

# The Injection of Fly Ash Slurries in Deep Geological Reservoirs for Improved Reservoir Integrity and Safe CO<sub>2</sub> Sequestration

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## INTRODUCTION

The South African electricity producer, Eskom, generated 36.01 million tons of coal-combustion fly ash (FA) in 2010. About 5.6% were reused for the production of cement. The remaining 33.89 million tons were safely disposed of and managed on Eskom ash dumps and dams which are located adjacent to their corresponding power stations<sup>1</sup>. South Africa has a long history regarding the development of new applications for this material. For instance, Ash Resources, South Africa's leading manufacturer and supplier of fly ash products, has pioneered the re-use of FA and has positioned itself as one of the world leaders in ash technology over the last 30 years. South Africa remains very active in the development of ash technologies. Concurrently, the power industry is also a major carbon dioxide (CO<sub>2</sub>) emitter, with Eskom's emissions approximating 225 million tons for 2010.

In this paper, the authors introduce a theoretical concept whereby FA in a slurry form could be injected at strategic sites of deep saline formations. The purpose of this injection strategy is to prevent the migration of injected anthropogenic CO<sub>2</sub> plumes beyond the confining layers of the formations, via induced *in situ* localized, accelerated mineral carbonation. The proposed application falls within the carbon capture and storage (CCS) initiative by geo-sequestration and aims at improving the integrity of deep saline formations which may be at risk of leakage upon injection of CO<sub>2</sub>.

## CONCEPTUAL STRATEGY FOR FLY ASH SLURRY INJECTION AND CARBONATION FOR IMPROVED GEOLOGICAL RESERVOIR INTEGRITY

The injection and storage of CO<sub>2</sub> in deep geological reservoirs, also called geosequestration, is the most widely adopted variant of carbon capture and storage

(CCS) by governments and industries worldwide. A critical aspect of geosequestration is the existence of suitable high-integrity geological sites for the safe, long-term storage of CO<sub>2</sub>. Saline formations located at depths greater than 800 meters are of particular interest for countries which do not possess large depleted gas and oil reservoirs, such as South Africa<sup>2</sup>. However, unlike depleted oil and gas reservoirs which are historically proven to be well-confined, saline formations may not have a similar proven sealing capacity. They are always characterized by some level of recharge and discharge of brines which may increase with CO<sub>2</sub> injection. Ultimately, the velocity of the flow will be dictated by the backpressure imposed by the brines onto CO<sub>2</sub> injection and by the injection process itself, and by *in situ* parameters such as rock porosity and permeability. Further important aspects are *in situ* geochemical processes influenced by CO<sub>2</sub>, which at reservoir conditions will be in supercritical stage (sc-CO<sub>2</sub>). In the main, the CO<sub>2</sub>-supplemented formation will host a myriad of intricate dissolution and precipitation reactions. These chemical and physical effects of CO<sub>2</sub> injection will strongly depend on the types of minerals forming the host environment and on the pore fluids. Thus, with the injection of CO<sub>2</sub> the equilibrium between the lithostatic pressure and pore pressure will be changed and together with the *in situ* mineral dissolution and precipitation processes, under the influence of sc-CO<sub>2</sub>, may have a strong bearing on the permeability and reservoir and sealing capacity of the given formation.

Understanding the reactivity of the storage reservoir rock (*e.g.* sandstone) in saline formations with injected CO<sub>2</sub> is essential to predict the short-, medium- and long-term fate of CO<sub>2</sub>. Whilst significant effort has been made to better comprehend CO<sub>2</sub> mineralization via carbonate precipitation<sup>3</sup>, a lesser amount of information is available on rock-brine-CO<sub>2</sub> interactions following CO<sub>2</sub> injection. It is however known, that depending on the nature of the interactions they may either cause (1) increased porosity and permeability<sup>4</sup> and (1.a) subsequent greater storage capacity of the intended reservoir or (1.b), unwanted CO<sub>2</sub> migration outside the boundary layers of the reservoir, or (2) decreased porosity and permeability with reduced injectivity due to carbonate precipitation<sup>3</sup>. Details on competing geochemical processes (*e.g.* dissolution of primary and secondary silicate minerals, precipitation of carbonates, entrainment and deposition of fine materials) were discussed elsewhere<sup>5-9</sup>. The concept presented in this paper aims at improving the integrity of deep saline formations to prevent the occurrence of scenario (1.b) under circumstances of increased porosity and permeability, due to the aggressive properties of supercritical CO<sub>2</sub> - saline brine mixtures, or where the presence of minor fractures in the saline formation cannot be excluded.

The injection of reactive mineral slurries at strategic sites of deep saline formations may help to prevent the migration of CO<sub>2</sub> plumes beyond their confining layers via induced *in situ* localized, accelerated mineral carbonation. Researchers at the Albany Research Center (USA) have previously suggested this possibility of co-injecting ultramafic mineral slurries (*e.g.* olivine, serpentine) with CO<sub>2</sub>, and reflected on several conceivable injection scenarios<sup>10</sup>. These scenarios were recently reviewed and critically discussed<sup>9</sup>. In the context of South Africa, coal-combustion fly ash may be better suited for this application. Fly ash is abundant and readily-available at no cost, and is much more reactive than primary minerals. In addition, it can be classified into very small sizes

(sub-45  $\mu\text{m}$ ), presents favorable rheological properties for easy transport and injection, and could therefore provide calcium (Ca) and to lesser extent magnesium (Mg) cations to accelerate the binding of  $\text{CO}_2$  in carbonate minerals.

The most conceivable application of induced mineral carbonation to geological sequestration of  $\text{CO}_2$  is offered by the possibility of engineering a “mineral slurry curtain” which will progressively convert into a “carbonated mineral slurry curtain”. The curtain must be placed between the primary injection well of  $\text{CO}_2$  and potential weakness points (*i.e.* fault zones, fractures, facies changes) in the target formation, where  $\text{CO}_2$  could migrate towards and across such boundaries, resulting in rapid leakage outside the borders of the formation. The “carbonate curtain” would form *via* the volume expansion occurring upon carbonate formation, and filling the pore spaces between the formation grains. Thus, the newly formed carbonate cements would thereby act as a barrier preventing the injected  $\text{CO}_2$  to migrate further towards the aforementioned weakness points. Such a migration process of  $\text{CO}_2$  and the injected fly ash slurry must be imagined as a progressing mineralization front, like probably occurred during the origin of *e.g.* hydrothermal ore deposits. The migration must however be bedding-confined, without blocking the porosity. Key to this scenario for horizontal isolation of the  $\text{CO}_2$  plume will be the selection of the appropriate locations and depths of the wells with regard to zones of faults or fractures within the target horizon, the appropriate well spacing, and the appropriate concentration of mineral reactant to inject into the secondary wells. This procedure will also require an extremely detailed knowledge of the lateral and vertical distribution of mineralogy, porosity and permeability of the storage horizon, and the sites of possible zones of weakness of the geological seals. Other important issues evolving around the feasibility of such a scenario are the kinetics of formation of the carbonate curtain and the range of fluid and lithostatic pressures the “mineral slurry curtain” and the “carbonated curtain” would be able to sustain.

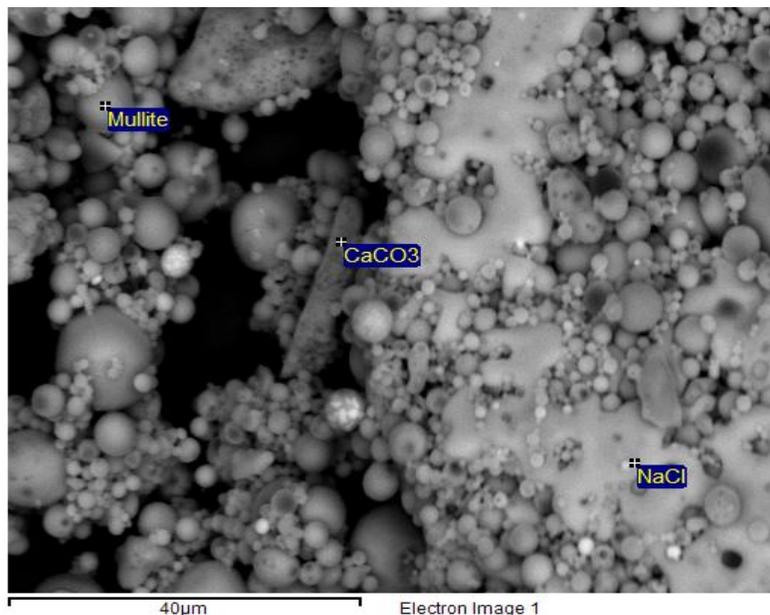
However, the proposed theoretical concept is only conceivable if it can be demonstrated that coal-combustion fly ash reacts with  $\text{CO}_2$  at reservoir conditions, to form carbonate minerals at acceptable rates.

## REACTION BETWEEN COAL-COMBUSTION FLY ASH AND SUPERCRITICAL $\text{CO}_2$

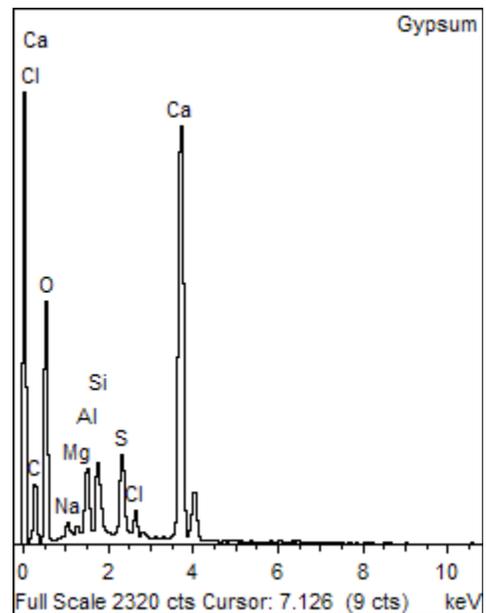
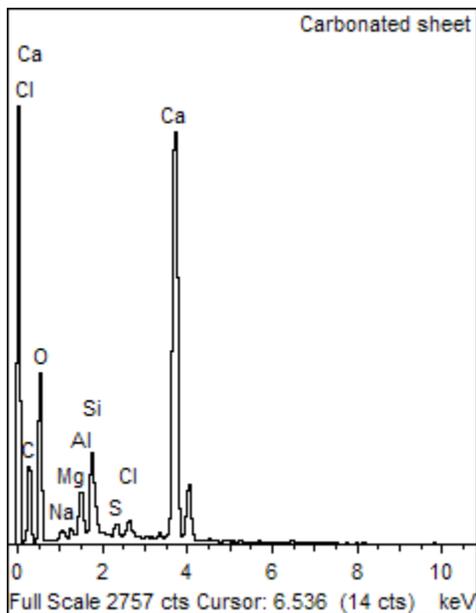
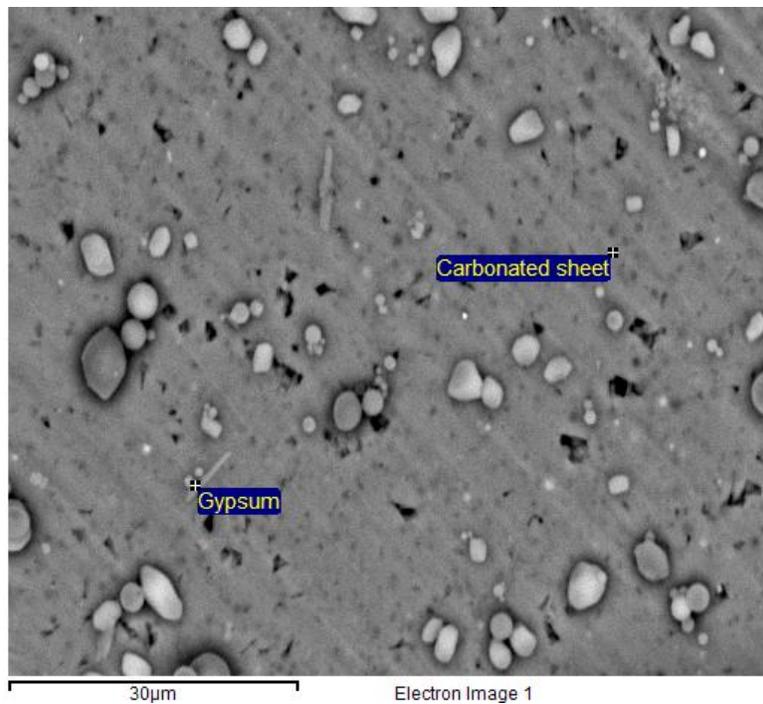
Within deep saline formations (below 800 meters),  $\text{CO}_2$  is in a supercritical state since its critical point lies at 30.98°C and 73.8 bars<sup>11</sup>. The aqueous carbonation of coal-combustion fly ash has been demonstrated under sub-critical  $\text{CO}_2$  conditions<sup>12-14</sup>, but not in brine waters under supercritical conditions.

The carbonation reaction of coal-combustion fly ash with supercritical  $\text{CO}_2$  (sc- $\text{CO}_2$ ) was tested in a model brine at temperature and pressure conditions of 90 °C and 90 bars respectively. At the end of the 2-hour contact time, and upon centrifugation and drying of the solid residue at 40 °C up to constant weight, the residue was examined under a scanning electron microscope (Figures 1 and 2). While a large number of fly ash particles appeared to be intact, fragments of carbonated sheets with widths of *ca.* 3.8  $\mu\text{m}$  were also observed (denoted “ $\text{CaCO}_3$ ” in Figure 1). The surface of a carbonated

sheet is depicted in Figure 2. The sheet was enriched in Ca and C; it is however unclear whether other elements identified in the spectrum (*i.e.* Al, Si, Na, Mg and Cl) are part of the sheet composition or are rather indicative of an effect of analytical volume being larger than the thickness of the sheet. Small amounts of S were also detected. Fly ash particles as well as a small number of needle-shaped gypsum crystals were also embedded in the sheet. The mineralogical composition of the carbonated sheet was confirmed using XRD, which demonstrated the presence of aragonite (23%), calcite (3%) and fly ash minerals (*e.g.* mullite, quartz). It also contained an XRD-amorphous phase of about 37%. The carbonated sheet illustrated in Figure 1 was most certainly a fragment of a larger sheet which formed at and coated the bottom of the high-pressure, high-temperature reactor. The thickness of this larger sheet was found to be 16.6  $\mu\text{m}$ . A thinner layer of white precipitate was also observed on the wall of the reactor; this precipitate was composed of aragonite and calcite, and contained an amorphous phase of *ca.* 1%. This was the first direct confirmation that coal-combustion fly ash reacts with sc-CO<sub>2</sub> to form carbonate minerals. Further investigations into the extent and rate of conversion of sc-CO<sub>2</sub> when reacting with fly ash in model brines, at different P/T conditions and solid-to-liquid ratios is underway.



**Figure 1** SEM micrograph of fly ash treated in CO<sub>2</sub>-saturated brine.



**Figure 2** SEM micrograph of the surface of carbonated sheet formed from fly ash treated in CO<sub>2</sub>-saturated brine, and elemental spectra (EDS) of the sheet and needle-like crystal of gypsum. Another crystal of gypsum is depicted in the middle top of the micrograph.

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