion levels are too low and higher temperatures and pressures should be investigated to determine whether the conversions could be increased. Tests were conducted with longer periods of recarbonation to determine whether the recarbonation would continue or was blocked by pore plugging and had reached some natural limit. Some tests on dried hydrated ash were done to determine whether liquid water made a difference to the carbonation process. The results are presented in Tables 6 and 7.

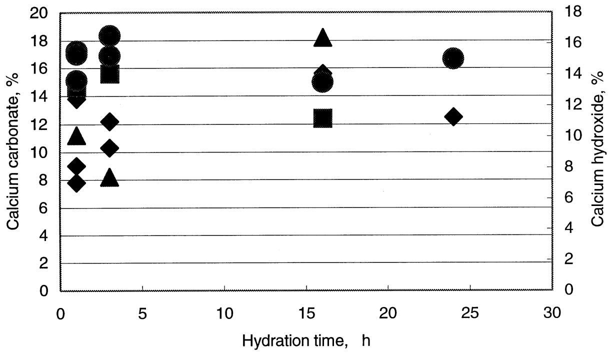

Fig. 5. Effect of hydration time on recarbonation levels of Point Aconi bed ash. Hydration and recarbonation were carried out at 75°C. ◆ $CaCO_3$, recarbonated for 3 hours; ▲ $CaCO_3$, recarbonated for 24 hours; ■ $Ca(OH)_2$, recarbonated for 3 hours; ● $Ca(OH)_2$, recarbonated for 24 hours.

Tables 5 and 6 provide some evidence that bed ash undergoing longer hydration times carbonate to a greater degree, although the variation of the data is large. Data in Table 5 indicated that when pacified at the same temperature and for the same duration, bed ash samples hydrated for 1 h showed an average CaO to $CaCO_3$ conversion of 33.5 ± 8.3%. Bed ash samples hydrated for 3 h gave an average CaO conversion ratio of 34.5 ± 4%. With hydration times of 16 and 24 h, the conversions were 46.2 and 38.3%. The absolute conversions are “lowered” because, as discussed above for longer runs, it is apparent that more “CaO” is being made available for carbonation. One important conclusion is that liquid water significantly enhances the carbonation rate. This is important because otherwise, in order to achieve higher conversions, higher temperatures are required. However, depending on the pressure, liquid water will not exist at temperatures much above 100°C, which will act to reduce the recarbonation levels.

One issue that has not been resolved is whether there is an effective upper limit to the carbonation level. The data in Table 7, despite some experimental scatter particularly for the shorter runs, increases almost linearly

Table 6
Hydration and carbonation levels for Point Aconi ash for periods of 20 and 24 h

Test	9	10	11	12	13	14
Hydration time, temp. (h, °C)	3, 75	1, 75	3, 75	16, 75	3, 75	24, 75
Pacification time, temp. (h, °C)	20, 75	24, 75	24, 75	24, 75	24, 50	3, 75
% $Ca(OH)_2$	12.7	14.6	15.6[a]	12.4	17.2	17.2
% $CaCO_3$	17.2	11.2	8.2	18.2	11.4	12.0
% CaO equivalent	19.3	17.3	16.4	19.6	19.4	19.8
% Corrected CaO equivalent	21.6	18.9	22.9	22.0	21.4	21.8
% Carbonate conversion	50.0	36.1	27.9	52.1	32.9	34.1

[a] Carbonation with dried samples.

Table 7
Hydration and carbonation levels for Point Aconi ash for periods above 24 h

Test	15	16	17	18	19	20	21	22	23	24
Hydration time, temp. (h, °C)	3, 75	3, 75	3, 75	3, 75	3, 75	3, 75	3, 75	3, 75	16, 75	24, 75
Pacification time, temp. (h, °C)	45, 75	46, 75	72, 75	72, 75	72, 75	96, 75	90, 75	115, 50	48, 75	72, 75
% $Ca(OH)_2$	12.2 (10.2)[b]	14.4[a]	14.4	12.7	15.2[a]	12.2	10.3 (8.2)[b]	10.0 (9.0)[b]	13.6	11.4
% $CaCO_3$	19.1 (14.0)[b]	12.6	16.9	12.2	10.7	22.6	22.7 (21.1)[b]	21.3 (20.0)[b]	15.3	17.6
% CaO equivalent	20.0	18.0	20.4	17.6	17.5	21.8	20.5	19.5	18.9	18.5
% Corrected CaO equivalent	22.5	19.7	22.9	21.9	19.1	25.1	23.5	22.1	21.0	20.6
% Carbonate conversion	53.5	39.2	46.4	50.5	34.1	57.9	61.9	61.1	45.3	53.4

[a] Test with dried sample.
[b] ( ) Data obtained using TGA.

with time over the time range examined, Fig. 6. However, this is probably an artifact of the presentation of the data, because the two conversions at the longest times, 96 and 115 h, are effectively identical, taking a value of about 60%, which is very close to the value obtained in Table 3 for the PTGA work. To resolve whether the carbonation was reaching a limit, a very long pacification test was carried out for 217 h. This gave a conversion to carbonate of 60%, which suggests that within experimental error a maximum conversion at these pressures probably occurs in the 60–70% plus range, with this limit arising presumably due to pore plugging.

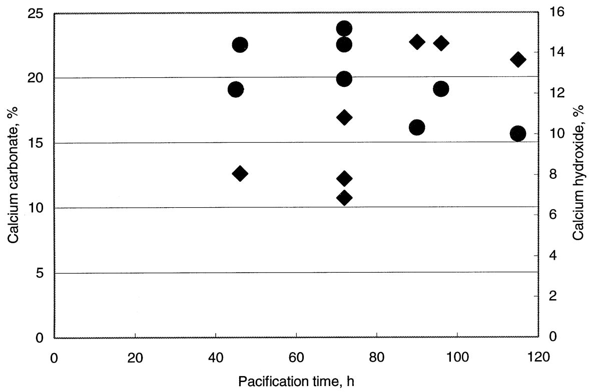

Fig. 6. Effect of pacification time. Point Aconi bed ash prehydrated at 75°C for 3 h. ◆ $CaCO_3$; ● $Ca(OH)_2$.

To confirm the results, repeat tests using TGA to determine the $Ca(OH)_2$ and $CaCO_3$ were performed. Although the agreement is not perfect, it is sufficiently close to give confidence in results obtained from oven tests.

4.6. CANMET pacification tests

A limited number of tests (five) were carried out using CANMET bed ash to determine whether the results were comparable with the Point Aconi bed ash (Table 8). Although the initial conversion was higher, there seems no evidence of hydration duration affecting the degree of conversion. An interesting difference between these two ashes is that the results of the 41 and 92 h tests are nearly identical, suggesting that pore plugging is again limiting the conversion to some maximum level, which here is about 70%. Unfortunately, as in the case of the Point Aconi bed ash it is clear that the conversions are simply too low to make a recarbonation strategy effective at these temperatures and pressures (75°C and up to 1 MPa of CO_2).

4.7. NISCO pacification tests

The initial PTGA experiments with NISCO bed ash indicated that it is more reactive than Point Aconi bed ash, at least for carbonation at atmospheric pressure.

Table 8
Hydration and carbonation levels for CANMET bed ash

Test	1	2	3	4	5
Hydration time, temp. (h, °C)	3, 75	16, 75	3, 75	3, 75	3, 75
Pacification time, temp. (h, °C)	3, 75	4, 75	20, 75	41, 75	92, 75
% $Ca(OH)_2$	16.0 (12.2)[a]	15.5	12.1	10.1	9.3
% $CaCO_3$	19.1 (26.2)	19.1	21.0	29.0	29.3
% CaO equivalent	22.8	22.4	20.9	23.8	23.8
% Corrected CaO equivalent	26.0	25.5	23.8	28.1	28.1
% Carbonate conversion	22.8	22.4	50.6	69.8	72.0

[a] ( ) TGA data.

This impression was confirmed by elevated temperature experiments at 102 and 550°C. In air the dried hydrated bed ash achieved weight gains from 1.5 to 2.8%/h, while for ash heated at 550°C the weight gains increased from 2.2 to 2.8%/h. Four determinations of carbonate from hydrated samples showed $CaCO_3$ contents of 7.5 ± 1.1%, while a direct TGA determination gave a $CaCO_3$ value of only 3.7%, and two chemical determinations indicated that $CaCO_3$ were 2.2 and 3.3%. Here all data have been corrected to a water-free basis, assuming that $Ca(OH)_2$ has been decomposed.

The TGA determination was presumably close to the chemical analysis because such tests are done in nitrogen, eliminating the opportunity for the samples to carbonate. This indicated that the oven method of determination of $Ca(OH)_2$ is flawed with this ash, because the sample could not be prevented from taking up CO_2 from the air and, therefore, hydroxide and carbonate conversions may be expected to be under- and over-predicted respectively. The apparent free lime content of 16.3%, determined by boiling in water and then measuring weight loss, in this case at 102°C, and then at 550°C, was significantly below the chemically determined content of 20–22.7%.

Based on the increased reactivity of the NISCO ashes, it was decided to verify whether different hydration times affect carbonate conversions, as suggested by the Point Aconi bed ash runs. Tests were done using the glass autoclave with hydration times from 0 (water was added and carbonation was started immediately) to 20 h. The results are given in Table 9 and Fig. 7. As with the first set of experiments, temperatures were maintained at 75°C for both the hydration step and the pacification step. Here only one pressure was employed, 1 MPa.

Table 9
Variation of mean $Ca(OH)_2$ and $CaCO_3$ levels with hydration times for NISCO ash

Hydration time (h)	0	1	2	20
% $Ca(OH)_2$	11.8	13.0	13.3	14.6
% $CaCO_3$	22.1	19.8	19.4	16.7
% CaO equivalent	21.3	20.9	20.9	20.5
% Corrected CaO equivalent	24.3	23.7	23.7	23.0
% Carbonate conversion	58.1	53.1	52.0	45.8

It is clear from Table 9 that the initial conversions are significantly higher than those associated with 3 h carbonation periods for Point Aconi bed ash, with a mean conversion of 52.4 ± 5.1% compared with only 36.3 ± 6.9% for the Point Aconi bed ash. This allows the possibility that some ashes, e.g., those with high dolomitic content, may indeed be reactive enough to use CO_2 in a pacification process. The data also suggest that, if anything, increasing hydration time decreases the conversion with CO_2. It would be possible to develop a hypothesis consistent with such an observation (e.g., increased hydration time corresponds to blocking of micropores due to some final conversion to portlandite). However, in the absence of confirming experiments it is probably inadvisable to make any conclusions other than that the hydration period may have an effect on the carbonation behaviour and, if so, it is ash specific and can only be determined experimentally.

One set of four experiments with 3 h hydration time and 18 h pacification time, again at 75°C and 1 MPa partial pressure was set up. For whatever reason, it is apparent that the conversions have not increased for

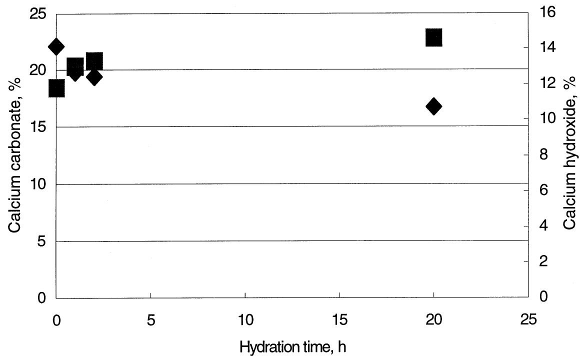

Fig. 7. Effect of hydration time on NISCO bed ash, hydrated at 75°C, recarbonated at 75°C for 3 h. ◆ $CaCO_3$; ■ $Ca(OH)_2$.

these runs over the 3 h pacification time and carbonate conversion was 43.4 ± 5.6%. The average $CaCO_3$ content is 15.3 ± 2.2%. These results may be explicable if long hydration times are in some way deactivating the ash. These conversions are marginally greater than those for Point Aconi bed ash for 20 and 24 h (mean value of 39.8 ± 10.7), but given the considerable scatter in the data it is impossible to be certain. It does seem clear that, even though NISCO ash is more reactive than Point Aconi ash, quantitative conversion cannot be achieved within reasonable times under these conditions. Given that the main aim of this work was to examine the feasibility of such an approach for the Point Aconi unit no further attempts were made to resolve some of the questions that exist with respect to the carbonation behaviour of NISCO bed ash.

4.8. Parr bomb pacification tests-Point Aconi ash

It is evident that experiments at lower temperatures do not ensure sufficient conversion of CaO in the bed ashes to make the development of a carbonation strategy practical. Therefore, it was decided to carry out some preliminary tests to investigate the effects of higher temperatures on the carbonation of hydrated CFBC ash. Initially two pressures, nominally 1 MPa and 1.8 MPa, and two temperatures, 150 and 300°C (300°C being the temperature limit for the Parr autoclave), were chosen. By the end of the run pressures might have fallen to as low as 0.4–1.0 MPa, depending on the initial pressure. In all cases, a prehydration strategy similar to the one followed with the glass autoclave, which involved putting 3–5 times the stoichiometrically required water in with the sample for a 3 h heating period at 75°C, was followed. Table 10 gives the results for per cent recarbonation, together with mean data for similar times (i.e. data obtained within ± 5 h of the Parr autoclave results) from work with the glass autoclave.

It seems reasonable to conclude that increasing reaction time increases the conversion and for the lower pressure results (< 1 MPa), it appears that the data for the 150°C condition are — within the range of experimental error — quite close to that for the 75°C tests with the glass autoclave. More surprisingly these data indicate that increasing the temperature from 150–300°C actually decreases the conversion. In line with the data from the PTGA, these results indicate that increasing pressure, at least over the range examined here, produces only a moderate increase in the conversion.

Table 10
Per cent recarbonation for Point Aconi bed ash with the Parr autoclave

Temperature (°C)	Time (h)	Lower pressure	Higher pressure	Mean data from GA[a]
150°C	3	38.9 ± 0.8%	–	38.7 ± 9.1%
	20	35.6 ± 4.8%	–	46.8 ± 11.4%
	24	–	60.0 ± 0.03%	
	96	64.1 ± 2.7%	–	75.5 ± 0.4%
	117	48.6 ± 6.6%	–	71.1
300°C	18	20.2 ± 0.5%	28.1 ± 1.7%	46.8 ± 11.4%
	70	39.5 ± 3.6%	58.0%	58.0 ± 1.4%

[a] Taken from Tables 5–7.

In order to investigate the effects of pressure in more detail, trials were carried out at 0.2, 1.5, 2, 3 and 6 MPa. Apart from the trial at 0.2 MPa, which was carried out in the glass autoclave, all tests were done in the Parr autoclave. In all cases, the hydration process was carried out at 75°C for 3 h, and the pacification period lasted 18 h at 150°C. Results are given in Table 11 and in Fig. 8.

This test work clearly shows a dramatic increase in conversion of CaO to $CaCO_3$ for the highest pressure (6 MPa). The conversions achieved at 6 MPa are at a level that would be interesting for a commercial recarbonation process. However, this pressure is probably too high for commercial application, as it would involve building a very expensive pressure vessel for an industrial-scale process.

There is also an increase in the percentage $CaCO_3$ as the pressure increases, i.e. from 0.2 to 1 MPa or more). However, the conversion does not reflect that increase because CaO in the system increases, again presumably due to the reaction of OCCs.

To complete the study of the effect of pressure on the conversion of free lime to $CaCO_3$, tests were also carried out at 1.5, 2 and 3 MPa. The results are given in Table 12. Quite remarkably, the decrease in conversion to $CaCO_3$ with increasing temperature appears to be confirmed. It is also evident that, even if the conversions for the earlier comparison trial are ignored, any increase in conversion as a function of pressure is quite small until very high pressures approaching 6 MPa are achieved.

More interesting is that for these runs the overall CaO content in the sample is very close to the experimentally determined value of 16.7%. There is no indication of any OCC being converted to carbonate at 300°C. The most obvious explanation is that tests at 150°C are below the saturation temperature for water at pressures of 1 MPa and above (i.e. the saturation pressure is 0.48 MPa at 150°C).

However, at 300°C, a pressure of 8.6 MPa would be required to reach the saturation pressure for steam and hence liquid water is absent for these tests [23]. The implication is that tests at 75 and 150°C are similar in that reaction with the OCCs is presumably occurring via reaction with CO_2 in liquid water. At 300°C, all heterogeneous reactions are associated with H_2O and CO_2 in the gas phase and not in the liquid state or in solution. Evidently OCCs cannot react at these low temperatures with CO_2. This hypothesis is further supported because

Table 11
Variation of mean $Ca(OH)_2$ and $CaCO_3$ levels with pressure at 150°C for Point Aconi ash

Test pressure (MPa)	0.2	1.5	2.0	3.0	6.0	1.0[a]	2.0[b]
% $Ca(OH)_2$	9.0	14.2, 12.5, 11.9 (14.3)[c]	14.9, 10.7	13.9, 14.4	6.8	16.0	10.6
% $CaCO_3$	14.3	16.7, 18.6, 15.7 (15.6)[c]	17.3, 21.3	18.5, 17.9	30.2	12.1	21.5
% CaO equivalent	14.8	20.1, 19.9, 17.8 (19.4)[c]	21.0, 20.0	20.9, 20.9	22.0	18.9	20.0
% Corrected CaO equivalent	16.2	22.5, 22.4, 19.7 (21.6)[c]	23.6, 22.7	23.6, 23.6	25.9	20.8	22.7
% Carbonate conversion	54.0	46.5, 52.4, 49.4 (45.0)[c]	46.1, 59.6	49.7, 48.0	76.9	35.8	60.0

[a] Comparison data from 20 h, comparison data for 24 h, at 150°C (see Table 10 for conditions).

[b] Comparison TGA data.

[c] ( ) Measured by TGA; multiple tests results are shown in the same table cell.

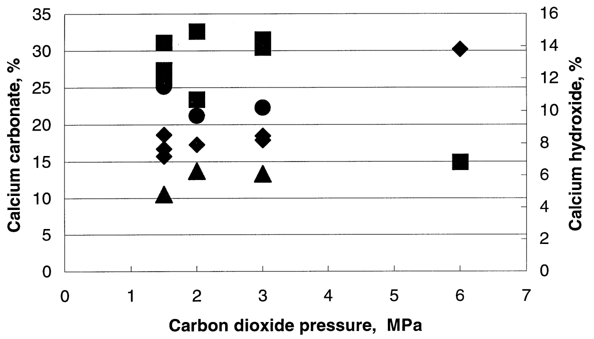

Fig. 8. Pressure effect on pacification. Point Aconi bed ash, prehydrated at 75°C for 3 h. ◆ $CaCO_3$, recarbonated at 150°C; ▲ $CaCO_3$, recarbonated at 300°C; ■ $Ca(OH)_2$, recarbonated at 150°C; ● $Ca(OH)_2$, recarbonated at 300°C.

Table 12
Variation of mean $Ca(OH)_2$ and $CaCO_3$ levels with pressure at 300°C for Point Aconi ash[a]

Test pressure (MPa)	1.5	2.0	3.0	2.0[a]
% $Ca(OH)_2$	11.5	9.7	10.2	14.6
% $CaCO_3$	10.5	13.7	13.3	7.7
% CaO equivalent	14.6	15.0	15.1	15.4
% Corrected CaO equivalent	15.8	16.4	16.5	16.5
% Carbonate conversion	40.3	51.1	49.3	28.0

[a] Comparison data from earlier trial for 18 h (see Table 10).

the one test carried out at 150°C and 0.2 MPa is also associated with a total CaO equivalent of 16.2, which is very similar to the values in Table 11, implying liquid water is essential if CO_2 is to rapidly carbonate the OCCs.

5. Conclusions

A commercially feasible recarbonation process cannot be achieved for the Point Aconi or NISCO FBC ashes unless very high pressures are used. It is also likely that dolomitic limestone is required. The kinetic rate for the carbonation reaction is effectively zero below 400°C. If the ashes are hydrated, the lower temperature limit for the carbonation reaction is reduced to 200–230°C for rapid conversion. At ambient temperature, recarbonation will occur, although it is very slow.

For bed ashes with high levels of OCCs, hydration permits these compounds to increase the free lime in the system. This is important because a fully hydrated ash will continue to react with CO_2 in the landfill.

An effective conversion limit of 60–70% has been suggested by this work. The rate of reaction with CO_2 is dependent on the limestone type. It is possible that a recarbonation process could work with more porous calcine (dolomite).

Acknowledgements

This work was performed with the support of the Committee on Atlantic Coal, Nova Scotia Power Inc. and Environment Canada. The helpful comments of Professor E.M. Bulewicz of Cracow University of Technology are also acknowledged.

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