

Carbonation of Brine Slurried Size Fractionated Coal Combustion Fly Ash

Muriithi, GN¹; Gitari, MW²; Petrik, LF¹

¹Environmental and Nano Sciences Group, Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville, 7535, Cape Town, South Africa, Tel: +27 (0) 21 959 3878, Fax: +27 (0) 21 959 3304

²Department of Ecology and Resource Management, School of Environmental studies, University of Venda. Private bag, X5050, Thohoyandou, 0950, Limpopo, South Africa. Tel: +27 (0) 15 962 8572

Abstract

Coal combustion by-products such as fly ash (FA), brine and CO₂ from coal fired power plants have the potential to impact negatively on the environment. Reaction of CO₂ with FA/ brine slurry can potentially provide a viable route for CO₂ sequestration through formation of mineral carbonates. Fractionated FA has varying amounts of CaO which not only increases the brine pH but can also be converted into calcite. Statistically designed controlled carbonation reactions were carried out in a reactor set-up to evaluate the effect of particle size, pressure, temperature and S/L ratio on the carbonation efficiency of FA. Input parameters: temperature and pressure were at two levels (30 °C and 90 °C; 1 Mpa and 4 Mpa), S/L ratio was at three levels (0.1, 0.5 and 1) while particle size was at four levels (bulk ash, <20 µm, 20 µm -150 µm and >150 µm). Carbonation using brine resulted in higher degree of calcite formation compared to ultra-pure water. The 20 -150 µm size fraction was observed to have the highest CO₂ sequestration potential while the >150 µm fraction had the lowest. Pressure was observed to have a slight influence on the % CaCO₃ yield while higher temperatures led to higher % CaCO₃ yield. The effect of S/L ratio was temperature dependent. The two most important parameters in the carbonation of FA/brine slurries were particle size and temperature.

KEY WORDS: Fly Ash, Brine, Carbonation, CO₂ sequestration, Carbonation efficiency, Size fractionation.

INTRODUCTION

Coal combustion provides 40 % of the world's energy needs; nevertheless this figure is projected to increase due to the increasing demand for electricity and the availability of large coal reserves in different parts of the world. However, coal combustion leads to emission of environmentally harmful gases such as CO₂, SO_x, NO_x, chlorofluorocarbons (CFC) and ozone (O₃). CO₂ is the most important greenhouse gas (GHG), being responsible for about two thirds of the enhanced green house effect. Currently, China's CO₂ emissions surpass those of the USA by 8 %. South Africa on the other hand generates 93 % of its electricity from coal combustion with CO₂ emissions of over 218 Mt annually.¹ Despite the numerous environmental issues associated with its combustion, coal will remain a major source of electric power in South Africa for years to come due to large coal deposits which can be exploited.² Thus technologies need to be developed to reduce emissions of CO₂ from coal fired power plants.

Other coal combustion by-products (CUB) include fly ash (FA), bottom ash, slag and flue gas desulphurization (FGD). Of the one billion metric tons of coal mined annually in the USA, about 90 % is burned to generate electricity with a production of over 100 million tons of CUB annually.³ Over 36.4 Mt of FA are produced by the electricity production industry in South Africa per annum with only 5 % put into beneficial use while the remaining is disposed in ash dumps or ponds.⁴ FA is enriched with a suite of trace elements such as V, Na, Cl, SO₄, PO₄, Hg, Ba, B, K, Th, Se, As, Mo, Ti, and

major species such as Ca, Mg, Fe, Al and Si. Furthermore, the particle size ranges between 0.5-200 μm , thus FA is prone to leaching in the event of water percolation.

Inland industries such as coal combustion plants in South Africa require huge volumes of water in their daily operations and most of them operate in areas where there is scarcity of water. Water recycling is necessary due to the scarcity. Pre-treatment of raw surface water and mine water for boiler feed and other plant operations is done through processes such as reverse osmosis (RO), electro reversal dialysis (EDR) which produce high ionic strength effluents (brines) that require disposal. These brines contains high levels of Na, Cl, SO_4 , Ca, Mg and a host of trace elements such as Fe, Mn, Cr, V, Ti, P, Si and Al. The main environmental concern with respect to the disposal of FA and brine is the release of inorganic contaminants including soluble salts and trace metals as a result of leaching processes.⁵ Brine handling techniques require further expensive treatment options or disposal into lined dams to minimize environmental impacts. These treatment options are generally capital intensive and have high operating costs. It is imperative that proper management of these three “wastes stream” i.e. CO_2 , FA and brine is devised so as to continue exploitation of natural resources like coal in an environmentally sustainable manner.

Current methods for the CO_2 sequestration include adsorption by physical and chemical wet scrubbing, adsorption by solids using pressure and temperature swing modes, cryogenic distillation and mineral carbonation.⁶ Mineral carbonation is an attractive alternative method for the removal of CO_2 as it results in permanent storage of carbon dioxide as mineral carbonates that are environmentally benign and can be used for mine backfilling⁶. Previous researchers^{7,8} have shown that carbonation of coal FA and brine has the capacity to sequester CO_2 in the form of carbonates. However there is no data available on the carbonation efficiency of brine impacted and size fractionated South African FA. The objective of this study is to correlate the carbonation efficiency between different size fractions of South African Class F FA, evaluate the factors controlling the carbonation efficiency of the FA/brine slurries. This study is especially attractive since the residual solid and liquid by-products from power plants could be used to mitigate the residual gaseous wastes produced by the same plants and also enhance in recycling of the brine effluents.

MATERIAL AND METHODS

The FA and brine samples were collected from coal burning power utility in Mpumalanga province of South Africa. Fractionation was achieved by use of an Endecott mechanical shaker. Morphological analysis was done by Scanning Electron Microscopy (Hitachi X-650 scanning Electron Microanalyser equipped with a CDU- lead detector at 25m kV). Crystalline phases present in the FA were determined by X-Ray Diffraction Spectroscopy(XRD) using a Bruker AXSD8 Advance diffractometer coupled with a Cu- $\text{K}\alpha$ radiation at 40 kV and 40 mA with a PSD Lynx-Eye, Si-strip detector at 0.03 deg/step 2 theta from 12°- 80° and 3 seconds counting time. Elemental analysis of FA was done by XRF using a Philips PW 1480 X-ray spectrometer fitted with a Cr tube and five analyzing crystals namely LIF 200, LIF 220, GE, PE and PX at 40 kV and 50 mA tube operating conditions. Chittick tests were carried out to determine the % CaCO_3 in the carbonated FA by reacting 1.70 g of the carbonated FA with 20 ml of 6N HCl and recording the amount of CO_2 evolved by reading the displacement of the reservoir fluid. TGA/DSC was carried out using a Mettler Toledo TGA/SDTA 851e with sample robot and a TSO800 GC gas control unit. Anions present in the brine as well as the carbonation leachates were analyzed with an Ion Pac AS14A column and AG14-4 mm guard column. Major cations were analyzed using a Varian radial ICP-AES while trace cations were done on an Agilent 7500ce ICP-MS using High Matrix Introduction (HMI) accessory and He as collision gas.

CARBONATION PROCEDURE

The carbonation reactions were carried out in a stainless steel autoclave reactor with a 600 ml volume capacity. The brine and FA slurry were contained in a teflon liner which was placed inside a steel jacket. A schematic of the reactor is shown in Figure 1.

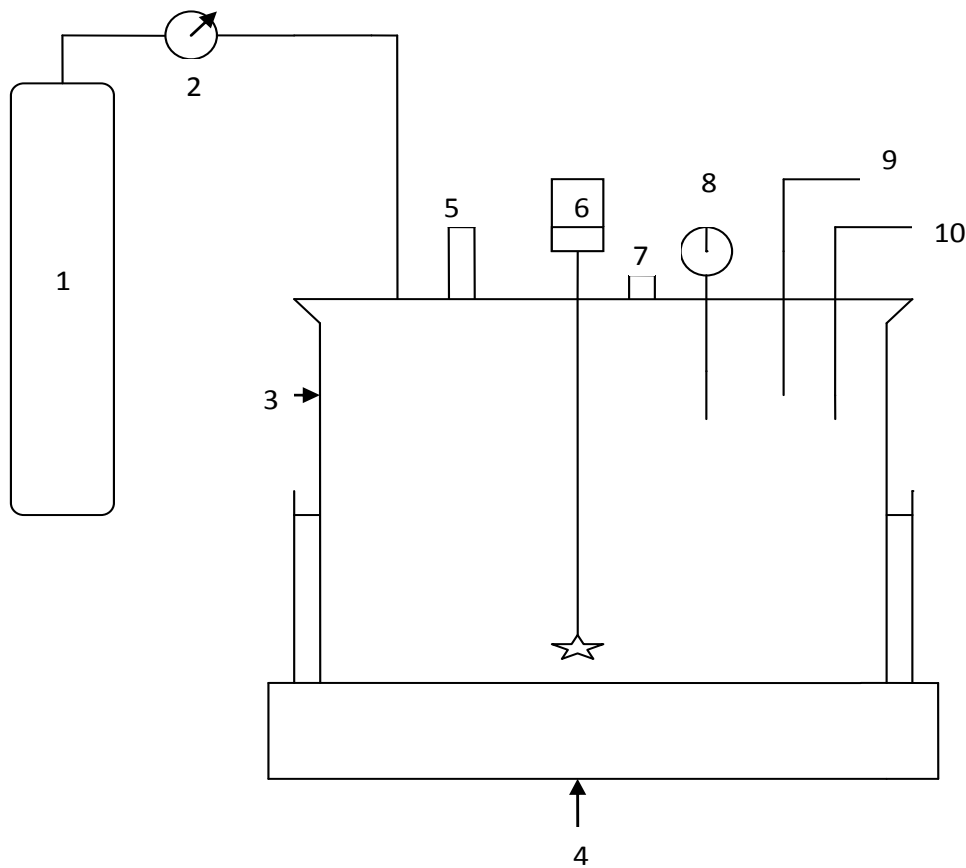


Figure 1: Schematic of the reactor

- 1) Carbon dioxide cylinder
- 2) Pressure regulator
- 3) Stainless steel reactor vessel (maximum temperature = 350 °C with teflon liner, maximum pressure = 345 bars)
- 4) Heating jacket
- 5) Pressure relief valve
- 6) Stirrer powered by a magnetic drive
- 7) Thermocouple
- 8) Pressure gauge
- 9) Liquid sampling point

Two different temperatures of carbonation were used (30 °C and 90 °C) while the pressure of CO₂ was varied between 1 Mpa and 4 Mpa. To investigate the influence of solid/ liquid (S/L) ratio on carbonation, S/L ratios were varied between 0.1, 0.5 and 1. The size fractions of FA used were < 20 μm, 20-150 μm, >150 μm and bulk ash. The dispersion (brine +FA at the required S/L ratio) was placed inside the teflon liner in the pressure vessel and closed. Following the sealing of the pressure vessel, the body of the reactor was placed in the heater assembly and the thermocouple, magnetic stirrer drive system, and water coolant supply controlled by a solenoid valve were put in place. The gas supply connection for the CO₂ (Afrox, technical grade) feed line was then attached. The system was then purged three times with CO₂ at 0.05 Mpa to ensure that all the air was expelled after which the heating system was switched on. When the specified temperature was reached, CO₂ was charged into the reactor to achieve the specified reaction pressure. The brine/FA/CO₂ mixture was then stirred at 600 rpm for 2 hours to prevent any settling of solids during the experiments. At the end of the experiment, the reactor was removed from the heating system and was quenched in cold water. The reaction cell was depressurized for 15 minutes during the water cooling period. Upon cooling to room temperature, the reactor was disassembled, and the solid product was separated by

centrifugation (30 minutes at 6000 rpm), thereafter the supernatant solutions were decanted. Finally, the solid product was dried in an oven for 8 h at 90 °C and analysed by XRD and Chittick test. The supernatant solutions were filtered through a 0.2 µm pore membrane. The filtered solutions for cation analysis were immediately acidified to pH < 2 while those for anion analysis were stored as they were i.e, without acidification. The samples were refrigerated at 4 °C until analysis.

RESULTS AND DISCUSSIONS

Chemical Analysis by X-Ray Fluorescence

The fractionated and un-carbonated FA were characterized chemically using XRF for major, minor and trace elements. Table 1 shows the results for major and minor elements.

Table 1: Major elements concentration (bulk and fractionated un-carbonated ash).

Majors (wt %)	Bulk	>150µm	150 µm-106 µm	106µm-90 µm	90 µm-75 µm	75µm-63 µm	63 µm-53 µm	53µm-45 µm	45µm-32 µm	32 µm-25 µm	25 µm-20 µm	<20 µm
SiO₂	51.227	42.458	50.640	51.770	52.417	52.668	51.400	52.641	52.373	52.709	52.761	51.118
TiO₂	1.548	0.979	1.214	1.333	1.514	1.580	1.616	1.630	1.655	1.684	1.695	1.844
Al₂O₃	26.000	17.968	22.034	24.055	25.270	25.979	27.224	26.355	27.352	26.554	27.353	28.510
Fe₂O₃	2.430	1.984	3.472	2.628	2.756	2.426	2.419	2.280	2.394	2.243	2.245	2.572
MnO	0.061	0.041	0.058	0.062	0.064	0.062	0.063	0.060	0.059	0.065	0.061	0.064
MgO	2.439	1.662	2.342	2.513	2.714	2.534	2.569	2.451	2.499	2.480	2.472	2.624
CaO	9.198	5.894	9.014	9.671	10.286	9.484	9.591	9.261	9.129	8.768	8.498	8.634
Na₂O	0.457	0.146	0.281	0.287	0.355	0.385	0.384	0.466	0.537	0.582	0.558	0.688
K₂O	0.787	0.652	0.778	0.746	0.768	0.778	0.781	0.796	0.815	0.823	0.823	0.872
P₂O₅	0.698	0.438	0.542	0.576	0.691	0.718	0.747	0.755	0.770	0.781	0.777	0.878
SO₃	0.358	0.360	0.261	0.264	0.301	0.351	0.317	0.368	0.375	0.379	0.385	0.395
Cr₂O₃	0.033	0.022	0.029	0.031	0.033	0.034	0.036	0.040	0.038	0.040	0.041	0.041

The fresh South African class F FA contained SiO₂, Al₂O₃, Fe₂O₃ and CaO as the major oxides. CaO in FA is present as free lime and embedded in glassy spheres. Usually the CaO content increases with decreasing particle size. However, the content can also decrease due to formation of glassy spheres from free lime and aluminosilicate melt or the reaction of free lime with SO₂ via CaSO₃ to anhydrite.⁹ Bearing in mind that the amorphous glassy spheres are the most important Al₂O₃ bearing phases, Al₂O₃ content of size fractions is an indicator of the amount of amorphous glassy phase in FA.⁹ An increasing trend with decreasing particle size is clearly visible for Al₂O₃ while the 75 -90 µm fraction had the highest lime content.

BRINE ANALYSIS AND CLASSIFICATION

The brine utilized for carbonation was obtained from the RO circuit of the coal combustion power utility in Mpumalanga. Table 2 gives the analysis of the various ions present in the brine while the classification is shown in Figure. 3.

Table 2: Brine solution concentrations.

Species	K	Al	As	Ca	Co	Cr	Cu	Fe	Mg	Mn
concentration (RO brine) ppm	104.1 ±0.31	0.044 ±0.06	0.007	101.76 ±0.15	0.015 ±0.01	0.014 ±0.01	0.067 ±0.02	0.051 ±0.01	158.73 ±1.24	0.082 ±0.03
Species	Mo	Na	Ni	Se	Sr	V	Zn	Cl	SO ₄	NO ₃
concentration (RO brine) ppm	0.039 ±0.01	4315 ±2.18	0.116 ±0.01	0.004	3.030 ±0.11	0.016 ±0.01	0.100 ±0.01	2036 ±3.26	9488 ±2.22	8.565 ±0.61

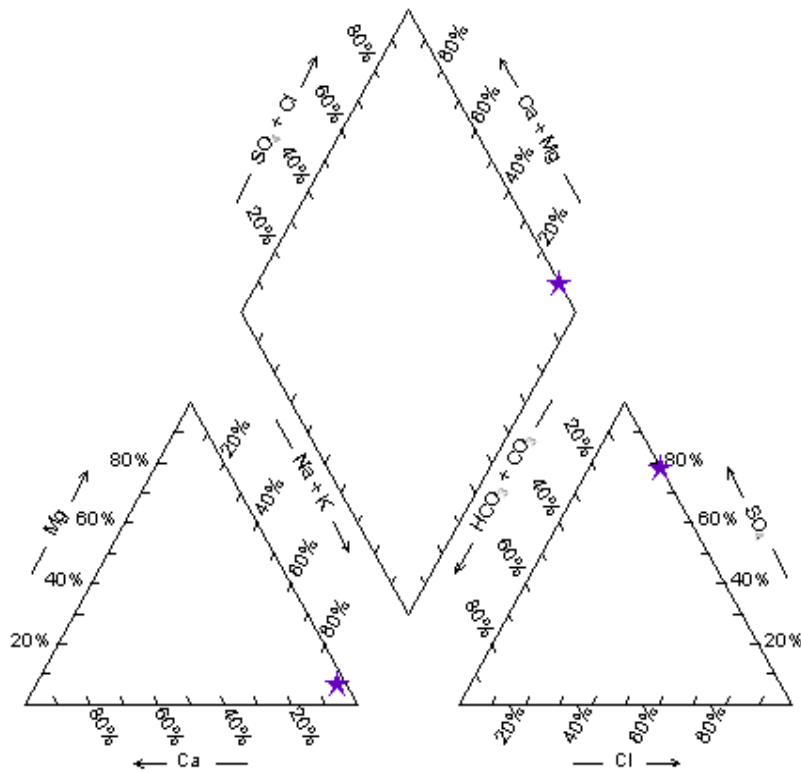


Figure 3: Piper diagram for brine classification.

The brine solutions can be classified as Na-Cl-SO₄ waters. Other significant ions include Ca, K, Mg and trace quantities of NO₃, PO₄, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sr, V and Zn.

MORPHOLOGICAL ANALYSIS

The morphology of un-carbonated and carbonated FA was evaluated by SEM (Fig. 4). This was in an attempt to evaluate the changing morphology as a result of carbonation and subsequent formation of secondary mineral phases.

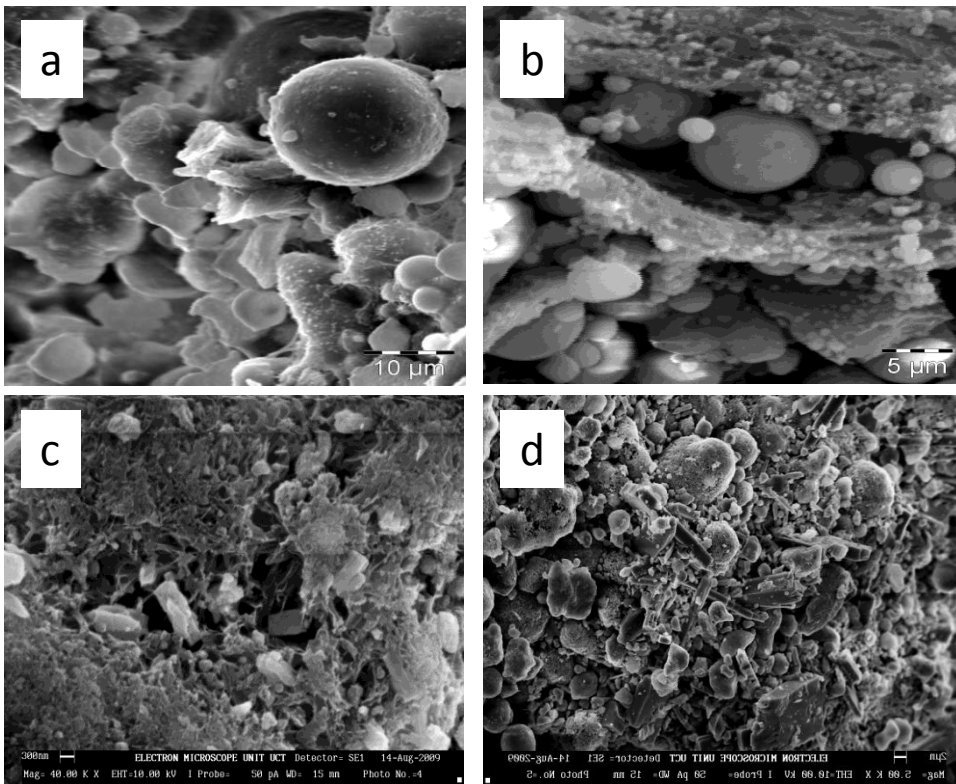


Figure 4: SEM micrographs showing un-carbonated (a & b) and carbonated (c & d) FA.

Micrographs of fresh un-carbonated South African FA show the presence of spherical particles (Fig. 4a), cenospheres (Fig. 4a) and plerospheres (Fig. 4b). The fine fraction of FA particles are typically well-rounded, solid spheres and the larger particles within the larger size fraction samples contain a few particles up to $0.5 \mu\text{m}$ with cenospheres common and an occasional plerosphere. Some of the larger particles are vesicular (i.e. made up of small spherical or oval cavity). Pieterse¹⁰ attributes the origin of the vesicles to generation of gases and vapors such as CO , CO_2 , SO_2 and H_2O giving FA its light weight characteristics. The carbonated FA however shows “cubic-like” structure of calcite (Fig. 4c); while in Fig. 4d “needle-like” structures of aragonite are observed. This was confirmed by XRD analysis (Fig. 5 and 6). Carbonation thus resulted in the transformation of the ash morphology due to formation of secondary phases such as calcite and aragonite. Similar morphologies of carbonated FA have been reported^{11,12,13} and calcite was identified as the main polymorph of CaCO_3 formed during the carbonation process.

X-RAY DIFFRACTION ANALYSIS OF FRESH ASH AND CARBONATED ASH

The diffraction pattern of the fresh un-carbonated ash as well as the carbonated ash are shown in Figures. 5 and 6 .

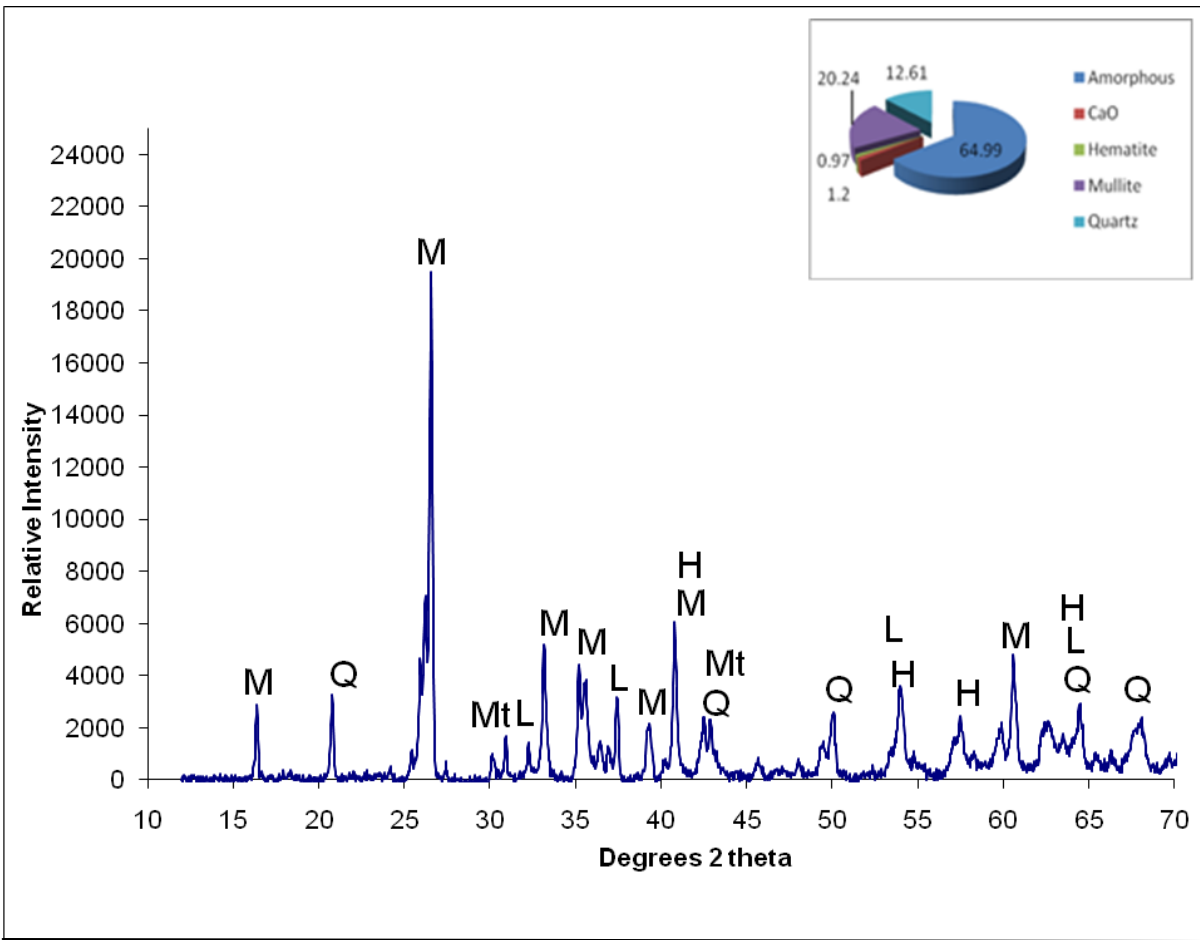


Figure 5: XRD spectrum and quantification of mineral phases in fresh FA; M (mullite), Q (quartz), Mt (magnetite), L(lime), H (hematite).

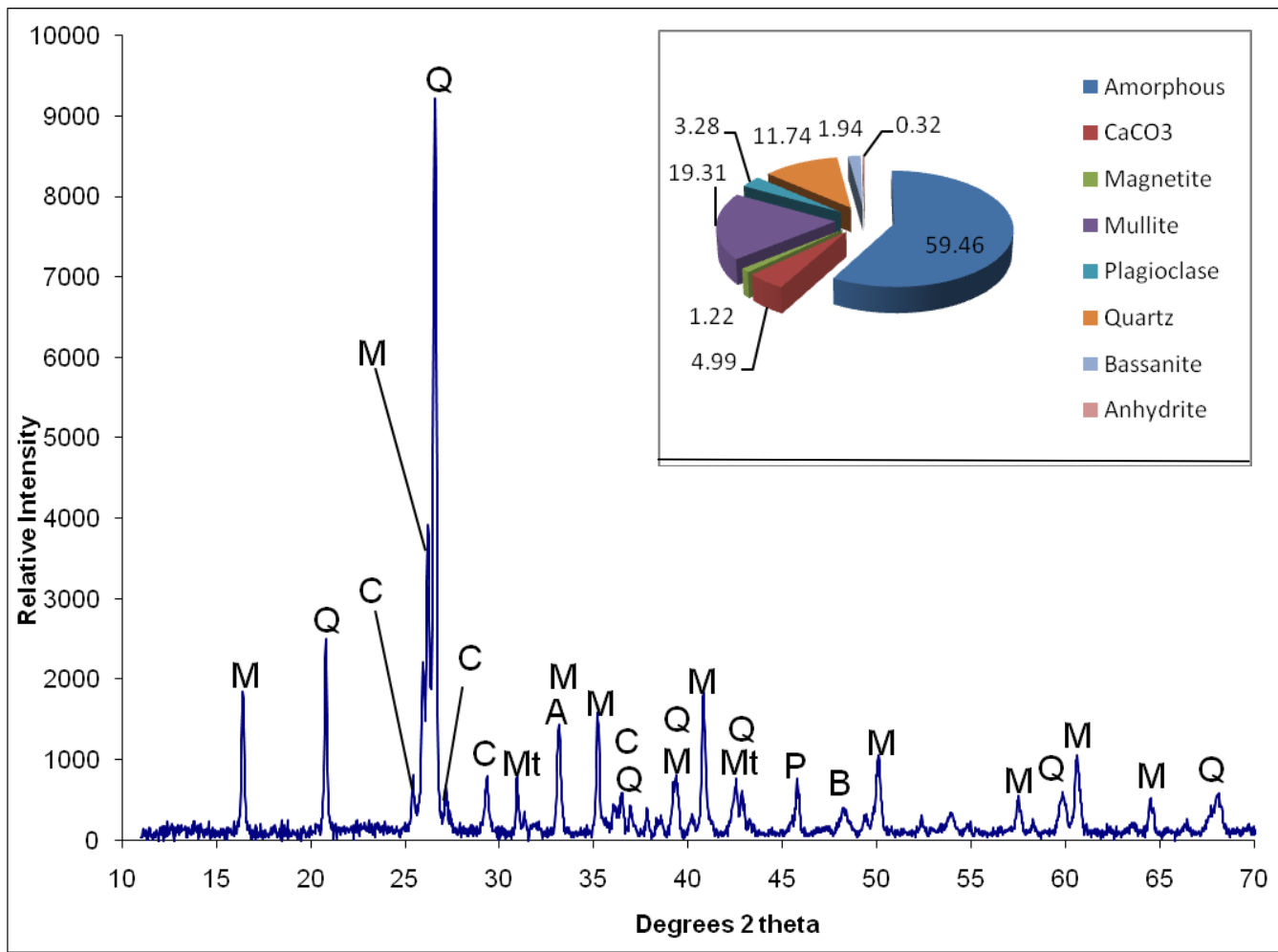


Figure 6: XRD spectrum and quantification of mineral phases for carbonated FA; (90 °C, 4 Mpa, bulk ash at a S/L ratio of 1); M (mullite), Q (quartz), C (calcite), A (anhydrite), P (plagioclase), B (bassanite), Mt (magnetite).

The CaO fraction present in the pre-carbonated ash (Fig. 5) is converted to calcite in the post-carbonated ash. Presence of calcite peak can be observed (Fig. 6) thus XRD confirmed the conversion of CaO to calcite during the carbonation process confirming the observations made from the SEM morphology for the carbonated ash.

COMPARATIVE STUDY OF THE FORMED CALCIUM CARBONATE

Figure 7 shows correlation of the mass % CaCO₃ yield as determined by quantitative XRD and Chittick tests. The two methods were applied in quantifying the mass % of CaCO₃ formed in the carbonation process.



Figure 7: Correlation of mass % CaCO₃ yield determined by quantitative XRD and Chittick test.

As is evident from Figure 7, the mass % of CaCO₃ could be determined by both methods. A strong correlation was observed except for runs R2, R14, R24, R25, R27 and R29. Statistical testing was carried out to determine whether Chittick tests gave a better estimate of the % CaCO₃ than XRD. Student t-test statistic was applied to test the hypothesis that Chittick test gave a higher overall % CaCO₃ yield than XRD.

The t-test calculations indicated the calculated value of t of 2.198 was greater than the tabulated value of 1.701. The null hypothesis was thus rejected and it was concluded that Chittick analysis gave a higher overall % CaCO₃ yield. Calculation of Pearson correlation coefficient gave a value of 0.799 which is indicative of a relatively high degree of correlation.

CARBONATION EFFICIENCY OF THE FRACTIONATED SOUTH AFRICAN FA

For pure oxides (e.g. CaO and Ca(OH)₂), the theoretical extent of carbonation is a function of basic stoichiometry (equation 1)¹⁴:



Using the simple equation of mass = moles * molar mass, and bearing in mind that the molar ratio is 1:1, it follows that every ton of CaO can potentially sequester up to 799 kg of CO₂. For wastes such as FA, the theoretical extent of carbonation can also be calculated as a function of stoichiometry, though in this case the extent of carbonation will also depend on the availability of the oxides for reaction. Theoretically the maximum CO₂ uptake capacity can be calculated as a function of the chemical composition of the original material in this case fly ash, using the Stenoir formula (equation 2)¹³:

$$\text{CO}_2 (\%) = 0.785 (\% \text{ CaO} - 0.7 \% \text{ SO}_3) + 1.09 \% \text{ Na}_2\text{O} + 0.93 \% \text{ K}_2\text{O} \dots \dots \dots (2)$$

The stoichiometric mass factors shown in Eq. (2) assumes that all of the CaO (except that bound in CaSO₄ and CaCO₃) will react to form CaCO₃, all the MgO will react to form MgCO₃, and all of Na₂O and

K₂O will convert to Na₂CO₃ and K₂CO₃. The mass factors for K₂O and Na₂O are doubled if bicarbonates form instead of carbonates¹⁴. Furthermore the degree of carbonation is strongly dependent upon calcium content, though the presence of certain components might influence the effective diffusivity and reactivity of the CO₂.¹³

Using equation 4 and the data in Table 1 for the different oxides present in the different partitions of the fresh FA, the maximum % CO₂ uptake for all the FA size fractions can thus be calculated (Table 3)

Table 3: Maximum % CO₂ uptake for different size fractions.

Particle size	Bulk ash	> 150 μm	150- 106 μm	106 - 90 μm	90 - 75 μm	75- 63 μm
% CO ₂	8.25	5.16	7.96	8.45	9.01	8.39
Particle size	63-53 μm	53-45 μm	45 -32 μm	32-25 μm	25-20 μm	< 20 μm
% CO ₂	8.49	8.30	8.30	8.07	7.830	8.12

From Table 3 above, it means that theoretically, assuming all available oxides react to form carbonates, the sequestration capacity of bulk fly ash for instance is 8.25 % i.e. for every 1 ton of bulk FA, 82.54 kg of CO₂ can be sequestered. Bearing in mind that the 20 -150 μm fraction was combined as one and its average CaO was 9.3 % the % CO₂ uptake would theoretically amount to 8.31 % meaning that the for every ton of 20 -150 μm fraction, 83.15 kg of CO₂ could be sequestered. It is thus clear that the higher the lime content of a fraction the higher the sequestration capacity of that fraction. The >150 μm fraction which had the lowest lime content (Table 1) gave the lowest theoretical % CO₂ sequestration capacity. CaO in the FA is the main source of the Ca²⁺ though the Ca²⁺ in brine also contributes towards the total Ca cations available for carbonation. Fernandez et al¹³ evaluated the effect of particle size in carbonation of municipal solid waste incinerator (MSWI) ash and observed that carbonation was higher with smaller particles sizes. They attributed this observation to the higher CaO content of the smaller particle sizes, homogeneity of the particle sizes as well as the higher surface area of these particles.

Knowing the pressure drop due to carbonation, the amount of CO₂ consumed by carbonate precipitation can be calculated using the ideal gas law^{11,12} as follows:

$$n_{CO_2} = \frac{P_{carbonation_pressure_drop}V}{RT} \dots\dots\dots(3)$$

Where V is the reactor volume occupied with gas. The teflon liner used together with the steel jacket was not a tight fit and hence the volume of gas was assumed to be the volume of the steel jacket minus volume of the teflon liner minus the volume occupied by the solid and liquid mixture in the teflon. The teflon volume was calculated by a simple displacement experiment where the volume displaced by the teflon was taken to be its volume (observed to be 200 cm³). The volume of the steel jacket was calculated from the equation for the volume of a cylinder i.e $V = \pi r^2 h$, (r = radius of the jacket (3.15 cm), h = height of the steel jacket (15 cm) which gave a value of 467.65 cm³. V was calculated for each run and the data used to calculate nCO₂ values for the runs. After the calculation of nCO₂, the carbonation efficiency (CE) of each run was calculated using equation 4.^{11,12}

$$CE = \frac{n_{CO_2} \cdot M_{CO_2}}{W_{CaO} \cdot M_{CaO}} * 100 \dots\dots\dots(4)$$

Where n_{CO₂} is the number of moles consumed, calculated by equation 3 above, M_{CO₂} is the molar mass of CO₂ (44.01 g/mol), W_{CaO} is the starting mass of the CaO in the reactor (the corresponding amount of

CaO in the size fraction in grams as seen in Table 1) and M_{CaO} is the molar mass of CaO (56.077 g/mol).

Applying Eq. 4 above and the information given in Table 3, the carbonation efficiency of fractionated FA was calculated, bearing in mind the conditions for each run. From Table 3, it can be observed that theoretically one ton of the 20 -150 μm fraction can sequester 83.15 kg of CO_2 . Bearing in mind the CE of this fraction it follows that a ton of this particle size range will actually sequester 71.8 kg of CO_2 . A total of 31 runs were carried out but only runs with $\text{CE} > 60$ and selected runs at 1Mpa pressure are shown in Table 4.

Table 4: Carbonation efficiencies (CE) for the various experimental runs.

Run no.	Temp (°C)	Pressure (Mpa)	Particle size (µm)	S/L ratio (g/ml)	Initial pressure (Mpa)	Final pressure (Mpa)	Pressure Drop due to carbonation	nCO ₂	CE (%)
5	90	4	>150	0.5	4	1.03	2.97	0.074197	70.59
10	30	4	Bulk	0.5	4	1.52	2.48	0.11616	70.82
14	90	4	<20	1	4	0.59	3.41	0.120327	78.15
20	30	4	Bulk	1	4	0.34	3.66	0.10126	61.73
21	90	4	<20	0.5	4	0.83	3.17	0.123937	80.5
22	30	4	<20	1	4	0.21	3.79	0.104856	68.1
23	30	1	Bulk	0.5	1	0	1	0.046839	28.56
26	90	1	20-150	0.1	1	0.07	0.93	0.004622	2.79
27	90	1	Bulk	0.5	1	0.07	0.93	0.03636	22.17
28	30	4	20-150	0.5	4	0.14	3.06	0.1433	86.4
29	30	1	>150	0.1	1	0.14	0.86	0.005121	4.87
31	90	4	Bulk	1	4	0.83	3.17	0.111858	68.2

It is evident (Table 4) that the input factors of pressure, temperature and particle size vary across the table. Overall, high pressure of 4 Mpa was necessary while both the temperatures (30 °C and 90 °C) gave high carbonation efficiency values.

The sequestration potential was calculated for the highlighted runs (i.e, runs 5, 10, 14, 20, 28 and 31) and the sequestration potentials per tonnage of fly ash are shown in Figure. 9 based on the different size fractions applied.

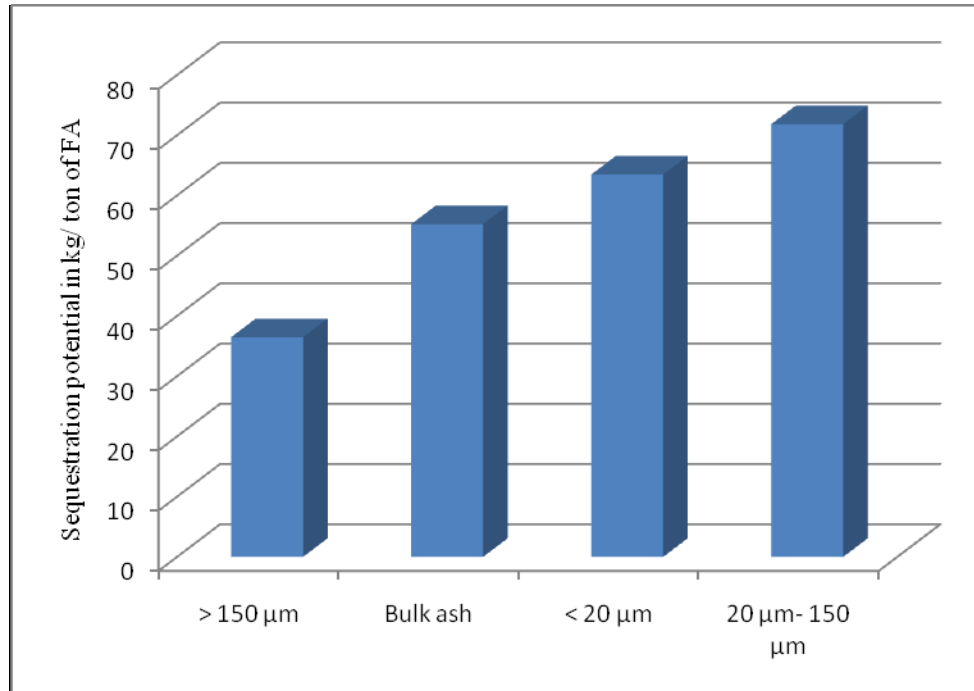


Figure 9: Sequestration potential of the different size fractions.

It can be concluded that based on particle size, the fraction with the highest CO₂ sequestration potential is the 20-150 μm while the least potent is the > 150 μm fraction. Montes-Hernandez et al.¹² in their study on the carbonation of non-fractionated FA obtained a carbonation efficiency of 82 % after 18 hours of carbonation at 30 °C. However the sequestration potential of their ash was lower i.e, 26.19 kg of CO₂ per ton of FA as opposed to the value of 62.35 kg of CO₂ per ton of bulk FA observed in this study. This is attributable to two factors, firstly, the fractionated FA used in this study (Table 1) had a higher CaO content as opposed to theirs with a value of 4.1 % of CaO and secondly, they used water for the carbonation experiments whereas brine was used in this study. This confirms that brine contributes additional Ca²⁺ for the carbonation process.

COMPARISONS OF ULTRAPURE WATER AND BRINE AS THE FA DISPERSION MEDIA IN THE CARBONATION EXPERIMENTS.

Carbonation was also carried out for Run R31 with ultra-pure water (at 4 Mpa, 90 °C, using bulk ash at a S/L ratio of 1) to compare the results with the findings from Montes-Hernandez et al.¹² and to determine the significance of using brine in place of ultra pure water. Table 5 gives a comparison of the aqueous extract (leachate) recovered after carbonation using either ultra-pure water or RO brine solutions.

Table 5: Concentrations of the raw brine, leachates obtained after carbonation using brine or ultra-pure water

Element	Raw brine (ppm)	Run 31 (ultrawater) (ppm)	Run 31 (brine) (ppm)
K	104.1±0.31	23.532±1.35	9.75±0.17
Al	0.044±0.06	0.063±0.01	Nd
As	0.007	0.003	Nd
B	NA	64.039±0.16	2.72±0.06
Ca	101.76±0.15	26.851±1.14	25.5±1.02
Co	0.015±0.01	Nd	0.002
Cr	0.014±0.01	0.010	0.001
Cu	0.067±0.02	0.044±0.01	Nd
Fe	0.051±0.01	0.030	Nd
Mg	158.73±1.24	103.238±2.01	1.522±0.02
Mn	0.082±0.03	Nd	Nd
Mo	0.039±0.01	1.204±0.03	0.069±0.01
Na	4315±2.18	58.048±0.09	3201±1.92
Ni	0.116±0.01	0.112±0.01	Nd
Se	0.004	0.094±0.01	Nd
Sr	3.030±0.11	2.019±0.12	Nd
V	0.016±0.01	4.559±0.81	0.15±0.01
Zn	0.100±0.01	0.140±0.01	Nd
Cl	2036±3.26	Nd	2193±2.03
SO ₄	9488±2.22	Nd	7511±1.57
NO ₃	8.565±0.61	Nd	Nd

NA - not analyzed; Nd- not detected.

The observation of lower concentrations of the various elements in the brine carbonated leachates can be attributed to the co-precipitation of the brine components with CaCO₃ as was suggested by Mooketsi et al.¹⁵ Table 5 shows that majority of the trace elements have a higher concentration in the water leachates than in the brine leachates except for Na. The Na content of the brine leachates is very high (3201 ppm) compared to the water leachates (58.05 ppm). From the brine classification given in Figure 3, it had been noted that the brine used were Na-Cl-SO₄ rich solutions hence the high Na content for the brine leachate compared to the Na content of the water/FA leachates. The magnesium content of the water leachates is higher than that for the brine leachates, 103.24 ppm and 1.522 ppm respectively. This signifies that Mg in brine takes part in the carbonation, though magnesite was not identified using XRD, maybe due to very low quantities being formed.

Quantification of the solid residues obtained after carbonation using water or brine for Run R31 was carried out to evaluate the effect of the liquid media used for fly ash dispersion on the relative amounts of the phases formed. Figure. 10 below shows the variation in the relative amounts of the mineral phases quantified in the solid residues recovered after water or brine carbonation.

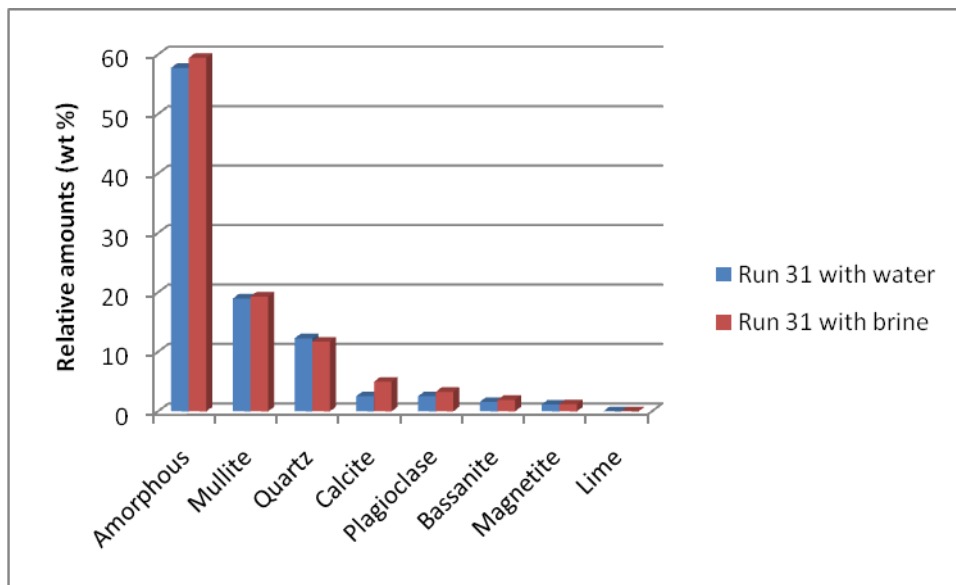


Figure10: Quantification of the phases present in the carbonation solid residues.

It is noted that the degree of calcite formation is higher in the brine carbonated residues compared to the water carbonated residues. The results confirm that brine contributes additional Ca^{2+} that enhances the degree of carbonation. Also evident is the fact that no lime was present in either the water or brine residues. The explanation for this would be that the lime in the brine reactions raised the brine pH for carbonation to occur while the lime in the water reactions hydrolyzed to the hydroxide form that later transformed to CaCO_3 . In both cases the lime dissolved to release Ca^{2+} and hydroxyl ions which contributed to the increase in pH.

CONCLUSIONS

Brine impacted class F size fractionated fly ash has been carbonated under various conditions of pressure, temperature and L/S ratio. Chemical analysis of the size fractionated fly ash showed that the 20-150 μm fraction had the highest % CaO (9.3 %) while the > 150 μm fraction had the least % CaO (5.89 %). Main trace elements present in FA were S, Sr, Ba, Zr, Mn, Cr and V. Cu, Ni, Zn, Ba, Sr, Cr and V. The trace species showed an increasing trend with decreasing FA particle size. Mn however showed no trend while Sr, S, Y, Th, Rb, Pb and Nb showed limited concentration trends. Chemical analysis showed that the RO brine solutions applied in this study could be classified as Na-Cl- SO_4 with major ions being Ca, K, Mg, Cl, SO_4 and Na.

The morphology of FA changed after carbonation from spherical particles, cenospheres and plerospheres to cubic-like structures of calcite and needle-like structures of aragonite. XRD confirmed the transformation of the CaO fraction in the un-carbonated FA to calcite in carbonated ash. Chittick tests and quantitative XRD gave a reliable measure of correlation of the % CaCO_3 yield for the different experimental conditions applied. Statistical testing however showed that Chittick tests to be a better estimator of the % CaCO_3 yield than XRD.

This study has clearly shown that the carbonation efficiency of fractionated FA is dependent upon the relative amount of CaO present in that fraction. From our experiments, the 20-150 μm fraction whose CaO content was 9.3 % had the highest carbonation efficiency and sequestration potential of 71.84 kg of CO_2 per ton of FA. The main product of the carbonation was observed to be calcite. Furthermore the study showed that carbonation of FA using brine leads to higher carbonation efficiency as the brine contributes Ca^{2+} which converts to CaCO_3 during the carbonation process.

The study has shown the feasibility of utilizing the two “waste products” i.e. FA and brine in the sequestration of CO₂. This would lower the treatment cost for RO effluents and contribute to brine stabilization in the form of mineral carbonates. Bearing in mind that some CO₂ point sources already produce pressurized and purified CO₂ emissions, these streams could be applied for carbonation at the source point as they do not require further purification or pressurization, thereby contributing towards cost reduction for CO₂ sequestration.

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