



## Comparison of CO<sub>2</sub> capture by ex-situ accelerated carbonation and in in-situ naturally weathered coal fly ash

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### Abstract

Natural weathering at coal power plants ash dams occurs via processes such as carbonation, dissolution, co-precipitation and fluid transport mechanisms which are responsible for the long-term chemical, physical and geochemical changes in the ash. Very little information is available on the natural carbon capture potential of wet or dry ash dams. This study investigated the extent of carbon capture in a wet-dumped ash dam and the mineralogical changes promoting CO<sub>2</sub> capture, comparing this natural phenomenon with accelerated *ex-situ* mineral carbonation of fresh fly ash (FA). Significant levels of trace elements of Sr, Ba and Zr were present in both fresh and weathered ash. However Nb, Y, Sr, Th and Ba were found to be enriched in weathered ash compared to fresh ash. Mineralogically, fresh ash is made up of quartz, mullite, hematite, magnetite and lime while weathered and carbonated ashes contained additional phases such as calcite and aragonite. Up to 6.5 wt % CO<sub>2</sub> was captured by the fresh FA with a 60% conversion of calcium to CaCO<sub>3</sub> via accelerated carbonation (carried out at 2 h, 4Mpa, 90 °C, bulk ash and a S/L ratio of 1). On the other hand 6.8 wt % CO<sub>2</sub> was found to have been captured by natural carbonation over a period of 20 years of wet disposed ash. Thus natural carbonation in the ash dumps is significant and may be effective in capturing CO<sub>2</sub>.

### 1. Introduction

Owing to the heavy reliance on fossil fuels for power generation in the world today, the level of carbon emissions has risen leading to enhanced global warming which is accompanied by climate change in various parts of the world (IPCC, 2007). Globally coal combustion accounts for over 42% of the carbon emissions while in South Africa, the electricity generating industry produced 230.3 Mt of CO<sub>2</sub> in 2011 (Eskom, 2011). Curtailing the CO<sub>2</sub> emissions from coal combustion is thus vital in climate change mitigation. Various mechanisms are being sought to deal with carbon emissions reduction and global warming mitigation. Among these are carbon capture and storage (CCS) in geological formations (e.g. deep saline reservoirs, unminable coal beds, depleted oil/gas reservoirs, basaltic rocks, enhanced coal bed methane, enhanced oil recovery etc.). Mineral carbonation is an increasingly promising option within the CCS portfolio

(Doucet, 2011) and demonstration plants of up to 1 Mt CO<sub>2</sub> per annum may be operational as early as 2020 (Zevenhoven et al., 2011). There are large deposits of natural silicate minerals that can be used for mineral carbonation, in addition to alkaline waste materials such as FA, steel furnace slag, cement slag and mine tailings.

One of the advantages of mineral carbonation over geo-sequestration is the stability of the formed carbonated products over extended periods of time. Thus there would be little need to monitor the disposal sites and the associated risks would be very low. Eskom, the main power generator in South Africa, consumed 124.7 Mt of coal producing 36.2 Mt of FA in 2011 (Eskom, 2011). Only 5% of generated ash is recycled in the form of building materials such as bricks and as a cement extender while the unused FA is disposed in ash handling dams which require maintenance and eventual rehabilitation. Water requirements are high in power generation; for instance the Sasol Secunda plant (South Africa) uses 255 Ml/day of fresh water for steam generation, process cooling and as feed water for its coal to liquid fuel and other chemical processes.

Pre-treatment of raw water (consisting of 90% mine water and 10% cooling water blow down) by desalination leads to the formation of waste brines. These are highly saline solutions usually containing total dissolved solids (TDS) of over 35,000 mg/L and enriched in Ca, Na, K, SO<sub>4</sub>, Cl and Mg (Petrik et al., 2007). Also present are traces of Fe, Mn, Cr, V, Ti, P, Si and Al (Mooketsi et al., 2007). In Secunda for instance, the brine streams are used for the hydraulic transport of FA usually in the form of a slurry which is then stockpiled in ash dams. Ingress of atmospheric CO<sub>2</sub> is believed to influence the weathering and maturation of FA. Basic oxides such as lime, portlandite and periclase present in FA are expected to convert to their respective carbonate forms with time (Yeheyis et al., 2009).

Accelerated mineral carbonation which mimics natural weathering processes in which calcium or magnesium silicates are transformed into carbonates could be significant in the proximity of the emission sources without the need of storing the gas into geological reservoirs. Several authors have noted that carbonation is effective in minimizing build-up of calcium in the leachate of landfills thus carbonation may reduce the mobility of trace metals in alkaline FA at elevated pH values (Reddy et al., 1994; Meima et al., 2002; Ecke, 2003; Kim et al., 2003). Carbonation has also been investigated as a technology for the stabilization of municipal solid waste incineration (MSWI) ash prior to disposal (Ecke (2003); Ecke et al. (2002); Wu-Jang et al. (2007) and Rendek et al. (2006)). Various authors (Montes-Hernandez et al. (2009); Soong et al. (2006) and Muriithi et al. (2011)) have studied the carbonation potential of coal combustion FA. They suggested that carbonation occurs in two successive reactions, firstly the irreversible hydration of lime present in the ash and secondly the spontaneous carbonation of the calcium hydroxide suspension. This paper seeks to investigate natural carbonation as a stabilization reaction during environmental weathering and as a CO<sub>2</sub> capture process, probing the mineralogical changes occurring and to compare this with accelerated

carbonation. The novelty of this study was first to investigate the potential of ash dams to capture CO<sub>2</sub> in the natural set-up as well as to compare the CO<sub>2</sub> capture capacity of the ash dams to accelerated *ex-situ* mineral carbonation in terms of time factor and the resultant changes in the carbonated ash and weathered ash. It is envisaged that this study will form a basis for further studies involving natural carbonation phenomena in the ash disposal sites.

## **2. Materials and methods**

### **2.1. Sample collection, preparation and characterization**

Both fresh and weathered coal FA was obtained from Secunda power plant owned by Sasol Synfuels (the petro-chemical company in South Africa).

For the weathered ash, a combination of air flush coring and direct circulation air percussion drilling were used to drill the boreholes at the ash dam while fresh ash was obtained directly from the precipitators. Air flush coring uses a conventional drilling rig and compressor with a specialized drill bit that cores the ash without the need for water or lubrication for cooling of the drill bit (Fig. 1 below).

The advantage of using this air drilling technique is that the coring method does not use water to cool down the drill bits as in normal rock coring. The samples therefore remain chemically unchanged and physically intact. An initial starter hole was drilled using air percussion through the overburden, to the top of the ash dam. The air flush coring technique was then used further down to the bottom of the ash (Akinyemi et al., 2012). Fresh FA was characterized and used in the carbonation experiments in the laboratory while weathered ash was characterized and evaluated for CO<sub>2</sub> capture potential. The power plant applies wet disposal technique for its ash disposal and the specific site cored has an approximate age of 20 years. During wet disposal, FA is mixed with brine effluents from the water circulation system to form a slurry which is transferred to the disposal site via pipes. The slurry is then stacked in a “pancake-like layering” as each layer is left to settle for some time before the next layer can be dumped. The ash settles and the brine percolates into clear effluent dams where the salty water is recycled. A schematic of the ash handling system at the power station is shown in Fig. 2.

An Abem SAS 1000 terrameter and ES 464 switching unit were used for geophysics survey. The electrical resistivity method was applied to establish variations in ash characteristics, salt deposition and water level distribution in the subsurface. Four multicore cables and stainless steel pegs were used with the “roll-along” surveying method. Measurement of the ground resistivity was carried out by transmitting a controlled current ( $I$ ) between two electrodes pushed into the ground, while measuring the potential ( $V$ ) between two other electrodes. The resistance ( $R$ ) was calculated using Ohm’s law. The profile was surveyed using a 10 m electrode separation with the Schlumberger protocol up to a depth of approximately 80 m.

The elemental and mineralogical compositions of fresh and carbonated FA samples were analysed using XRF (Philips PW 1480 X-ray fluorescence spectrometer equipped with a chromium tube operating at 40 kV and 50 mA for major elements and at 50 kV and 40 mA for trace elements) and XRD (PANanalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence and receiving slits with Fe filtered Co-Ka radiation) respectively. Morphological analysis of fly ash samples was performed using high vacuum SEM (Hitachi X-650 Scanning Electron Microanalyser equipped with a CDU-lead detector at 25 kV and a tungsten filament). Anions in the brine were analyzed using a Dionex DX-120 ion chromatograph with an Ion Pac AS14A column and AG14-4 mm guard column. Major cations on the other hand were analyzed using a Varian Radial ICP-OES, while trace cations were analyzed on an Agilent 7500ce ICP-MS, using a High Matrix Introduction (HMI) accessory and He as collision gas.



Fig. 1. Air flush core barrel and core inside the barrel.

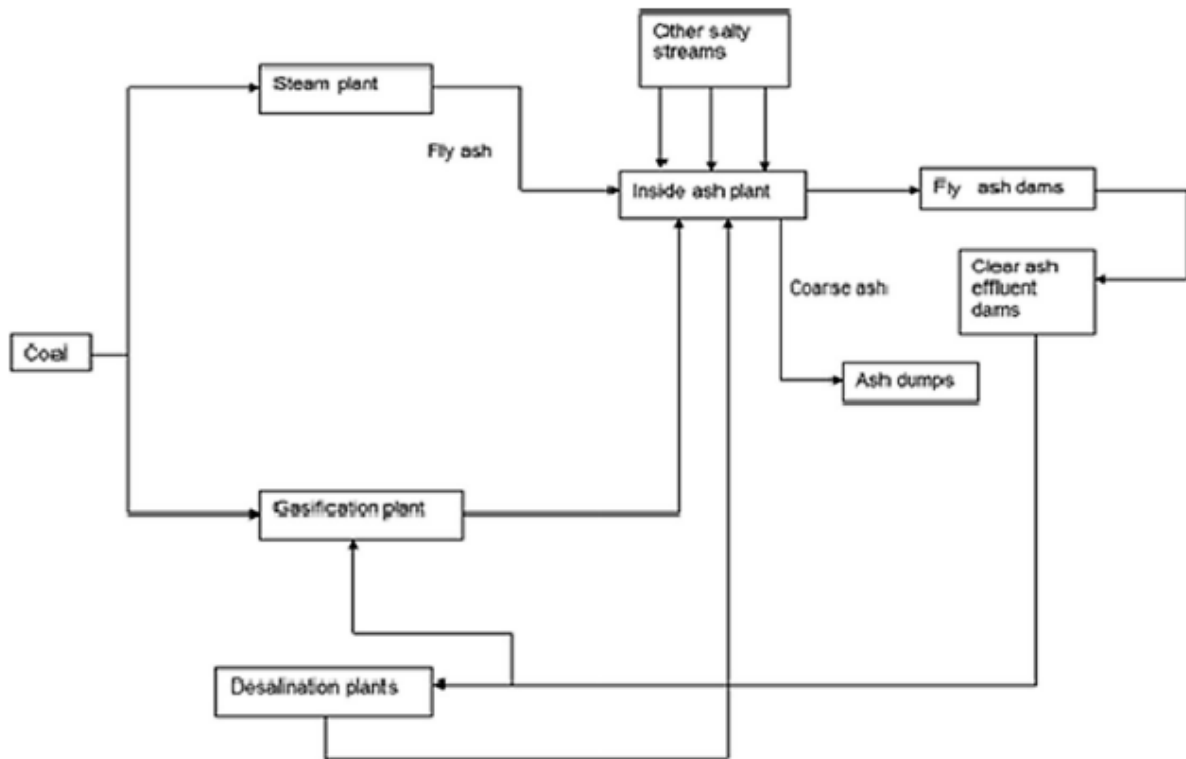


Fig. 2. Waste handling process at Secunda (Mahlaba, 2007).

The total carbon content of weathered ash was determined by carbon and sulfur analysis (C&S) (Eltra CS 800 Double Dual Range system equipped with four infrared absorption detectors), while their carbonate content was obtained using Chittick tests according to Dreimanis (1962). The Chittick tests were done by reacting FA suspensions (1.70 g of FA suspended in a 1-L solution containing 100 g of NaCl, 1 g of NaHCO<sub>3</sub>, 2 ml of methyl orange, where sufficient H<sub>2</sub>SO<sub>4</sub> was added to turn the solution a deep pink color) with 20 ml of 6 N HCl and recording the amount of CO<sub>2</sub> evolved by reading the displacement of the reservoir fluid. The displacement of the colored liquid in the burette by evolving CO<sub>2</sub> was read after 1 min and after 20 min. The reading at 1 min was recorded as  $R_1$  while that at 20 min was recorded as  $R_{20}$ . A schematic representation of the Chittick test set-up is illustrated in Fig. 3.

Correction factors were calculated for each reading and used to determine the % CaCO<sub>3</sub>. This was done by reacting 0.10 g of pure CaCO<sub>3</sub> through the same process as for the FA samples. The factor is given as:

$$f = \frac{W*T}{1.22*V} \quad (1)$$

where:

W = weigh of pure CaCO<sub>3</sub> (g)  
T = temperature of measurement (K)  
V = volume of CO<sub>2</sub> produced (ml)

The above correction factor was used to calculate the % CaCO<sub>3</sub> (based on 1.7 g of dried FA) as follows:

$$E = CR - (0.04)(CR_{20} - CR_1) \quad (2)$$

Where

CR<sub>1</sub> = reading at 1 min \*f  
CR<sub>20</sub> = reading at 20 min \*f  
%CaCO<sub>3</sub> = 0.232E

## 2.2. Accelerated mineral carbonation

Four parameters were investigated in the accelerated carbonation experiments. These include particle size (<20 μm, <150 μm, > 150 μm and bulk ash), temperature (30 °C or 90 °C), pressure (1 Mpa or 4 Mpa) and solid (FA) to liquid (brine) ratio (S/L; 0.1, 0.5 or 1). 80 ml of brine was used in all the experiments. The FA/brine dispersions were carbonated in a high-pressure Parr reactor with an internal volume of 600 ml, maximum pressure of 34.5 Mpa and maximum temperature of 350 °C. A statistical design was utilized to generate the experiments by inputting the various levels of the chosen parameters and generating a D-Optimal model. A table of the input factors considered in the statistical design is given in Table 1.

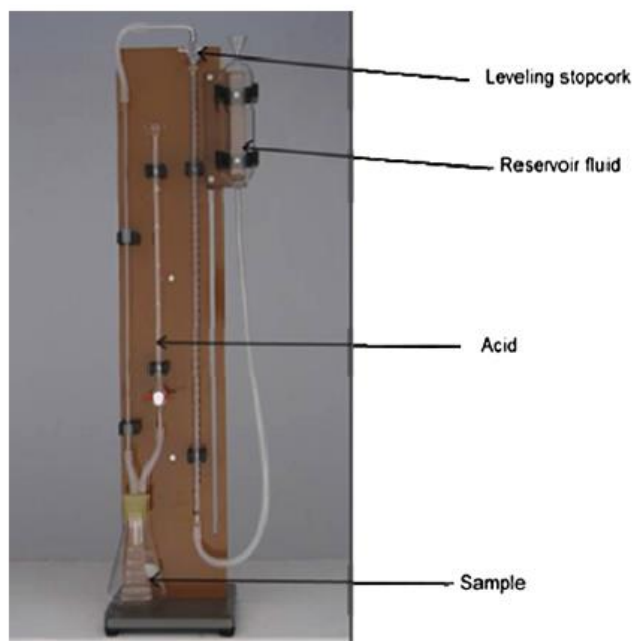


Fig. 3. Picture of the Chittick test apparatus used.

**Table 1**

Table of input factors and response factor for accelerated mineral carbonation as generated by the design of experiments (DOE) software.

	Factor 1	Factor 2	Factor 3	Factor 4
Run No.	A:Pressure Mpa	B:Temperature °C	C:Particle size µm	D:S/L ratio g/ml
R1	1	90	<20	0.5
R2	1	90	<150	0.5
R3	4	90	Bulk	0.1
R4	1	30	<20	0.5
R5	4	90	>150	0.5
R6	1	90	<150	1
R7	1	90	>150	0.1
R8	1	30	<150	0.1
R9	4	90	<150	0.1
R10	4	30	Bulk	0.5
R11	4	90	<150	0.1
R12	1	30	Bulk	0.1
R13	4	30	<150	1
R14	4	90	<20	1
R15	4	90	>150	1
R16	1	30	Bulk	1
R17	1	30	<20	0.5
R18	1	30	<20	0.1
R19	1	30	>150	0.5
R20	4	30	Bulk	1
R21	4	90	<20	0.5
R22	4	30	<20	1
R23	1	30	Bulk	0.5
R24	4	90	<20	0.1
R25	4	30	>150	0.1
R26	1	90	<150	0.1
R27	1	90	Bulk	0.5
R28	4	30	<150	0.5
R29	1	30	>150	0.1
R30	1	90	>150	1
R31	4	90	Bulk	1
R32	4	30	>150	1

The FA/brine dispersion was placed inside the Teflon liner in a high-pressure vessel. 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 CO<sub>2</sub> feed line was then attached. The system was then purged three times with CO<sub>2</sub> at 0.05 Mpa to ensure that all the air was expelled. After the final purge, the heating of the system began. When the specified temperature was reached, CO<sub>2</sub> (technical grade) was charged into the reactor to achieve the specified testing pressure. The FA/brine/CO<sub>2</sub> mixture was then stirred at 600 rpm for 2 h. 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 min during the water cooling period. Upon cooling to room temperature, the reactor was disassembled, and the solid product was separated by centrifugation (30 min at 6000 rpm), thereafter the supernatant solutions were decanted. Finally, the solid product was dried in an oven for 8 h at 90 °C.

### 3. Results and discussions

#### 3.1. Geophysical mapping of the dam

Geophysical mapping of the ash dam was done at the specified sites with different salt content as seen in Fig. 4.

Core S1 was drilled at 960 m (latitude 26.560411, longitude 29.119348), Core S2 was drilled at 800 m (latitude 26.559099, longitude 29.119039) and S3 was at 600 m (latitude 26.557826, longitude 29.118943) along a fault line (marked f on the tomograph) (Fig. 5). The surface of the three cores is of medium resistivity between 9.3 and 12.2  $\Omega$  as shown by the color scheme scale at the bottom of the tomograph. The mid-section for all the three cores is of low resistivity of between 4 and 7  $\Omega$ . The base section however varies for the three cores with S1 at above 28.3  $\Omega$ , S2 at 16.2e21.4  $\Omega$  and S3 at 12.2e16.2  $\Omega$ . Resistivity is inversely proportional to conductivity according to Ohms law and thus the higher the resistivity the lower the conductivity, further implying the lower the salt content. This means the salt content at the base of S1 is the lowest while S3 has the highest salt load at the base. This information is collaborated by the moisture content data in Fig. 6 below. It is assumed that the site is underlain by dolerite and that no ash was dumped north of the existing dam in the past. The red-brown contours are associated with less weathered to fresh dolerite while the purple contours at the bottom of the profile are associated with highly weathered dolerite as has been reported previously by Akinyemi (2011). Between 560 and 880 m, the red contours are not present indicating a highly conductive region. The implication is that the ash leachate is in direct contact with the bed rock and hence there is potential for ground water pollution. An investigation of the moisture content in the three cores is given below.

Unlike cores S2 and S3, core S1 had higher moisture content at the surface. For S2 and S3, the samples deeper down the profile were water logged and paste like in nature. The higher moisture values at lower depths are due to hydraulic seepage of rain water or the brine used to slurry the ash and gravitational forces. Differences in the moisture content distribution can be attributed to the uneven preferential flow paths due to inconsistent placement conditions or variations in ambient weather conditions during placement. The high water content in the ash dam leads to the flushing out of the soluble elements in the ash down the depth profile.



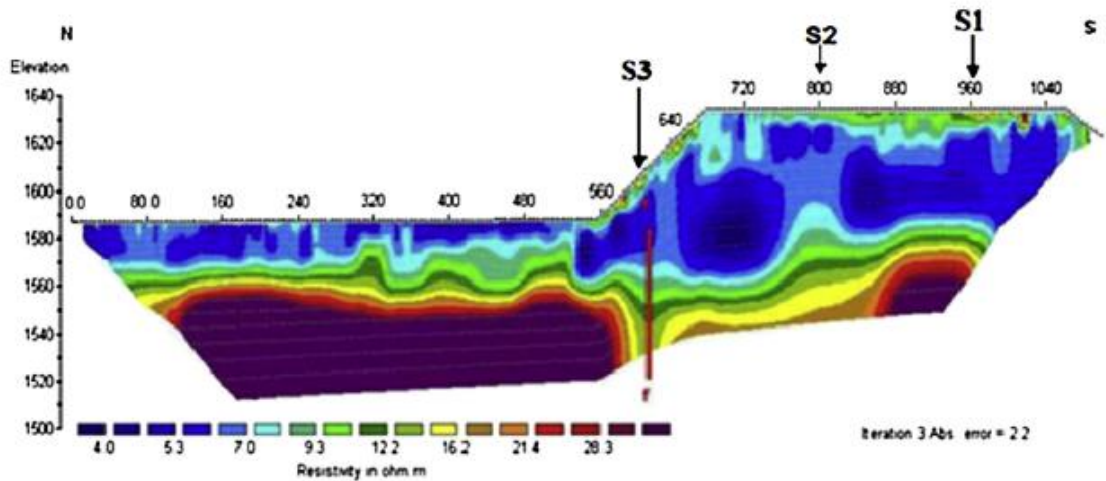


Fig. 4. Resistivity tomograph of the three cores obtained.

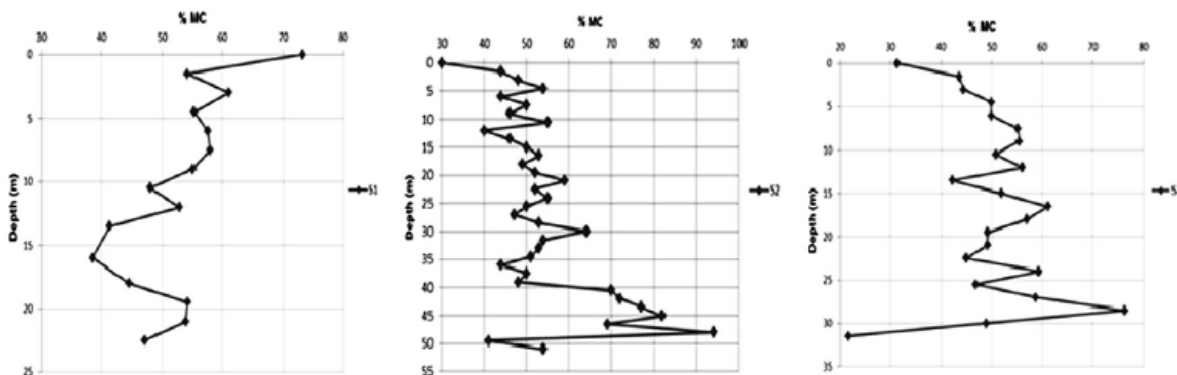


Fig. 5. Percentage moisture content of the three cores ( $n = 3$ ).

### 3.2. Brine analysis

Analysis of the brine solutions used for the carbonation is given in Table 2 below.

The solutions can be classified as  $\text{NaSO}_4$  waters from the main cations and anions present. Major elements present in the brine are  $\text{SO}_4$ , Na, Cl, Mg and K; minors are Sr,  $\text{NO}_3$ , Si, Ni and Pb, while the traces comprise of V, B, Ba, Cu, As, Fe, Se, Mn, Mo, Ti, Zn, Cr, Al and Co. Elements such as Ca,  $\text{SO}_4$  and Mg can be transformed into calcite, gypsum and magnesite respectively, although reports of gypsum and magnesite formation during carbonation of FA are limited in the literature. Gitari et al. (2009) observed mobilization of species such as Se, As, B, Mo and Cr from ash which was in contact with brine. They thus concluded that the presence of these elements will influence the chemistry of ash in contact with brine. Conversion of Ca present in brine solutions used in this study (as shown in Table 2 above) would lead to 0.021 wt % of  $\text{CaCO}_3$  being formed. This value is lower than the values obtained by both C&S analysis as well as Chittick test. Moreover, Ca from both brine and the dissolution of CaO in FA are expected to take part in this

conversion. It is estimated that the ash dam has been exposed to an estimated 117.65 billion litres of brine over the 20 year period of its existence.

### 3.3. Chemical characterization of fresh and weathered ash

A comparison of the chemical composition of fresh, weathered and carbonated ash is given in Table 3.

Enrichment of Nb, Y, Sr, Th and Ba with weathering is observed. It's important to note that weathered and carbonated ash have come into contact with brine which is a source of some of the elements such as Sr and Ba. [Mahlaba et al. \(2011\)](#) postulated that the increase of some elements such as Na is from the brine which is used to transport the ash. The waste brine is usually rich in elements such as Na, Cl, SO<sub>4</sub>, K, Sr, Ba etc. ([Nyamhingura, 2010](#)) and this may explain the increase of some of these elements in the weathered ash. On the other hand a reduction in Rb, Pb, Ni, Co, V and Zr is observed with weathering which is consistent with leaching over time. Calcite has been known to bind some heavy metals such as Pb, Cd, Cu, Ni and Zn via chemical fixation ([Bertos et al., 2004](#); [Meima and Comans, 1999](#)). According to [Sweeney et al. \(1999\)](#), carbonating solidified waste before landfilling reduces the alkalinity from the pH range of 11-12 to a range of 8-9 where the waste is in equilibrium with the atmosphere. This corresponds with the minimum solubility of metals such as Al, Ca, Cd, Cu, Fe, Mn, Ni, Pb and Zn, hence their immobilization.

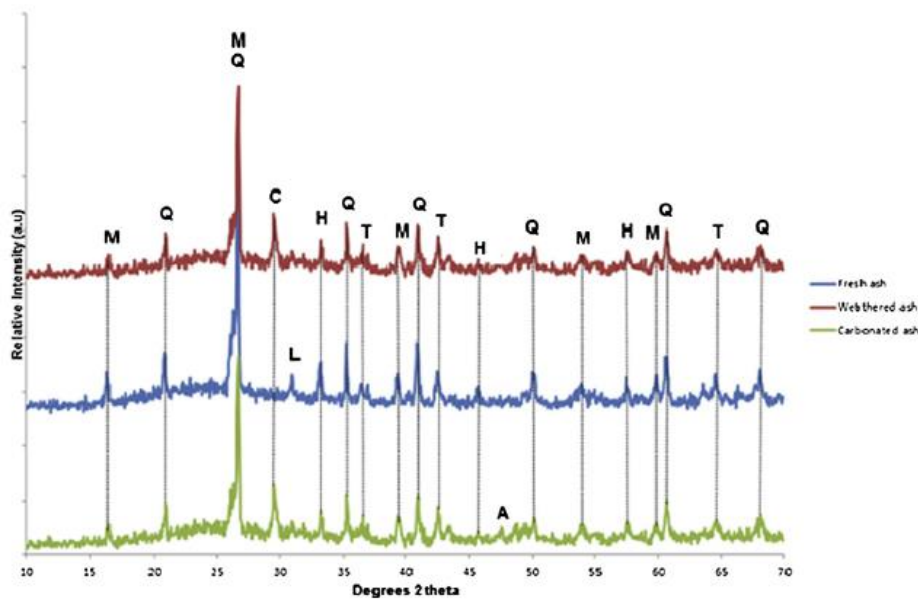


Fig. 6. XRD spectra of fresh, weathered and carbonated fly ash; M = mullite; Q = quartz; C = calcite; H = hematite; Mt = magnetite; A = aragonite; L = lime.

**Table 2**  
Major, minor and trace ion analysis of the raw brine solutions  
( $n = 3$ ).

Elements	Concentration (ppm)
SO <sub>4</sub>	11,704 ± 14.28
Na	3355 ± 25.46
Cl	1365 ± 7.78
Ca	210.2 ± 10.47
Mg	111.85 ± 0.07
K	78.75 ± 2.05
Sr	11.06 ± 0.18
NO <sub>3</sub>	6.5 ± 1.44
Si	2.54 ± 0.03
Ni	2.5 ± 0.02
Pb	1.6 ± 0.01
V	0.4898 ± 0.04
B	0.154 ± 0.01
Ba	0.15 ± 0.01
Cu	0.118
As	0.076 ± 0.01
Fe	0.068 ± 0.02
Se	0.058 ± 0.01
Mn	0.057 ± 0.01
Mo	0.037
Ti	0.029
Zn	0.028
Cr	0.023
Al	0.023
Co	0.020

Yeheyis et al. (2009), observed that trace metals such as Cu, Fe, Co, Mn, Mo, Ni, Pb and Zn are usually co-precipitated with hydroxides of Fe and Al as well as neo-formed clay minerals in weathered municipal solid waste incineration (MSWI) ash. They further argued that the cementitious and precipitated minerals could serve as a physical barrier to the constituents of the disposed FA by clogging the pores of the ash and hence preventing mobilization. Calcite is the predominant newly formed mineral during ash maturation, combined with aluminum hydroxides and various sulfates (Freyssinet et al., 2002). For all the ashes, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and CaO are the major oxides thus they can be classified as class F since the sum of the percentage composition of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> is greater than 70% according to the American Society for Testing and Materials (ASTM 618-1993). Furthermore, the CaO content is lower than 10% which is also a grading criterion for class F FA.

Calcium-containing minerals such as CaO in fresh FA control the alkalinity of waste materials (Meima and Comans, 1999). As weathering occurs, processes such as leaching, sedimentation, oxidation, carbonation and pH reduction are prevalent. This leads to the conversion of lime and portlandite to more stable carbonate forms as pH of the ash stabilizes to about 8, at which level calcite is in equilibrium with the atmosphere. This phenomenon can explain the observed CaO decrease with weathering.

Accelerated carbonation has lower levels of CaO than weathered ash. The carbonation efficiency for this protocol was calculated to be 75.54% (reader referred to Muriithi et al., 2011), moreover, the conversion of CaO to CaCO<sub>3</sub> is at increased kinetics since higher pressures and temperatures are used as opposed to natural carbonation. Quenching of the ash with brine before and at the disposal site converts CaO to Ca(OH)<sub>2</sub>, CaSO<sub>4</sub>.2H<sub>2</sub>O

and  $\text{Ca}_6\text{Al}_2(-\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$  (in the presence of sufficient Al and  $\text{SO}_4$ ). MgO is another alkalinity impacting mineral in fresh FA and its behavior is thus expected to be similar to that of CaO. Al, Fe, K and P content remained fairly similar for all three samples.

### 3.4. Mineralogical characterization using XRD

The mineralogical composition of the fresh, carbonated and naturally-weathered FA was determined to identify the presence of carbonate minerals (Fig. 6).

The major phases present in the three different ashes are quartz and mullite, and to a lesser extent hematite and magnetite. Lime was present in the FA, but not in the weathered ash and carbonated ash which contained calcite, and calcite and aragonite respectively. A tabulation of the mineral phases present in the ash is shown below (Table 4).

Transformation of lime to calcite and its various polymorphs with carbonation has been reported by other researchers (Mlambo et al., 2011; Perez-Lopez et al., 2008; Rendek et al., 2006). According to Bertos et al. (2004), vaterite and aragonite can be formed first and then they transform to the most stable form of  $\text{CaCO}_3$  which is calcite. Vaterite was however not identified in our study.

### 3.5. Morphological characterization of fresh, weathered and carbonated ash

SEM analysis was carried out in order to understand the morphological changes occurring as the fresh ash was carbonated as well as its variation from weathered ash as shown in Fig.7 below.

Fresh ash (Fig. 8A) is mainly characterized by spherical particles, with a proportion of cenospheres (hollow sphere filled with  $\text{N}_2/\text{CO}_2$  that gives FA its light weight characteristics (Fenelov et al., 2010)). The spherical shape is an indication that the particles were formed under un-crowded free-fall conditions and a relatively sudden cooling, which helps to maintain the spherical shape (Li et al., 2003; Saikia et al., 2006).

Carbonated FA (Fig. 8B) is made up of acicular particles of calcite and some aragonite, the two polymorphs of  $\text{CaCO}_3$  observed in the XRD analysis (Fig. 7) and previously reported by Fairchild and Thatcher (2000). The calcite particles are clearly observed around a bigger spherical particle.

**Table 3**XRF analysis of fresh, weathered (at 20 m depth of the dam) and ex-situ mineral carbonation product. (NB:  $n = 3$ , Weathered ash value is from the average of the 3 cores).

Majors (wt %)	Fresh ash	Weathered ash	Carbonated ash	Traces (ppm)	Fresh ash	Weathered ash	Carbonated ash
SiO <sub>2</sub>	51.23 ± 1.64	44.28 ± 0.42	47.83 ± 0.05	Nb	35.30 ± 0.79	149.43 ± 2.15	33.50 ± 0.42
TiO <sub>2</sub>	1.55 ± 0.09	1.76 ± 0.07	1.50	Zr	638.80 ± 21.60	598.32 ± 9.16	485 ± 9.45
Al <sub>2</sub> O <sub>3</sub>	26.00 ± 1.65	25.49 ± 0.75	25 ± 0.08	Y	81.12 ± 0.95	171.28 ± 0.93	80.50 ± 0.74
Fe <sub>2</sub> O <sub>3</sub>	2.43 ± 0.06	2.59 ± 0.08	2.17 ± 0.11	Sr	4059.27 ± 48.76	4659.54 ± 20	3409 ± 37.58
MgO	2.44 ± 0.71	2.73 ± 0.04	1.68 ± 0.06	Th	52.76 ± 2.18	186.11 ± 1.11	21 ± 3.62
CaO	9.20 ± 0.85	5.41 ± 0.91	3.87 ± 0.35	Rb	33.14 ± 0.93	6.86 ± 0.75	24.50 ± 2.89
Na <sub>2</sub> O	0.46 ± 0.01	2.53 ± 0.57	0.47 ± 0.13	Pb	30.00 ± 0.08	14.48 ± 0.58	13 ± 0.92
K <sub>2</sub> O	0.79 ± 0.02	0.81 ± 0.02	0.79 ± 0.01	Ni	43.29 ± 0.79	32.78 ± 2.05	65 ± 4.75
P <sub>2</sub> O <sub>5</sub>	0.70 ± 0.03	0.94 ± 0.04	0.85 ± 0.01	Co	36.78 ± 1.89	11.18 ± 1.64	86 ± 2.30
SO <sub>3</sub>	0.36 ± 0.01	0.09 ± 0.01	NA	V	138.23 ± 3.64	59.89 ± 0.34	147 ± 0.03
				Ba	2290.65 ± 29.15	3207.61 ± 1.0	2315 ± 31.35

**Table 4**

Tabulation of the mineral phases present in fresh, weathered and carbonated ash.

Fresh ash	Weathered ash	Carbonated ash
Mullite	Mullite	Mullite
Quartz	Quartz	Quartz
Hematite	Calcite	Calcite
Magnetite	Magnetite	Hematite
Lime	Hematite	Magnetite
		Aragonite

Bertos et al. (2004) reported this morphology of calcite characterized by small tightly packed crystals <3 mm in size. Accelerated carbonation thus leads to changes in the ash morphology due to the formation of secondary phases such as calcite and aragonite. Similar morphologies of carbonated FA have been previously reported (Perez-Lopez et al., 2008; Montes-Hernandez et al., 2009; Fernandez et al., 2004), although these studies identified calcite as the only polymorph of CaCO<sub>3</sub> formed during the carbonation process. However SEM can only provide qualitative information and thus cannot be used to quantify the amount of CaCO<sub>3</sub> formed in the carbonation process.

Irregularly shaped particles and agglomerates are observed in the weathered ash (Fig. 8C). This transformation occurs as the ash matures through processes such as hydration, carbonation and co-precipitation. Major alteration reactions reported during weathering of fly ash are dissolution/precipitation of salts, glass corrosion, hydration of anhydrite to bassanite and gypsum, oxidation reactions of metals or metal oxides, slaking of lime and hardening reactions (cementation and carbonation of reactive lime and periclase by air). The reported alteration/weathering products are anhydrite, ettringite, gypsum, bassanite, calcite, iron oxides and hydroxides as well as gibbsite (Speiser et al., 2000; Vassilev and Vassileva, 2007).

### 3.6. Carbonation potential of the ash dams

The natural carbonation potential of the ash dams was evaluated by titrating the weathered Secunda ashes using the Chittick test procedure. Fig. 8 shows the calcite content variation along the depth profile in the ash dam.

For all three cores, the surface sample has the highest CO<sub>2</sub> content with core S1 having a value of 6.8%, core S2 a value of 6.7 and core S3 a value of 6.5%. The three values have a standard error of 0.158 and hence not significantly different from one another. Interestingly, the CO<sub>2</sub> concentration profile in core S1 is similar to its moisture content profile (Fig. 6) with highest concentration at the surface and lowest value down the depth profile. No correlation is observed for cores S2 and S3 however. Core S2 had the lowest value of 5.3 wt %, which was recorded at a depth of 22 m. A “zigzag” trend is observed for all three cores. This is due to the fact that after disposal, the ash is allowed to settle while the excess brine drains via the penstock and toe drain into the clear ash effluent dams for re-circulation before the next layer of ash slurry is applied. As a result, the ash dams are characterized by stacking of “pancake-like layering”. This stacking allows for a period of interaction with the atmosphere and hence the zigzag pattern implies the longer the exposure to the atmosphere the higher the CO<sub>2</sub> content. Yeheyis et al. (2009) also found that carbonation was predominant at the surface of one of the sites they cored (DFA-I) with additional phase formation of ettringite in the other two cores they used (DFA-II and DFA-III). They further argued that metals in the FA are immobilized in the dump site. Some components of the disposed ash may be converted to less soluble hydroxide and carbonate minerals via adsorption, co-precipitation and/or physical encapsulation. This implies a lower concentration of elements such as Cu, Fe, Co, Mn, Mo, Ni, Pb and Zn, which is confirmed in the XRF analysis reported in Table 2.

### **3.7. Evaluation of CO<sub>2</sub> capture by Chittick test and C&S analysis**

To authenticate the amount of CaCO<sub>3</sub> formed during accelerated carbonation process, Chittick test results were compared to C&S analysis results obtained for cores S2 and S3 (Fig. 9).

In both cores, C&S analysis gave lower values than the Chittick test. This could be due to the fact that Chittick test involves titration with a high concentration of acid (6 N HCl) and thus both the organic and inorganic carbon are easily released. On the other hand C&S analysis involves combustion of the ash in oxygen and the subsequent detection of the evolved CO<sub>2</sub>.

A comparable trend is clear in core S2 but missing in core S3. Interestingly, the highest CO<sub>2</sub> concentration by C&S analysis is not on the surface as can be seen for Chittick test. For core S2 the highest value obtained was 4.568% CO<sub>2</sub> at a depth of 33 m while for core S3 the highest value was 6.517% CO<sub>2</sub> at a depth of 28.5 m. The discrepancy between these two analytical techniques has not been demonstrated before and thus should be investigated further.

### **3.8. CO<sub>2</sub> capture via accelerated ex-situ mineral carbonation**

It was important to evaluate how the CO<sub>2</sub> capture in disposed, weathered ash via natural carbonation processes compared with accelerated mineral carbonation carried out in the

laboratory. A graphical representation of the CO<sub>2</sub> formed in wt. % for the various factor combinations as stipulated in Table 1 is given in Fig. 10.

The highest CO<sub>2</sub> content upon accelerated carbonation was 6.5 wt %; this experiment was conducted at 4 Mpa, 90 °C using bulk ash at a S/L ratio of 1 for 2 h. The lowest content on the other hand was found to be 2.75 wt % and was obtained at 1 Mpa, 30 °C, >150 and a S/L ratio of 0.1 for 2 h.

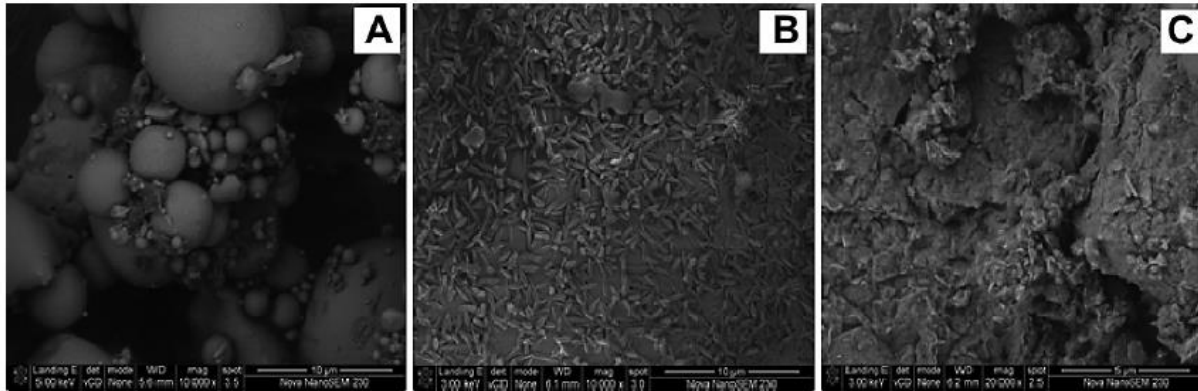


Fig. 7. SEM micrographs of fresh ash (A), carbonated ash (B) and weathered ash (C).

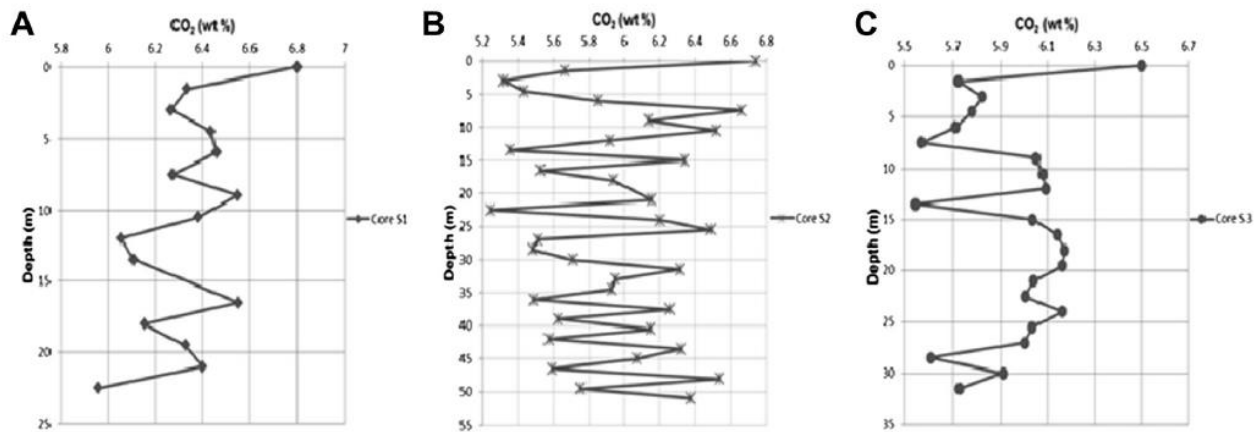


Fig. 8. Chittick test results for weathered ash (three cores were obtained: S1, S2 and S3) (n = 3).

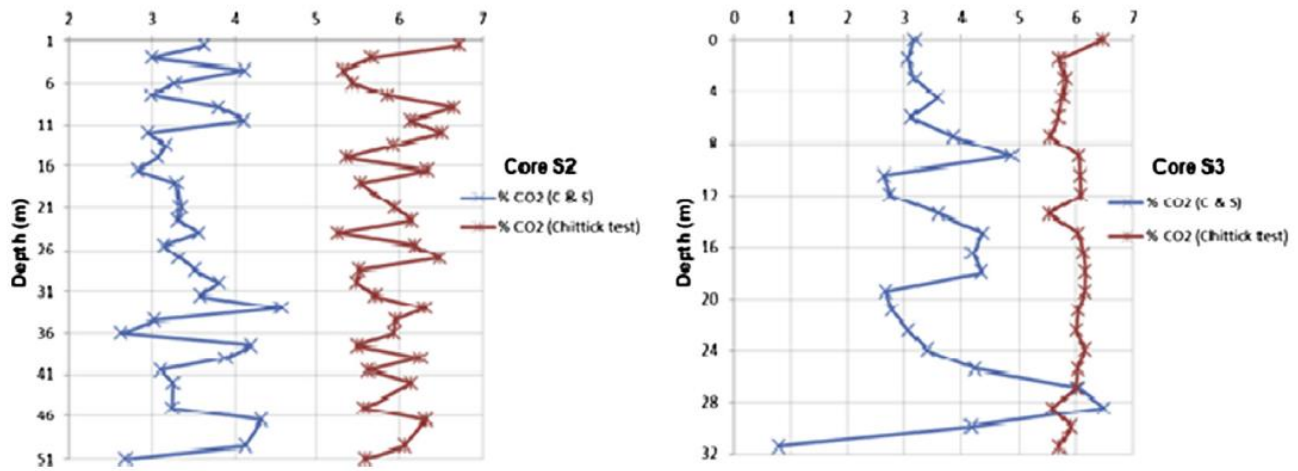


Fig. 9. Comparison of Chittick test and C&S analysis of weathered ash ( $n = 3$ ).

Comparison with the Secunda weathered ash revealed that core S1 had a maximum value of 6.8 wt %, core S2 6.7 wt % and core S3 6.5 wt %. These values do not vary significantly with the accelerated carbonation value of 6.5 wt %. It thus can be said that natural carbonation in the ash dumps is significant and can be effective in capturing CO<sub>2</sub>. Moreover, supercritical CO<sub>2</sub> from coal combustion may be dissolved in the waste brines and the resulting mixture used to transport or irrigate the ash dams, further enhancing the rate of natural carbonation. The parameters found to be of most significance in the carbonation process were the main effects of temperature, particle size and S/L ratio while the interactions of temperature and particle size as well as the interaction of temperature with S/L ratio were also found to be significant (Muriithi et al., 2012).

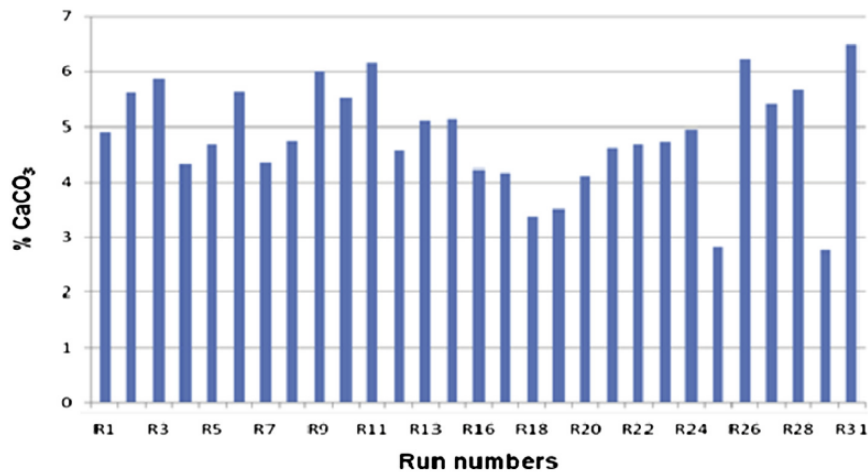


Fig. 10. Carbonation of the Secunda FA dispersed in brine as determined by Chittick test ( $n = 3$ ).

#### 4. Conclusions

Natural carbonation occurs in the ash disposal site although longer time scales are required to achieve the same results as 2 h of accelerated mineral carbonation. This could imply that supercritical CO<sub>2</sub> can be used to slurry the ash before disposal thus using up



some of the waste CO<sub>2</sub> emissions from power stations. This can be applied at a plant like Secunda where the CO<sub>2</sub> is already highly concentrated (90e98%). The morphology of the ash changes from sphero-particles in fresh ash to acicular particles in carbonated ash and finally to irregular shaped particles as weathering process takes place at the dumping site. Some elemental forms remain unchanged in concentration as fresh ash weathers. Others are enriched (e.g. Ti, Fe, Mg, Na, K, Nb, Y, Ba and Sr) while some are depleted in the weathered ash. These include Ca, S, Zr, U, Rb, Pb, Ni, Co and V. Analytical techniques such as C&S and Chittick test can be applied in the evaluation of carbonates in carbonated ash.

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