BRINE REMEDIATION USING FLY ASH AND ACCELERATED CARBONATION

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ABSTRACT

Coal combustion by-products such as brines, fly ash and CO_2 from coal fired power plants have the potential to impact negatively on the environment. Brines are loaded with salts which can contaminate the soil, surface and ground waters. Fly ash on the other hand is made up of toxic elements which can leach out due to rain water percolation while CO_2 is the major green house gas contributing to global warming. It has been shown that brine can react with CO_2 leading to formation of carbonates such as calcite, magnesite, siderite and dolomite. These carbonates have the capacity to encapsulate major elements from brine, sequester CO_2 as well as trapping within their matrices trace elements present in brine leading to cleaner brine effluents. This study aims to evaluate and optimize the factors that influence the brine/fly ash/CO_2 interaction chemistry. The CO_2/ brine reactions in the presence of fly ash can potentially provide a viable route for brine clean-up and beneficial remediation of fly ash.

Chemical characterization of brine effluents indicates that they are rich in Cl, SO_4, Na, Ca, K and Mg as well as traces such as Fe, Mn, Cr, V, Ti, P, Si and Al and can therefore be utilized as a source of Ca^{2+}, Mg^{2+} and Fe^{2+} for the carbonation reactions. Quantitative XRD results reveal that different size fractions of the fly ash have varying proportions of free lime. This lime fraction can be used to raise the brine pH to alkaline levels, maximizing the carbonation efficiency.

Key words: brine effluents, fly ash, major and trace elements, free lime, carbon dioxide, carbonation.

1. INTRODUCTION

South Africa is a semi-arid country thus making fresh water its most limiting natural resource. On a global scale, manmade pollution of natural sources due to increasing industrial and agricultural activities is the largest cause for fresh water shortages. Added to this is the problem of uneven distribution e.g. Canada has a tenth of the world's surface fresh water but less than a percent of its population (Dirach et al., 2005).

Three main driving forces affect South Africa's fresh water environment. Firstly, the natural conditions, particularly the climate, which is characterized by low rainfall and high evaporation rates creates low available run-off. Second is the rapid population growth and need for economic development while meeting the basic needs of its population. These socio-economic activities drive water use and lead to a greater water demand and increased pollution of available resources. The third driving force is the policy pertaining to national management of water resources, which determines the approach taken by the relevant authorities at all levels of government to managing the fresh water resources. Indirectly, policy pertaining to land use practices throughout the country impacts water quality and availability in South Africa (Walmsley et al., 1999). Only 8.6 % of the rainfall is available as surface water, while the mean annual run-off is estimated at only 50 million m^3a^{-1} and yet this is not evenly distributed throughout the country. The scarcity is compounded by pollution of the surface and ground water resources. Typical pollutants in South Africa include industrial effluents, domestic and commercial sewage, acid mine drainage, agricultural runoff and litter (Walmsley et al., 1999).

According to Fan He et al., (2006), coal accounts for 65 % of total primary energy consumption in China while on the other hand USA generates 51.7 % of its electricity from coal combustion (Klass, 2003). South Africa generates 93 % of its electricity from coal combustion and despite numerous environmental issues associated with its combustion, coal will remain a major source of electric power in South Africa for years to come owing to the relative lack of suitable alternatives to coal as an energy source, coupled with the large coal deposits which can be exploited at extremely favourable costs (Fecher, 2002). Consequently, large amounts of coal utilization by-products such as brines, fly ash, flue gas desulphurization products (FGD), bottom ash and slag are produced. Their disposal is of concern to the power generating industry due to their potential to harm the environment. Fly ash consists of fine particles that contain leachable heavy metals and is therefore, classified as a toxic waste (Ural, 2005). Brines on the other hand are heavily loaded with salts that can seep to the ground water and even lead to soil salinization.

In 2005, USA produced 71.1 Mt of fly ash of which 29.1 Mt; (about 40 %) was reused in various applications such as building and construction and portland cement production while a target has been set for 50 % utilization by 2011. Snigdha and Vidya (2006) reported that the major portion of fly ash produced in India is disposed in ash ponds and landfills while only 13 % is utilized. In South Africa, the quantity of fly ash generated per annum by Eskom power plants was estimated to be over 20 million tons (Eskom Annual Report, 2001; Reynolds et al., 1999) and only about 5 % of it is utilized while the remaining is disposed of in ash dumps. According to Engelbrecht and co-authors, (2004), South Africa produces over 218 Mt/a of CO_2 in the power generation industry. These emissions are mainly present in the form of flue gas with a CO_2 concentration of 10-15 % (186 Mt/a). The remainder of the CO_2 (32 Mt/a) is emitted in a concentrated form (90-98 %) and is also available under pressure (20 bars) (Engelbrecht et al., 2004; Scholes and Van der Merwe, 1998). This burden of wastes, namely brines, fly ash and CO_2 emissions from the coal fired power plant is a threat to sustainable energy production. Thus the power generation industry is looking for alternatives to the usual disposal methods so as to make coal based power generation not only more environmental friendly but also more sustainable.

Mooketsi et al., (2007), investigated the interaction of fly ash with brine and observed that brine treated sintered ash residues have elevated leachate electrical conductivity as well as Na^+, K^+, Ca^{2+}, Cl^- and SO_4^{2-} concentration compared to non brine treated sintered ash residues. They attributed this to the applied brine, concluding that the lime had an effect on the improved leachate quality. They further suggested that the decrease in leachate SO_4 concentration was due to the formation of insoluble anhydrite which reduces the labile form of sulphate species such as $NaSO_4$ in the brine. Furthermore it has been shown that carbonation leads to a reduction in mobility of species such as Pb, Zn, Cu, Ba, by about two orders of magnitude (Freyssinet et al., 2002, Meima et al., 2002, Van Gerven et al., 2005, Ecke et al., 2003). On the other hand carbonate stabilization has been found to be robust in demobilizing environmentally relevant metals such as Pb and Zn (Ecke et al., 2003). It was postulated that carbonation leads to a reduced mobility of Pb and Zn due to the predominance of $PbCO_3$ at a pH range of between 6 and 9 and $Zn(OH)_2$ in the pH range of between 9 and 11. Carbonation is thus a process that enhances the sequestering of a variety of cations namely Pb, Cd, Cu and Zn among others, through adsorption onto $CaCO_3$ leading to co-precipitation (Soong et al., 2006).

It is thus envisaged that the interaction of brine with South African class F fly ash should reduce the concentration of sulphate, potassium, sodium and chloride salts while carbonation could lead to a reduction in leaching of Ca, Mg, Fe as well as trace elements such as Pb, Zn, Ba, Cu and Cd thus resulting in cleaner brine effluents. This study was carried out to evaluate the application of carbonation of brine impacted fly ash for the remediation of these waste effluents.

2. MATERIALS AND METHODS

The fly ash and brine samples used in this study were collected from coal fired power plants in the Mpumalanga province of South Africa. The ash was fractionated using an Endecott mechanical shaker to obtain sieve sizes of <20 µm, 20 µm -25 µm, 25 µm-32 µm, 32 µm-45 µm, 45 µm-53 µm, 53 µm-63 µm, 63 µm-75 µm, 75 µm-90 µm, 90 µm-106 µm, 106 µm-150 µm and >150 µm which were analyzed for their mineralogical, morphological and chemical characteristics.

Carbonation Experiments

The statistical design of experiments (DOE) will be applied to optimize the following input variables: - L/S ratio, particle size, pressure and temperature. A D-Optimal design which allows one to choose any number of levels for each categorical factor was chosen as the factors are at mixed levels.

Procedure

The carbonation reactions were carried out in an autoclave reactor made of stainless steel and with a 600 ml volume capacity. The photo of the reactor is shown below (Figure 7):

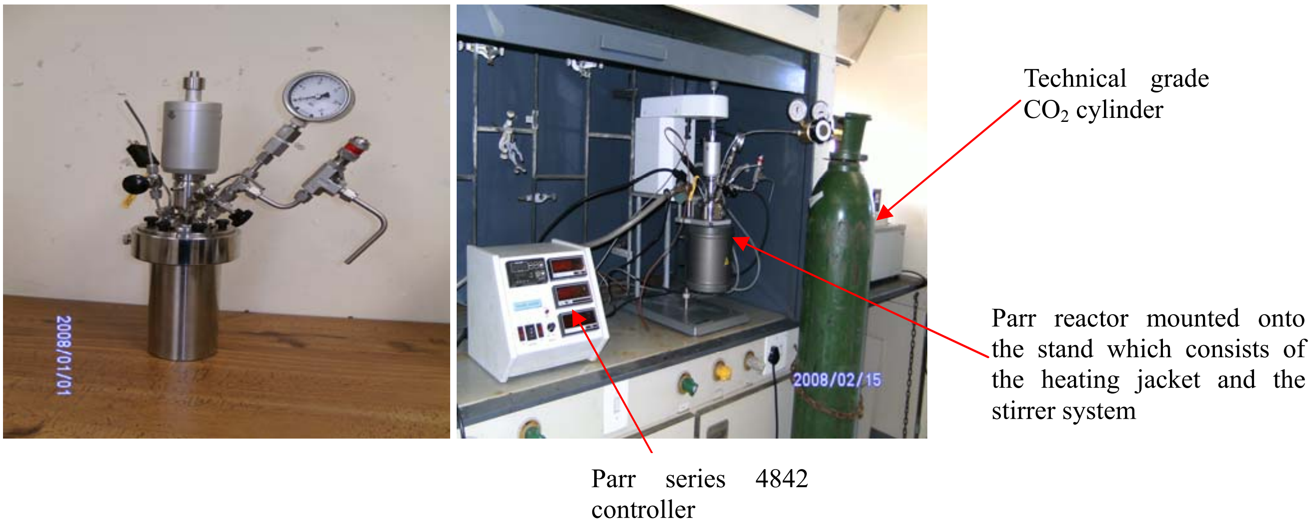


Figure 7. The autoclave reactor used in the study and the assembly consisting of the controller, mount and gas cylinder.

The dispersion (brine + fly ash) was placed in the reactor and closed. Following the closing of the bomb cylinder, the body of the reactor was placed in the heater assembly and the thermocouple, stirrer drive system, and water coolant supply put in place. The gas supply hook-up for CO_2 was then attached. The system was then purged three times with CO_2 at 0.05 Mpa to ensure that all the air was expelled. After the final purge, the heating of the system began, when the dispersion temperature was reached, CO_2 (technical grade) was charged into the reactor to achieve the desired testing pressure. The brine/fly ash/CO_2 mixture was then agitated at 500 rpm 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 immersed into cold water to cool. The reaction cell was depressurized for 15 minutes during the water cooling period and upon cooling to room temperature, the reactor was disassembled, and the solid product was separated by filtration through 0.2 µm pore sized membranes. Finally, the solid product was dried in an oven for 8 h at 90 ^{o}C. 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 concentration of the major, minor and trace elements in the leachates were analyzed using ICP-MS while the anions were analyzed using IC. Mineralogical and elemental characterization of the solid residues was done using XRD while morphological analyses were done using SEM-EDS. The carbonate content of the solid residues is to be determined using differential thermal analysis and thermal gravimetric analysis (DTA/TGA).

Characterization

The structural and morphological analysis was done by Scanning Electron Microscopy- Energy Dispersive Spectroscopy (SEM-EDS) using a Hitachi X-650 scanning Electron Microanalyser equipped with a CDU- lead detector at 25 kV. Diffraction patterns for each fraction were collected using a Bruker AXS D8 Advance diffractometer coupled with a Cu-Kα radiation at 40 kV and anode current of 40 mA with a PSD Lynx-Eye, Si- strip detector. The measured range of 2θ angles were from 10 ^{o} to 70 ^{o} while the diffraction patterns were collected with a step of $\Delta 2\theta = 0.03\ ^{o}$ and counting time of three seconds in every step.

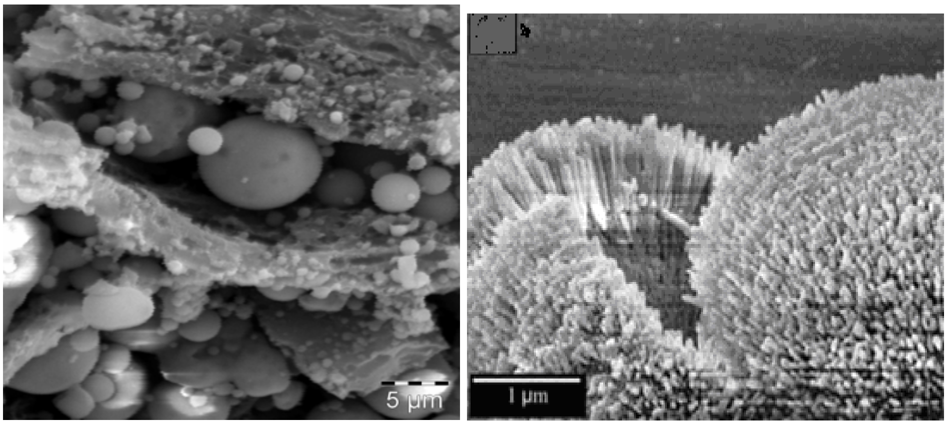
Elemental analysis was done by XRF using a Philips PW 1480 X-ray spectrometer fitted with a Cr tube and five analyzing crystals namely LIF 200, LIF 220, GE, PE and PX at 40 kV and 50 mA tube operating conditions. Matrix effects in the samples were corrected for by applying theoretical alpha factors and measured line overlap factors to the raw intensities measured with the SuperQ Philips software.

Anions were characterized using Dionex DX-120 IC with an Ion Pac AS14A column and AG14-4 mm guard column while the cations (majors) were analyzed using a Varian Radial ICP-AES and the trace elements on an Agilent 7500ce ICP-MS using a High Matrix Introduction (HMI) accessory and He as collision gas.

3. RESULTS AND DISCUSSIONS

Morphological Analysis

As shown in the micrographs below fresh fly ash (Figure 1a) was observed to be spherical while the carbonated ash (Figure 1b) showed the presence of needle-like particles that were identified as aragonite.



(a) (b)

Figure 1. SEM micrographs of fresh fly ash (a) and carbonated fly ash (b).

Other authors, Saikia et al., (2006), Kutchko and Kim (2006), Li et al., (2003) and Pieterson (1993) have reported similar morphologies of fresh fly ash. They concluded that the spherical shape is an indication that the particles were formed under un-crowded freefall conditions and a relatively sudden cooling, which helps to maintain the spherical shape while the agglomerated nature of some particles is an indication that the particles were produced due to high temperature sintering reactions. Morphological study of fly ashes is of importance as morphology has a bearing on the leachability of heavy metals. Ramesh and Koziński (2001) in their study on morphology of fly ash and its relationship with heavy metal release found that the presence of a non-porous continous outer surface and a dense particle interior may prevent heavy metal leachability from the fly ash.

Of the three polymorphs of calcium carbonate, calcite is the most stable while vaterite is the least stable. No authors have reported the formation of aragonite from carbonation while vaterite has been identified by Li et al., (2007). This is an interesting observation to be investigated further.

Mineralogical Analysis

Mineralogical characterization of the fresh ash indicated the presence of mullite, quartz, hematite, magnetite as well as lime as the major phases (Figure 2 below). The carbonated fly ash however had aragonite, calcite, anhydrite, mullite and silica as the major phases (Figure 3).

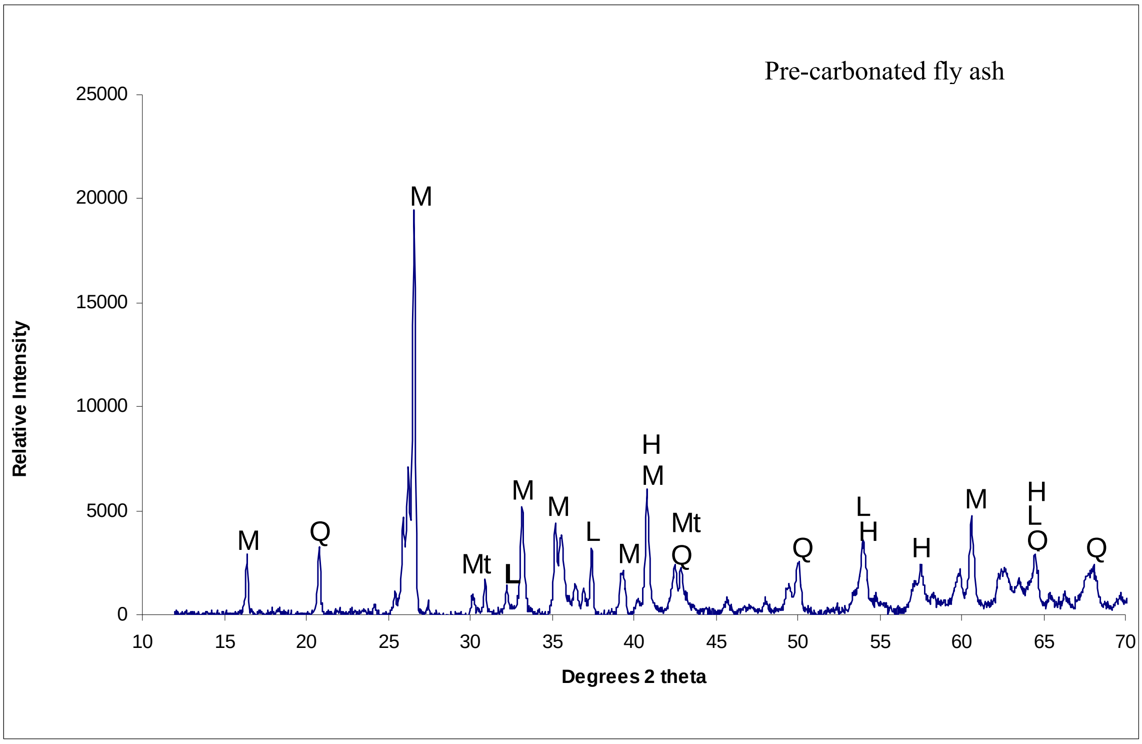


Figure 2. XRD spectra of fresh fly ash showing the major phases;
mullite (M), quartz (Q), lime (L), hematite (H) and magnetite (Mt).

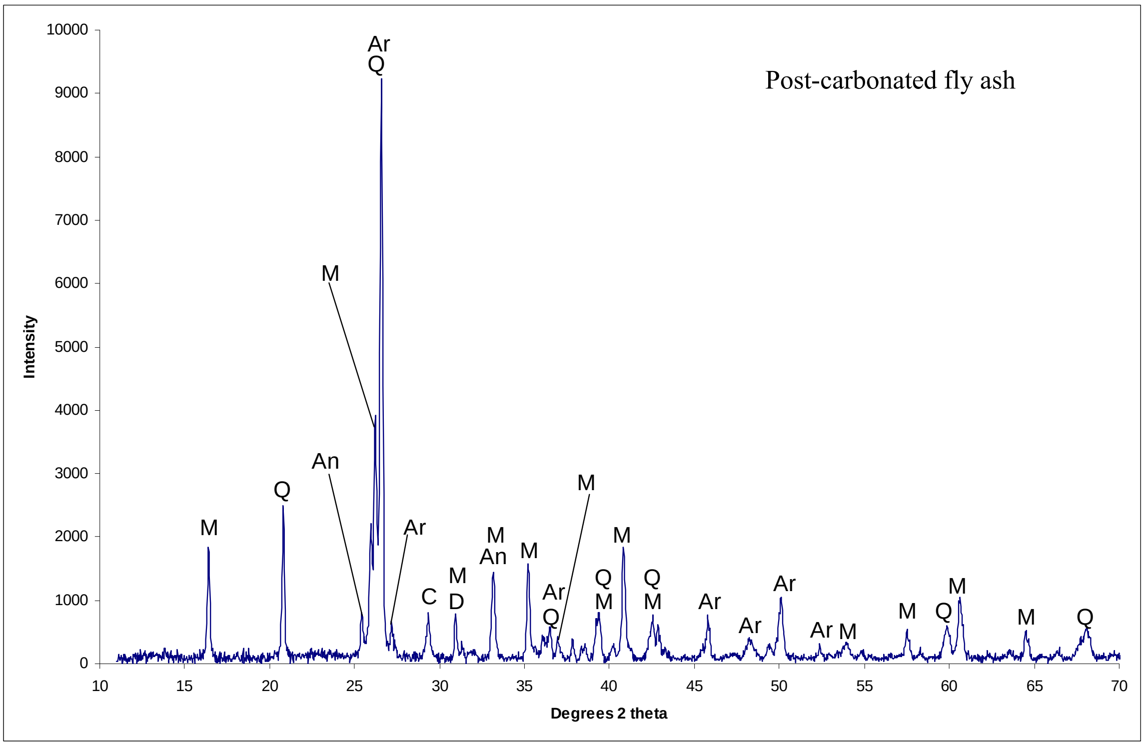


Figure 3. XRD spectra of carbonated fly ash showing the major phases; mullite (M), quartz (Q), anhydrite (An), aragonite (Ar), calcite (C) and dolomite (D).

This confirms the conversion of the Ca^{2+} present both in brine and from the lime dissolution into the two polymorphs of calcium carbonate namely calcite and aragonite. Calcite is the most common polymorph owing to its stability and has been reported numerously from carbonation experiments (Soong et al., 2006; Li et al., 2007; Fernandez, 2004; Hernandez et al., 2008, Perez et al., 2008). Vaterite, the least stable polymorph of calcium carbonate has also been reported (Li et al., 2007) while no study has shown the formation of aragonite. The anhydrite observed is from the reaction of some of the Ca^{2+} with the SO_4^{2-} present from brine to form the insoluble anhydrite.

Elemental Analysis

From elemental analysis, fly ash is observed to be enriched in silica, alumina and ferric oxides and can thus be classified as Class F with a sum content of over 70 % of the aforementioned oxides (Table 1). This classification is also based on the amount of lime present (<10 %). The ash is also enriched in traces of Zn, Pb, Rb, Zr, Sr, Sc, S, Th, Cu, Ni, Mn, Cr, V, Rb, U, Y and Ba (Figure 4). Presence of these trace elements in fly ash makes it an environmental hazard as the traces can leach into the ground water.

Table 1. Major elements in the fly ash in wt %

Majors	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	Cr_2O_3
(wt %)	51.227	26	2.43	1.548	0.061	2.439	9.198	0.457	0.787	0.698	0.358	0.033

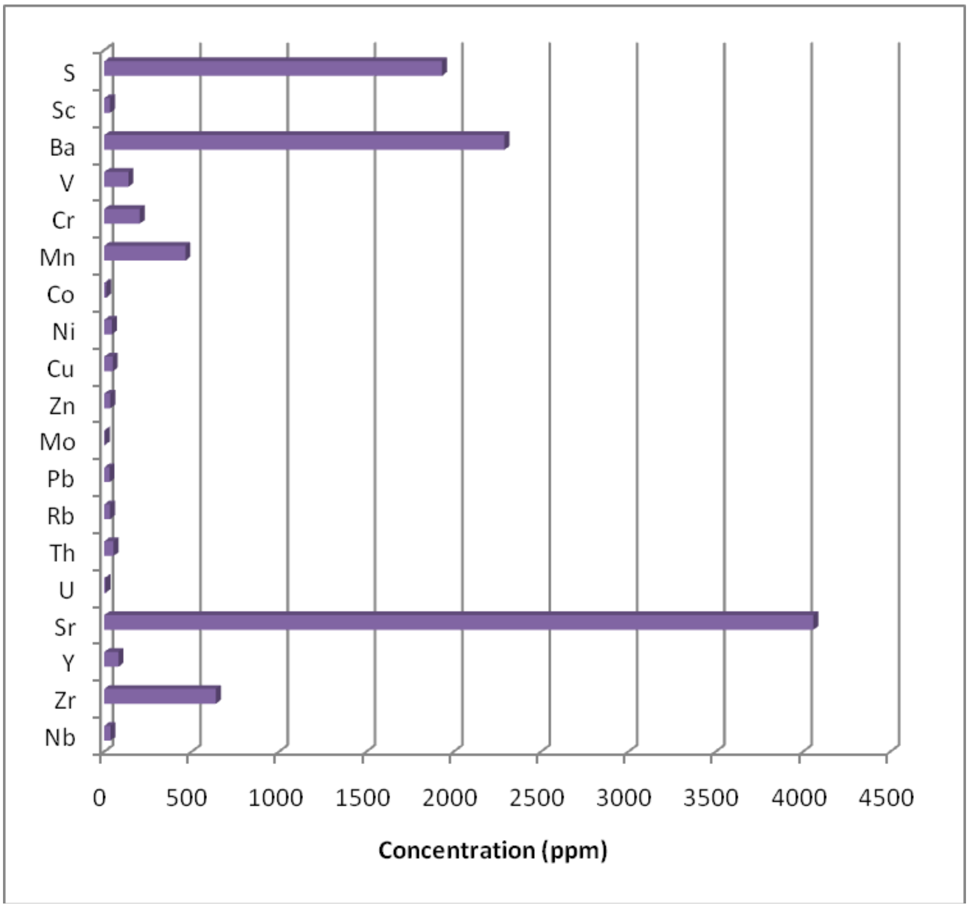


Figure 4. Trace elements concentration in fly ash (ppm)

Brine Analysis

Below is the analysis results of the RO brines used in the study. Utilization of the AqQA analysis program gave the following results:-

Water Type	Na-SO_4		
Dissolved Solids	16274 mg/kg	16424 mg/L	Calculated
Density	1.0092 g/cm^3		Calculated
Conductivity	14286 µmho/cm		Calculated
Hardness (as $CaCO_3$)			
Total	568.14 mg/kg	573.38 mg/L	Calculated
Carbonate	N/A		
Non-Carbonate	N/A		
Primary Tests			
Anion-Cation Balance			
Anions	258		
Cations	212		
% Difference	9.816		Not within ± 5%

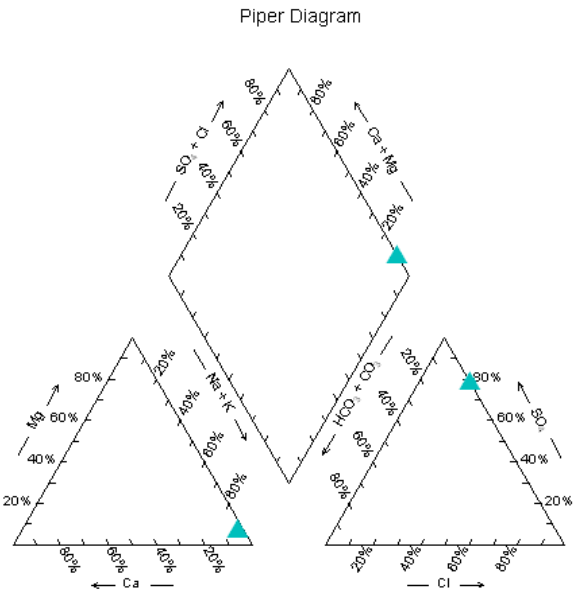


Figure 5. Piper Diagram of the raw brines showing the major anions, cations and the water type.

This classifies the waters as $NaSO_4$ type waters as can be seen on the piper diagram above with a 9.816 % ionic balance.

The brines are rich in SO_4, Na, Cl, Ca, Mg and K while traces of Ba, Sr, Cu, Si, B, Fe and P are also present. This has been reported elsewhere (Petrik et al., 2007; Buhrmann et al., 1999) who found the brines to be rich in similar ionic species.

Table 3. Concentration of major, minor and trace elements in the brines before and after carbonation

Elements	Before carbonation (ppm)	After carbonation (ppm)
B	1.4095	2.71989
Mg	76.6	1.52232
Al	0.02289	Nd
P	0.383	Nd
K	57.065	9.74966
Ti	0.000529	Nd
V	0.009007	0.14999
Cr	0.006415	0.00109
Mn	0.07573	0.00045
Fe	0.052555	Nd
Co	0.007197	0.00169
Ni	0.05618	Nd
Cu	0.1008	Nd
Zn	0.0529	Nd
As	0.003619	Nd
Se	0.001875	Nd
Mo	0.019275	0.69299
Cd	5.78E-05	Nd
Ba	0.03123	0.007563
Pb	0.000873	Nd
Ca	101.2	25.46357
Na	4488.4	99.13063
Sr	2.9	0.69002
NO3	8.565	Nd
Cl	2036.0	3235
PO4	4.69	Nd
SO4	9488.91	7511

From the table it can be seen that the concentration of the elements in brine reduces considerably after the carbonation process with the exception of B, V and Mo which leach from the fly ash into the brine. The increase in the chloride species after carbonation could not be explained; however absence of compounds such as halite and sylvite which were expected in the carbonated fly ash could explain this phenomenon. The above observation confirms the suggestion of Mooketsi et al., (2007) who observed that most of the brine components can be stabilized in the ash matrix.

Analysis of the major cations and anions before and after contacting the ash shows a clear trend of decreased concetration after contacting the ash (Figure 4 below). The calcium concentration is however observed to increase in the fly ash/brine mixture. This is attributable to the leaching of the lime present in fly ash into solution.

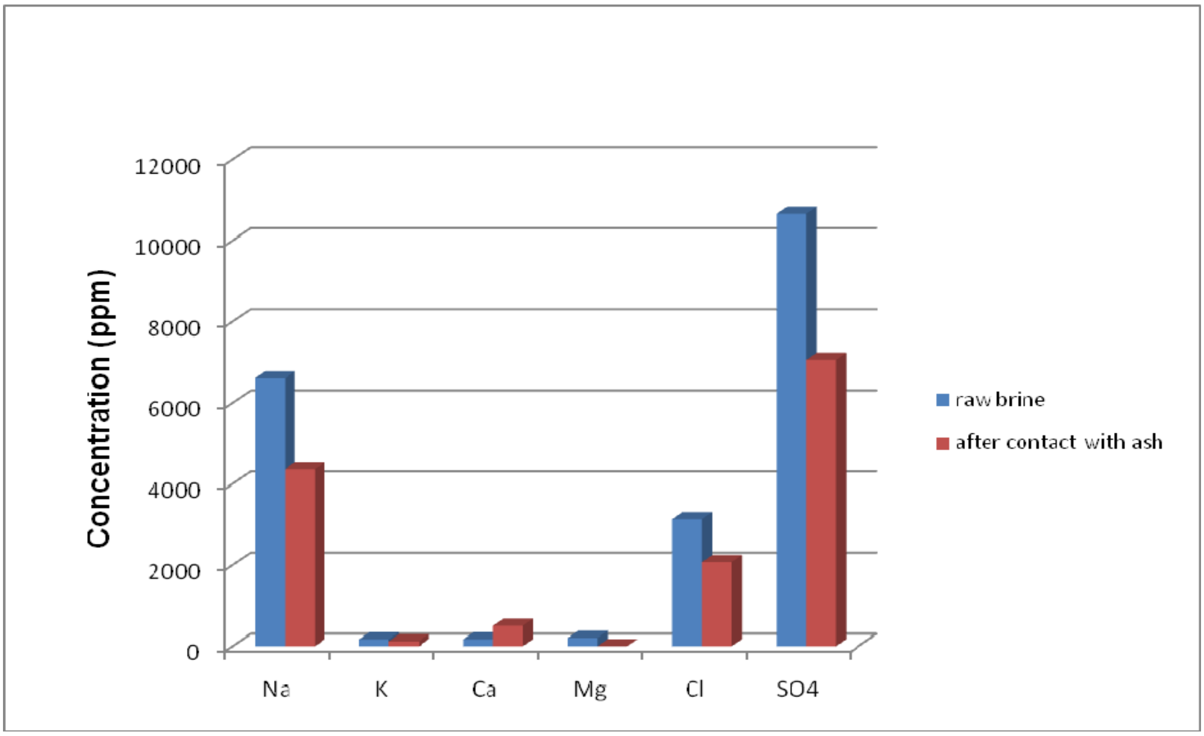


Figure 6. Comparison of raw brine and brine after contacting fly ash before carbonation

Fly ash is known to be alkaline in nature due to the high content of lime. The lime thus acts to increase the brine pH. Mooketsi et al., (2007) observed that contacting of brine with fly ash leads to irreversible retention of brine species in the fly ash matrix which could lead to an environmentally safe brine disposal option. Accordingly to the authors, brine treated sintered residues have improved leachate quality in terms of overall TDS as well as EC, Na, K, Ca, Cl and SO_4. They further postulated that the observed decrease in the SO_4 concentration is a result of reaction between the sulphates species present in brine and lime to form insoluble $CaSO_4$. This reaction consumes the SO_4 thus reducing the labile form of S species such as Na_2SO_4 in the brine. They concluded that most of the brine species like Na, Cl and SO_4 could be stabilized within the ash matrix.

4. CONCLUSIONS

It can be concluded that most of the brine species with the exception of B, V, Mo and Cl are stabilized within the ash matrix and that enhanced carbonation leads to co-precipitation of some of the traces present in brine hence producing cleaner effluents. On the other hand carbonation yielded aragonite as the major carbonate species with a small amount of calcite also being formed.

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